DECOLORIZATION OF PROCESS WATERS IN DEINKING MILLS AND SIMILAR APPLICATIONS: A REVIEW

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Process waters in deinking mills often feature a strong coloration, due to dyes and pigments released from the recovered paper. This can usually be remediated by pulp bleaching treatment with appropriate chemicals. However, the red shade (from rhodamine dye) is resistant to conventional bleaching treatments. This largely limits the use of deinked pulp in white paper grades. In this review, the available technologies for process water decolorization are discussed (chemical methods, physico-chemical methods and biological treatments). Ozonation of the process water appears to be the most promising technique for decolorization of process water in deinking mills. Other emerging technologies such as photo-catalytic treatment or mineralization by white-rot fungi (after adsorption on low-cost agricultural residues) should be considered as well.

INTRODUCTION

Color of process water in deinking mills arises from printing inks pigments and dyes, together with dyes used for tinting and shading paper. Most of these dyes and pigments can be efficiently degraded by conventional bleaching treatments, especially by dithionite bleaching. The main problem arises from the occasional but persistent red shade of process water, which is mostly caused by lithol rubine pigment and rhodamine dye (Muller-Mederer et al. 2001). While lithol rubine can be degraded by dithionite bleaching, rhodamine on the other hand is recalcitrant to conventional bleaching treatments (dithionite, FAS, peroxide) (Carré et al. 2000; Muller-Mederer et al. 2002). This red color limits the use of deinked pulp (DIP) in graphic papers. Therefore, reduction or elimination of rhodamine from the deinking process waters could increase usage of DIP and improve recyclability of printed products.

This review deals with color stripping techniques for effluents and process water; such techniques may be applied to decolorize process water in DIP circuits. Most of these techniques have been developed for the textile industry, which has to deal with large volumes of dyed effluent. The emphasis is put on methods that can degrade rhodamine dye, as it is at the origin of most color-related problem in DIP process water, and it is recalcitrant to conventional bleaching. As a starting point, a quick review of color stripping chemicals used for bleaching recycled pulp is presented.

ORIGIN OF COLOR IN DEINKING MILLS PROCESS WATERS

The color of deinked pulp results primarily from either pigmented inks or dyes. Pigmented inks are added mainly at printing, whereas dyes are mainly added during paper manufacturing for either tinting (high applied dosage, to produce colored paper) or shading (low applied dosage, combination of dyes to adjust or control DIP shade). Dyes are also sometimes part of pigmented inks formulation to enhance their color.

Dyes are made of conjugated molecules that give them their color. The color depends on the number and type of conjugated bonds. Most dyes contain aromatic, carbonyl, and azo groups as well. Decolorization involves breaking at least one of the conjugated bonds.

The most commonly used dyes in tinting paper are direct dyes. They are water-soluble anionic dyes and have high affinity with cellulosic fiber (in the presence of electrolytes), which is why they are sometimes called substantive dyes. They are mostly used to dye chemical pulp fibers. They may be cationized to improve their affinity with fibers. Generally, direct dyes are polyazo compounds. As an alternative, basic dyes are sometimes used, especially for dying of mechanical pulp, or in printing inks. Basic dyes are salts of different organic substances. They possess a cationic charge. Basic dyes attach readily to lignin-containing fibers (mechanical pulps, unbleached sulphate pulp, and semi-chemical pulp). Their chemical structure is variable, typically being based on triphenylmethan derivatives, cyanine, thiazine, or xanthene.

