



Critical Evaluation of Some Available Treatment Techniques for Textile & Paper Industry Effluents: A Review

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Authors' contributions

This work was carried out in collaboration between both authors. Author IQ reviewed the concerned literature, designed the study and wrote the final draft of the manuscript. Author RCC reviewed the manuscript and did the necessary corrections. Both authors read and approved the final manuscript.

Article Information

DOI: 10.9734/ACSJ/2015/15484

Editor(s):

(1) Yunjin Yao, School of Chemical Engineering, Hefei University of Technology, China.

Reviewers:

(1) Randa M. Osman, Chemical Engineering and Pilot Plant Department, National Research Center, Egypt.
(2) N. Murugalatha, Department of Applied Sciences and Humanities, Quatum School of Technology, Uttarakhand Technical University, India.

Complete Peer review History: <http://www.sciencedomain.org/review-history.php?iid=900&id=16&aid=8009>

Review Article

Received 28th November 2014
Accepted 29th December 2014
Published 2nd February 2015

ABSTRACT

The disposal of untreated effluents from the textile & paper industries is a major environmental concern these days. Textile effluents are colored & contain carcinogenic aromatic amines, dyes, organic & inorganic molecules. However, paper mill effluents are dark in colour due to the presence of wood extractives, lignin, resins, tannins, synthetic dyes & their degradation products. Both textile & paper industry wastewaters are characterized by extreme fluctuations in many parameters such as pH, color, temperature, suspended solids, biological oxygen demand (BOD), chemical oxygen demand (COD), adsorbable organic halides (AOX) & salinity. The recycling of wastewater of textile & paper industries has thus been recommended due to the high levels of contamination in dyeing and finishing processes. So this review discusses the various methods of treatment available in the literature for textile and paper industry effluents. Use of low cost adsorbents obtained from various plant materials such as neem leaves, bark of babul & maize corn carbon (MCC) are highly encouraged for the decolorization of aqueous solutions of dyed effluents of industries because they are not only cost effective but sometimes more efficient than the commercially available activated charcoal. A combination of anaerobic-aerobic treatments to effluents of textile and paper industries

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has been found to be more economical & effective in terms of reduction of pollution. Also the degradation of dyes by mixed cultures has been found to be more effective than those of the individual strains of microorganisms. Among all these methods, advanced oxidation processes are the most promising treatment techniques these days as these processes can be used to oxidize the more complex organic compounds without production of any secondary components to be handled.

Keywords: Effluent; decolorization; adsorbents; bioremediation; Advanced Oxidation Processes (AOP).

1. INTRODUON

Next to air, water is the most important natural resource necessary for the survival of life on earth. Industries such as textiles, paper, engineering & electronics determine the wide range of water chemistry. With the increased demand for textile products, the textile industry and its waste waters have been increasing proportionally, making it one of the main sources of severe pollution problems worldwide [1,2]. More than 80,000 tons of dyes used mainly in food industries, cosmetics, paper mills and especially in textile industries which absorb alone more than 70% of the produced total quantity [3]. There are more than 8,000 chemical products associated with the dyeing process and over 100,000 commercially available dyes exist with over 7×10^5 metric tons of dyestuff produced annually [4]. In particular, the discharge of dye-containing effluents into the fresh water environment is undesirable because of their color, released directly and the breakdown products are toxic, carcinogenic or mutagenic to life forms mainly because of carcinogens such as benzidine, naphthalene and other aromatic compounds [5]. Much of the water pollution is caused due to diversity in the composition of chemical reagents used in textile industries. The reagents range from inorganic compounds to polymers and organic products [6]. Wastewater generated by different production steps of a textile mill have high pH, temperature, detergents, oil, suspended solids, dissolved solids, dispersants, leveling agents, toxic metals, non-biodegradable matter, color and alkalinity [7]. Textile effluents are rich in recalcitrant organics, color, toxicants, surfactants and chlorinated compounds. These industries also use synthetic dyes including VAT dyes, AZO dyes and mordents. Mordents are used for fixing of colours and contain heavy metals like iron, copper, chromium, cadmium etc. which are toxic in nature. Many synthetic dyes are toxic mutagens and carcinogenic [8]. The textile wastewaters are characterized by extreme fluctuations in many parameters such as

biological oxygen demand (BOD), chemical oxygen demand (COD), pH, color and salinity [9].

Large quantities of freshwater and lignocellulosic materials are also used by the pulp and paper industries in various processing steps of paper production and thus large quantities of undesired effluents are generated. In addition to dark color & unpleasant odour, the generated effluents also show extreme fluctuations in the values of biological oxygen demand (BOD), chemical oxygen demand (COD), pH & organic content [10]. The dark colour results due to the presence of certain organics such as wood extractives, lignin, resins, tannins, synthetic dyes & their degradation products [11,12].

In addition to the harmful degradation products, the effluents of pulp & paper industry also contain chlorinated phenols. These chlorinated phenols, generated during the pulp bleaching stages of paper are toxic in nature & affect the fish community severely. Thus the direct discharge of these untreated dark colored effluents into water bodies is a major environmental concern because due to the presence of dark color, these effluents can largely reduce the sunlight entering the water bodies & thus inhibit the process of photosynthesis of aquatic biota. Studies have also revealed the potential toxic effects of these effluents on aquatic biota [13,14].

In textile & paper industries, opportunities exist for the release of potentially hazardous compounds into the ecosystem at various stages of operation. Color is the first contaminant to be recognized in wastewater and has to be removed before discharging wastewater into water bodies or on land. Major pollutants in textile & paper mill effluents are high suspended solids, chemical oxygen demand, heat, color, acidity, lignocellulosic materials, adsorbable organic halides (AOX) and other soluble substances. Wastewater of pulp & paper industries is also an important reservoir for *E. coli* and represents significant acute toxicity if released into the receiving fresh water bodies without being

adequately treated. Results have revealed the presence of both gram negative and gram positive bacteria in effluent samples [15].

Conventional bio treatment methods are not effective for most of the synthetic dyestuffs due to the complex polyaromatic structure and recalcitrant nature of dyes. Aromatic amines formed as the metabolites of reductive cleavage of the azo bond under anaerobic conditions are more toxic than intact dye molecules while aerobic conditions are desirable as total mineralization can be achieved [16].

The unplanned intrusion has negative effect on the environment. Efficiency of any physico-chemical or biological effluent treatment greatly depends on the nature, quality & concentration of the organic compounds. In addition, characterization of the effluent is important to determine its reuse as a safe option due to high water consumption. The recycling of wastewater has thus been recommended due to the high levels of contamination in dyeing and finishing processes (i.e. dyes and their breakdown products, pigments, auxiliary chemicals and heavy metals) [17,18].

2. Physico-chemical Treatment of Paper Industry Effluents

The physico-chemical techniques commonly employed for the treatment of paper mill effluents are sedimentation, dissolved air floatation systems, coagulation, ultrafiltration, reverse osmosis, ozonation, photo-Fenton, wet oxidation & advanced photocatalysis. Physico-chemical treatment processes are widely used for the treatment of pulp & paper industries. However, there are two important disadvantages of physico-chemical treatment processes; (a) the formation of sludge and its disposal; (b) the requirement of large space [19].

2.1 Sedimentation

Sedimentation is the simplest method of pre-treatment of waste water. It is used to remove the undissolved solids such as bark particles, fibre debris, filler and coating material from the paper mill effluents but is not effective for the removal of BOD or COD. Sedimentation tanks can remove more than 80% of the suspended solids at a surface loading rate (SLR) of $1.4 \text{ m}^3/\text{hr}$ [20].

2.2 Dissolved Air Floatation (DAF)

Dissolved air floatation (DAF) is a wastewater treatment process that can be used to clarify the wastewaters by removing the suspended matter such as oil or solids. The oil or suspended solids can be removed by dissolving air in the wastewater under pressure & then allowing the air to get released under the atmospheric pressure in a flotation tank or basin. The released air helps the suspended matter to float on the surface of water by adhering it to the tiny bubbles formed under atmospheric pressure. The floated matter is then removed easily by skimming [21].

Dissolved air floatation finds a good application in treating the effluents of paper mills. The wastewater in DAF tank is often dosed with coagulants like ferric chloride or aluminium sulphate to flocculate the suspended matter. After the coagulation & flocculation processes, fine bubbles are created by the air diffusers on the bottom of DAF tanks that adhere to the floc, resulting in a mass of concentrated floc that floats on the surface. The blanket of floating floc is thus removed from the surface by skimming. Also the clarified water thus obtained is withdrawn from the bottom of the dissolved air floatation tank [22].

Dissolved air floatation (DAF) can thus be used as a pre-treatment unit for the biological treatment process [23]. Ultra filtration combined with dissolved air floatation has been revealed to be more effective & efficient for the removal of 70% TOC, color & heavy metals from the same effluent [24].

2.3 Coagulation

Coagulation is one of the cheapest processes for the treatment of various organic effluents. Activated carbon is a commonly used coagulant to remove COD. 90% of COD removal has been observed during the adsorption studies of activated carbon [25]. Various coagulants like aluminium sulphate, polyethyleneimine, polyelectrolytes, calcium sulphate, aluminium sulphate & chitosan have also been found effective in reducing the BOD, COD, AOX & turbidity of the paper mill effluents.

Coagulants such as aluminium chloride, poly aluminium chloride (PAC) and copper sulphate were used for the batch coagulation process [26]. The initial pH of the effluent has been found to

have tremendous effect on COD and color removal. Poly aluminium chloride (PAC) as coagulant reduced COD up to 84% and 92% of color was removed at an optimum pH 5 and coagulant dose of 8 ml/L. With aluminium chloride at an optimum pH = 4 and coagulant dose of 5 g/L, 74% COD and 86% colour removal was observed. The results using copper sulphate as coagulant were encouraging. At an optimum pH 6 and mass loading of 5 g/L, 76% COD reduction and 78% color reduction was obtained. It was also observed that after addition of coagulant, the pH of the effluent decreased. The decrease in pH was highest for $AlCl_3$ followed by PAC and $CuSO_4$.

2.4 Reverse osmosis & Ozonation

Reverse osmosis (RO) is an important membrane based process technology used for the desalination of salt water and effluent wastewater treatment. Reverse osmosis can be used to remove the dissolved solids, organics and organic pollutants present in effluent wastewater. Ozonation on the other hand is used to treat the wastewater samples for bacteria, viruses, hydrogen sulphide, iron & manganese. In addition to this, ozonation can also be used to eliminate the taste or odor problems in wastewater. The oxidizing property of ozone is due to the formation of free oxygen radical after its degradation. The free oxygen radical is highly unstable, more reactive & very short lived. Reverse osmosis can be used for 80% BOD reduction, whereas ozonation has been observed to reduce COD, toxicity of paper mill effluent & also 80% reduction of effluent color [27,28].

3. ADVANCED OXIDATION PROCESSES

The conventional methods of wastewater treatment are not effective for the complete degradation of color and low molecular weight chloro organics [29]. Hence advanced oxidation processes (AOPs) need to be adopted for meeting the increasingly stringent wastewater discharge standards. AOPs rely on the in-situ generation of very reactive oxidizing species, the hydroxyl radicals (OH^\bullet) for the degradation of organic compounds [30]. The production of (OH^\bullet) radicals can be accelerated by combining various systems like UV/ catalyst, UV/ catalyst/ H_2O_2 (semiconductor photocatalysis), UV/ O_3 , UV/ H_2O_2 , O_3 / H_2O_2 , UV/ O_3 / H_2O_2 , UV/ O_3 /catalyst, Fe(II)/ Fe(III) with H_2O_2 (Fenton reaction) and UV/{Fe(II)/Fe(III)+ H_2O_2 } (photo- Fenton) [31]. However, semiconductor photocatalysis is an attractive technique among various AOPs

because it causes the complete mineralization of a wide range of organics without any harmful environmental impact [32]. TiO_2 is the most widely used semiconductor photo-catalyst for wastewater treatment because it is chemically and biologically inert, photo-stable over a wide range of pH, operates at low cost, and relatively easy to produce and use.

Advanced oxidation of elemental chlorine free (ECF) bleaching wastewater for the reduction of environmental load through D1 (first chlorine dioxide) and E stages (alkaline extraction) of the DED and ODED sequences (O, D & E refer to oxygen delignification, chlorine dioxide oxidation and alkali extraction with Na OH respectively) was studied using TiO_2 photocatalysis [33]. The wastewaters were generated from the mixed hardwood Kraft pulp by first chlorine dioxide (D1) bleaching & alkaline extraction (E) under controlled conditions. The bleaching wastewaters were treated in a slurry-type reactor by photocatalytic oxidation under UV radiation for 4hr at pH 7 & 0.5 g/L of TiO_2 . Removal efficiencies for ODED sequence wastewaters were more as compared to DED sequence. The percentage removal of biological oxygen demand (BOD), chemical oxygen demand (COD), color and adsorbable organic halides (AOX) for D1 stage of ODED sequence using UV/ TiO_2 oxidation treatment was observed as 46.3, 64.2, 88.3 & 59.3 respectively while for E stage wastewaters, the percentage removal of BOD, COD, color & AOX was observed as 55, 66.5, 86.7 and 64.2 respectively. Also BOD/COD ratio was much enhanced for ODED sequence wastewaters as compared to DED sequence. Thus, it can be concluded that the wastewaters from ODED sequence can be subjected better to photocatalytic degradation than the DED sequence

Pollution load of paper mill effluents has been effectively reduced by the use of photo-Fenton & wet oxidation in combination with ozone or the advanced photocatalysis with O_2 / TiO_2 /UV [34,35,36].

3.1 Solar Photo-Fenton Process

Solar photo-Fenton process is a promising attractive & alternative treatment technology among advanced oxidation processes for the treatment of wastewater containing recalcitrant organic compounds. The feasibility of solar photo-Fenton process for the effluents of pulp & paper industry was investigated [37]. The complete color and chemical oxygen demand

(COD) removal was obtained under optimal conditions of pH=4, Fe^{2+} = 1 g/L, H_2O_2 = 5 g/L and an irradiation time of 90 min. Also it has been observed that the biodegradability of wastewater was enhanced with increase in the ratio of (BOD_3)/COD from 0.028 to 0.83.

3.2 Wet Oxidation (WO)

Wet oxidation (WO) is also a very well-established treatment process involved in the purification of wastewaters. Wet oxidation process has thus been employed for the treatment of pulp & paper industry effluents. To increase the efficiency of wet oxidation process, many attempts have been made to create a suitable combination of processes with the WO process. In order to modify the WO process, the later was integrated with coagulation for the treatment of sludge remaining after coagulation [38]. Also an attempt was made to regenerate the used coagulant. For this purpose, two types of wastewaters from the paper industry were used for the studies; a) thermo mechanical pulp (TMP) circulation water &b) membrane concentrate. By using $\text{Fe}_2(\text{SO}_4)_3$ as coagulant, about 50% of the COD removal in the original water was achieved. From the WO experiments, it has been observed that iron shows the positive effect as the catalyst in the treatment of chemical sludge.

Treatment of pulp and paper mill effluents by wet air oxidation (WAO), using heterogeneous catalyst was also studied [39]. The heterogeneous catalyst used was CuO- ZnO supported on alumina and ceria as well as lanthanum based perovskites. The activity test was carried out at 95°C & one atmospheric pressure. In a reaction time of 2hr and a catalyst concentration of 5 Kg/m³ and an initial pH of wastewater sample as 3.0, a maximum COD reduction of 83% for (CuO-ZnO)/CeO₂ catalyst was obtained. The efficiency of wet oxidation process was enhanced almost by 100% by integrating it with coagulation.

4. BIOREMEDIATION OF PAPER INDUSTRY EFFLUENTS

Pulp and paper mill effluents are rich in recalcitrant organic compounds and cause aqua pollution. These industries use conventional activated sludge treatment process wherein nonspecific microorganisms are used and the food/microbe (F/M) ratio is kept low in the aeration tank.

A sequential batch reactor was employed for removing the pollutants from the effluents of pulp & paper industry by using the bacterial consortium (*Alcaligenes* sp., *Klebsiella* sp. and *Cronobacter* sp.)[40].

In this study, the influence of F/M ratio and dissolved oxygen concentration on the microorganism's growth and pollutant removal was taken. Taguchi approach was used for the bioremediation process. It has been observed that bioremediation resulted in the reduction of chemical & biological oxygen demand up to 72.3% & 91.1% respectively. Thus the treated wastewater can be released into the environment without any potential risks. Also, a significant reduction in color (55%), absorbable organic halides (45.4%), total suspended solids (86.7%) & total dissolved solids (22%) has been reported within 14hrs, while the sludge volume index was found 52.

In case of pulp and paper mill effluents, a two stage process i.e. anaerobic-aerobic are more effective both in terms of BOD and sulfur removal [41]. Anaerobic process not only requires low energy input but also comparatively fewer nutrients are required and interestingly less amount of sludge is produced during this process. It is suggested by many authors that use of anaerobic treatment process for paper mill effluents removes more than 80% COD [42].

Treatment of paper industry effluents using a stage anaerobic reactor was studied to confirm whether the effluents can be tolerated by methanogenic sludge & to assess the stability of reactor for the measured parameters including methane composition & COD removal [43]. It has been observed that up to 98% COD reduction could be attained when the anaerobic reactor was operated at an OLR of 1.560 kg COD/m³.d. It has thus been suggested that anaerobic digestion can be used to provide high treatment efficiency for the recalcitrant organics by generating the robust microorganisms (methanogenesis & acidogenesis) for the degradation of recalcitrant organic compounds in the paper mill effluents.

The three important disadvantages of bioremediation are; (a) growth of microorganisms is affected due to the presence of toxic metals in the effluent; (b) non-biodegradable dyes cannot be treated and (c) long time is required for the treatment process [44].

5. TREATMENT TECHNIQUES OF TEXTILE INDUSTRY EFFLUENTS

Various physico-chemical methods such as flocculation, coagulation, sedimentation, ozonation, bleaching, membrane filtration, ultra filtration, adsorption by activated carbon & heterologous photocatalytic treatments are commonly employed for the treatment of textile effluents.

The treatment of textile effluents is categorized into three broad steps i.e. primary, secondary and tertiary processes.

5.1 Primary Treatment of Textile Effluents

Primary process is the first step of treatment process & involves the removal of suspended solids, excess of oil, grease and gritty materials after coarse screening of the effluents [45]. Sedimentation can remove the heavily suspended and easily settleable particles under the effect of gravity, but is not effective in the removal of small sized colloidal particles. The colloidal particles can be removed by coagulation & the process of coagulation is carried out by adding the chemical coagulants like ferrous sulphate, ferric sulphate, lime, ferric chloride & alum [46]. Flocculation of small particles can be carried out mechanically by slow mixing of effluents with paddles which helps the small particles to coalesce together to form the heavier particles that get settled and are finally removed as sludge [47,48].

However, there are two important limitations of flocculation systems; a) the risk of getting short circuited & b) the difficulty to control the flocculation in the flocculation system.

5.2 Secondary Treatment of Textile Effluents

The Secondary treatment process is mainly concerned about the reduction of color, oil content, phenol and BOD of the effluents. Treatment of dye wastewater has become a matter of great concern, and several advanced treatment methods such as physical and chemical methods have been suggested [49]. Dyes can be removed from the waste waters of textile effluents by using commercially available activated carbon. However, in addition to commercially available activated carbon, being expensive, other low cost adsorbents obtained from various plant materials such as neem leaves, bark of babul & maize corn carbon

(MCC) can also be used for the decolorization of dyed textile effluents. The degradation of textile dyes can also be carried out by bioremediation using individual bacterial strains, mixed cultures of bacteria or advanced oxidation processes. However, studies have revealed that the decolorization of dyed textile effluents by using mixed cultures of bacteria is more effective than by using the individual strains of bacteria.

5.3 Bioremediation of Dyed Textile Effluents using Individual Strains of Bacteria

Biological approaches like activated sludge systems give rise to the accumulation of concentrated sludge and emission of toxic substances, which still remains as a disposal problem during dye removal. In this context there is a need to improve those biological treatments systems that are effective in removing dyes from large volumes of effluents at a low cost [50]. The bacteria are used to oxidize the dissolved organic matter present in the effluents to CO₂ and water & also degrade the nitrogenous organic matter into ammonia. Aerated lagoons, trickling filters & activated sludge systems are the important aerobic systems used for the secondary treatment. The BOD removal efficiency of aerated lagoons is up to 99% & phosphorous removal is 15-25% [51].

Removal of dyes from textile effluents is carried out by various microorganisms like bacteria, fungi, yeast, algae & plants. Recent work has shown that the existence of wide range of microorganisms is capable of decolorizing wide range of dyes and is also cost effective.

However the bioremediation of industrial effluents is greatly influenced by various operational parameters like temperature, pH, dye concentration, amount of oxygen & nutrients. Thus these factors are needed to be optimized for the efficient removal of color in the dyed textile effluents.

The complete degradation of con go red by *Bacillus* sp. ACT 1 & *Bacillus* sp. ACT 2 has been found quite effective in the temperature range of 30-45°C [52]. Thus, the bacterial activity towards decolorization is enhanced at an optimum temperature. However the activity of bacteria towards decolorization is decreased at elevated temperatures due to denaturation of enzymes in bacteria, necessary for the degradation of dyes.

Enterobacter agglomerans has been found to decolorize 90% of methyl red at pH 5-7 (acidic range) under viable period of incubation [53]. The concentration of dye present in the effluent also influences the decolorization by bacteria because high concentration of dyes in the effluents cause toxicity to bacteria & inhibit their metabolic activities. Therefore an optimum concentration of dye is also important for the effective removal of dyes by the bacteria. *Bacillus subtilis* was evaluated for the acid blue 113 at different dye concentrations & the optimum concentration of effective dye removal by *Bacillus subtilis* was found to be 200 mg/l [54].

Likewise the decolorization process of effluents by microorganisms largely depends on the nutrient concentration in the aqueous solution of dyes [55]. The decolorization of methyl red by Enterobacter agglomerans has been found to occur when the glucose concentration was 1, 2 & 4% whereas the decolorization decreased as the glucose concentration was less than 1%.

5.4 Degradation of Dyes by Mixed Cultures

Degradation of dyes by mixed cultures enhances the decolorization process because the individual strains attack the dye molecule at different sites or the decomposed products produced by one strain will be further decomposed by another strain [56,57].

Degradation of textile dyes by *Aspergillus tamarii*, mixed fungal culture (*Trichoderma* sp., and *A. flavus*) and *Penicillium purpurogenum* was studied and the decolorization was thought to occur by metabolism rather than by adsorption [58]. After studies, it was revealed that *A. tamarii* decolorized >90% of coomassie brilliant blue (CBB), bromophenol blue (BPB) & malachite green (MG) dyes. Also mixed fungal culture was observed to decolorize CBB 74, BPB 78 & MG 45%. However, *Penicillium purpurogenum* has been observed to decolorize CBB 91, BPB 92 & MG 52%. It has been suggested that isolated fungal strains could be effectively used in the development of alternative & ecofriendly methods for the degradation of textile dyes.

Azo dyes which are used most widely by textile industries are not degraded effectively by aerobic treatment can be treated by using anaerobic bacteria [59,60]. The by-products of the anaerobic treatment are toxic, mutagenic & carcinogenic in nature and therefore require further aerobic treatment for their complete

biodegradation [61]. Thus combined biological treatment i.e. anaerobic treatment followed by aerobic treatment, with some physico-chemical pretreatments are the most economical ways of decolorizing the dyed effluents [62]. The biological treatment is effectively used for the removal of nitrogen, organics, phosphorus and metals.

However due to the complicated molecular structure of dyes, the effluents of textiles are difficult to be treated by these conventional methods because of the expensive nature, less efficiency & limited applications due to which the wastes generated are difficult to dispose.

5.5 Use of Low Cost Adsorbents for Decolorization of Dyed Textile Effluents

The low cost adsorbents obtained from various plant sources have been found to be more economical & sometimes more effective than commercially available activated carbon for dye removal from the industrial wastes. Dyed effluents can be treated by using low cost adsorbents such as fly ash, bagasse pith, neem leaf powder, babul bark, sewage treatment bio solids (sludge) & coconut coir [63].

The use of low cost adsorbents such as fly ash for the removal of various dyes like Methylene blue, Malachite green & Rhodamine-B was studied for the decolorization of aqueous solutions of dyed effluents [64]. The color removal percentages observed were 93%, 89% & 77% for Methylene blue, Malachite green & Rhodamine-B respectively.

Another low cost adsorbent used for the decolorization is bagasse pith. Bagasse pith was used to study the color removal of dyed effluents from the aqueous solutions of Astrazone blue, Maxillon red & Telon blue [65].

The removal of basic dyes like Basic blue 3, Basic red 22 & Basic black 9 was studied by using sewage treatment plant bio solids [66]. The results revealed the optimum adsorption capacity at an adsorbent dosage of 0.5-0.75% w/v.

The adsorption capacity of neem leaf powder for the water soluble dyes like Congo red, brilliant green & methylene blue from the aqueous dyed solutions was studied for the varying conditions of temperature, pH, concentration of dyes and the adsorbent dosage [67]. It has been observed

that neem leaf powder is a cost effective and efficient low cost adsorbent.

In an another experiment adsorption capacities of locally available low cost activated bio-adsorbents obtained from neem leaves, orange peels, peanut hulls and coconut coir pith powders were studied to remove color in a textile industry wastewater [68]. The maximum color removal percentage in textile industry wastewater is about 74.2, 79.3, 85.6 and 80.7% respectively for neem leaves, orange peels, peanut hulls and coconut coir pith powders. From this experiment, it was concluded that peanut hulls are more efficient adsorbents for the color removal from the aqueous solution of dyed effluents.

The other low cost adsorbents (activated carbon) prepared from maize corn (MMC), teak leaf (TLC) & babul tree bark (BTBC) were prepared to study the removal of red industrial dye under various experimental conditions like adsorbent dosage, initial pH, initial concentration, particle size & contact time [69]. A high value of 21.28 obtained from Langmuir plot for maize indicated that maize corn carbon (MCC) is an ideal low cost adsorbent among babul tree bark (BTBC), teak leaf (TLC) & maize corn (MMC).

The adsorption characteristics of Eriochrome Black-T dye on the activated nilgiri leaves (*Eucalyptus globulus*) conducted at different pH, adsorbent dosage, initial concentration of dye and different contact time were studied [70]. From the present studies, it was concluded that activated nilgiri leaves could be employed as an alternative low cost adsorbent to the commercially available activated carbon for the decolorization of dyed textile effluents.

5.6 Tertiary Treatment of Textile Effluents

Tertiary treatment of textile effluents mainly involves the removal of COD and dissolved solids from the samples of the wastewaters. Tertiary treatment of textile effluents is carried out in various ways like reverse osmosis, electro dialysis, membrane filtration, ultra filtration, ion exchange & electrolytic precipitation.

5.6.1 Electrolytic precipitation

Electrolytic precipitation is an electrochemical destruction of dyes carried out by passing electric current through the effluents of textile

industries using electrodes. Due to the passage of electric current, electro chemical reactions occur, as a result of which the dissolved metal ions present in the solution combine with the finely dispersed particles in the same solution. Thus heavier metal ions are formed which can be removed after precipitation [71]. The electrochemical destruction of dyes is usually very good for the COD reduction because of the strong oxidizing potential of oxygen, chlorine, hydroxyl radicals and other oxidants produced [72]. Another important advantage of this technique is that no sludge is generated & also there is no consumption of chemicals.

5.6.2 Membrane filtration

Most of the commercial dyes can be efficiently removed from the effluents by membrane filtration [73,74]. However membrane filtration methods cannot be used to degrade the dyes, hence they get concentrated in the residue, causing secondary pollution that needs to be handled carefully. In addition to this, ultra filtration can also be used to remove the dyes, although the low molecular weight dyes may pass through the membrane. In such cases nano-filtration can be used.

5.6.3 Electrodialysis

Electrodialysis is a method which uses the membranes that are able to separate the dissolved salts. In case of electrodialysis, due to the passage of electric current through the solution, the ions are transported through a semi-permeable membrane [75]. Charge specific membranes are used for the process of electrodialysis. In an anion-selective membrane, only negatively charged particles can pass through whereas the positively charged particles are trapped & vice versa. Numerous membranes are placed throughout the system to hinder the flow of effluent & also to get the ions trapped or settled down [76]. It has been observed that by removing the turbidity, suspended solids & colloids prior to electrodialysis, membrane fouling (a process where solute particles usually go into the membrane pore or get attached to the membrane) can be prevented [77].

5.6.4 Electrochemical coagulation

Dyes can also be removed by electrochemical coagulation in which aluminum and iron sheets are used as consumable anodes to generate the coagulants [78]. The combination of aluminum &

iron is found to be effective for the coagulation & degradation of dyes. Aluminum coagulation involves adsorption only & there is no degradation of dyes, while ferrous ions generated may further degrade the dyes in ion-based coagulation. However the main drawback of this method is the generation of sludge to be handled [79].

6. ADVANCED OXIDATION PROCESS OF EFFLUENTS- PHOTO OXIDATION

Photo oxidation processes are induced by light. The common processes involved in photo oxidation are a) loss of electrons due to photo-oxidation of a chemical species & b) the reaction of a substance with oxygen under the influence of light. The basic mechanism involved in the advanced oxidation processes is the generation of OH° radicals which have the potential of destroying the components that are difficult to be oxidized [80,81,82]. The reactivity of OH° radicals is due to their electron loving nature which helps them to react rapidly towards the electron rich organic compounds. The basic advantage of photo-oxidation is that it can take place at any temperature & pressure, besides no secondary components are produced [83]. Generation of OH° radicals can be accelerated by the combinations of UV, electron beam irradiation, H_2O_2 , TiO_2 , O_3 , Fe^{2+} , and ultra sound.

Advanced oxidation processes hold a great promise for the improved treatment of textile dye effluents. A recent study carried on the effectiveness of $\text{H}_2\text{O}_2/\text{UV}$ system for the decolorization of Remazol Brilliant Blue was investigated under the optimum conditions for dye removal in two reactors (coil & conventional) [84]. It was revealed that the coil reactor had a higher temperature profile than the conventional reactor. It was also observed that at 25°C , UV radiation alone was not effective for the decolorization in both conventional & coil reactors. However, when the concentration of H_2O_2 was increased, the decolorization also increased with residence time. At a residence time of 56 min, more than 93% color removal of Remazol Brilliant Blue was achieved whereas 100% decolorization was achieved with a residence time of 65min at H_2O_2 concentration of 12.50 ml/L.

Advanced oxidation process involving TiO_2/UV and $\text{H}_2\text{O}_2/\text{UV}$ were evaluated for their potential use in the decolorization of Remazol Brilliant Blue using a coil photo reactor consisting of UV

radiation source & a spiral coil coated with TiO_2 [85]. The effects of UV radiation, TiO_2 coatings & dye concentration were studied & the results compared to the dye treatment involving H_2O_2 . The maximum dye removal efficiencies were 7.3, 12.2, 12.5, 4.1 & 99.9% respectively for uncoated, single coat & dual coat of TiO_2 respectively. However, the comparative studies among UV only, TiO_2 only, $\text{UV}+\text{TiO}_2$, H_2O_2 only & $\text{UV}+\text{H}_2\text{O}_2$ showed the per cent reduction in the color removal of 7.6, 2.3, 12.5, 4.1 & 99.9 respectively. The maximum decolorization was observed to occur in ≤ 100 min in all the cases.

7. CONCLUSION

Due to the high levels of contamination in dyeing and finishing processes, the recycling of wastewaters of textile & paper industries has been recommended. Both textile and paper industry waste waters are characterised by extreme fluctuations of pH, BOD, COD & adsorbable organic halides (AOX) due to presence of various organic compounds in them which pose serious problems to aquatic life. The recalcitrant organic pollutants & azo dyes which are carcinogenic in nature are to be treated effectively for safe reuse of the wastewater. So this review has been taken to discuss the various methods of treatment available in the literature for the treatment of textile and paper mill effluents. In addition to pre-treatment techniques like sedimentation, various physicochemical treatment techniques like dissolved air floatation, coagulation, flocculation, reverse osmosis, ozonation, ultra filtration, electrolytic filtration, membrane filtration, electro dialysis, electrochemical coagulation, adsorption, advanced oxidation processes & bioremediation have been discussed. Use of low cost adsorbents obtained from leaves and barks of plant materials such as neem leaves, bark of babul & maize corn carbon (MCC) are highly encouraged for the decolorization of aqueous solutions of dyed effluents of industries because they are not only cost effective but sometimes more efficient than the commercially available activated charcoal. A combination of anaerobic-aerobic treatments to effluents of textile and paper industries has been recommended because it is more efficient both in terms of pollution reduction & operational cost. The degradation of textile dyes can also be carried out by bioremediation using individual bacterial strains, mixed cultures of bacteria or by advanced oxidation processes. However, studies have revealed that the decolorization of dyed textile

effluents by using mixed cultures of bacteria is more effective than by using the individual strains of bacteria. Degradation of dyes by mixed cultures enhances the decolorization process because the individual strains attack the dye molecule at different sites or the decomposed products produced by one strain will be further decomposed by another strain. Advanced oxidation processes are more promising treatment techniques as these processes can be used to oxidise the more complex organic compounds due to the production of highly reactive OH° radicals which have the potential of destroying the components that are very hard to be oxidized. The production of OH° radicals can be accelerated by combining various systems like UV/catalyst, UV/catalyst/H₂O₂ (semiconductor photocatalysis), UV/O₃, UV/H₂O₂, O₃/H₂O₂, UV/O₃/H₂O₂, UV/O₃/catalyst, Fe(II)/Fe(III) with H₂O₂ (Fenton reaction), and UV/{Fe(II)/Fe(III)+H₂O₂} (photo-Fenton). The basic advantage of photo-oxidation is that it can take place at any temperature and pressure and does not produce any secondary components to be handled, thus it is the most effective technique.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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