As mentioned in the introduction, DIP process waters show an occasional but persistent red shade, mostly caused by lithol rubine pigment (PR 57:1) (together with Red lake C (PR 53:1) and Fast scarlet BBN (PR 48:1)). In addition, rhodamine dye (a basic dye) used for either color enhancement of pigment inks, or dying of rotogravure inks, is also found in process water (Muller-Mederer et al. 2001). Their chemical structures are given in Fig. 1.
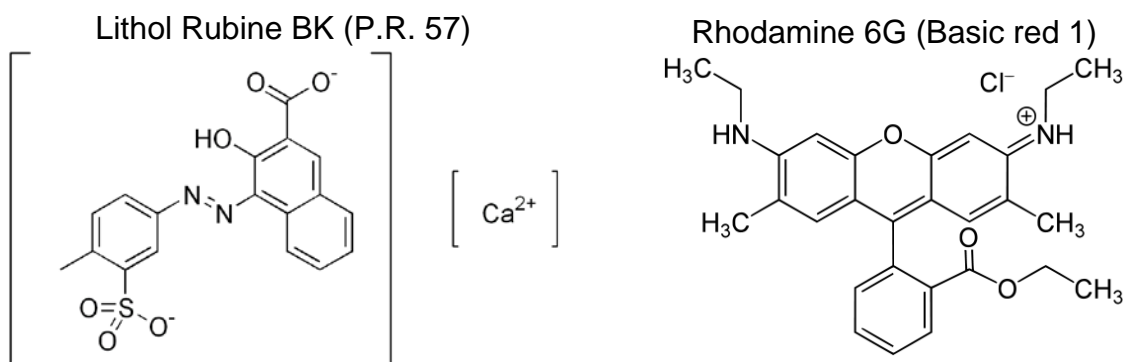

Fig. 1. Chemical structure of most frequent red colored compounds in DIP process water

COLOR STRIPPING IN RECYCLED PULP

Efficient color stripping of recycled pulp bleaching can be achieved by applying ozone (Kogan and Muguet 1992) (Muguet and Kogan 1993), usually with better results at

medium or low consistency (Magnin et al. 2000). Ozone has been shown to be efficient as a color stripping agent in recycled pulps against a wide spectrum of paper colorants (Karp and Trozenski 1996). Also, ozone can destroy optical brighteners, which have a chemical structure close to that of anionic direct dyes (typically di-amino-stilbene-n sulfonic acids) (Kogan et al. 1994; Patt et al. 1996; Magnin et al. 2000). Ozone bleaching works best at acidic pH; however (Kogan et al. 1994) have shown that ozone is efficient as a color stripping agent in alkaline conditions as well (up to pH=10), as this favors generation of highly reactive hydroxyl radical (very efficient but less selective than molecular ozone towards unsaturated bonds). Magnin and Angelier (1997) showed that a bleaching sequence consisting of an ozonation at low concentration (performed at slightly alkaline pH) followed by a peroxide stage was the best sequence to decolorize a floated pulp slurry made of SC paper printed with rhodamine gravure ink (among various oxidative and reductive bleaching sequences including P, D, Z, Y, FAS, and peracids stages); the red shade of the pulp was however not totally destroyed by this treatment, performed in presence of high ink load. To date, the use of ozone has not played any significant role in the bleaching of deinked pulp. That is partly due to the fact that ozone's reaction with mechanical pulp fraction causes pulp darkening (Szadeczki et al. 1997), and also because ozone may decrease mechanical properties of the wood-free pulp fraction (van Lierop and Liebergott 1994; Patt et al. 1996).

Chlorine dioxide has been reported to be a very efficient chemical for color stripping in recycled pulp (Sharpe and Lowe 1993; Magnin et al. 2000) and fluorescence destruction (Quinnett and Ward 1995). However chlorine dioxide has not gained acceptance as a bleaching chemical in recycled fiber mills.

Hydrogen peroxide usually has little color stripping ability when used as recycled pulp bleaching agent (van Lierop and Liebergott 1994; Patt et al. 1996; Magnin et al. 2000). Combination with oxygen provides no benefit for color stripping of pulp (Marlin et al. 2003).

Dithionite, a reducing agent, remains the most effective color stripping agent in recycled pulp (Dumont et al. 1994; Fluet and Shepperd 1997; Magnin et al. 2000; Carré et al. 2000). Formamidine sulphinic acid (FAS) also provides good color stripping ability in recycled pulps (Kronis 1992).

DECOLORIZATION METHODS FOR PROCESS WATERS

Chemical Methods
Oxidative chemicals

Ozone is an extremely strong oxidant (E° = 2.07 V) and reacts rapidly with most organic compounds. It is now widely accepted that ozone reacts in aqueous solution with various organic and inorganic compounds, either by a direct reaction of molecular ozone or through a radical type reaction involving the hydroxyl radical produced by the ozone decomposition in water. Ozone and hydroxyl radicals generated in aqueous solution are able to open the aromatic rings. The ozone molecule is selective and attacks preferentially the unsaturated bonds of chromophores, resulting in efficient color stripping.

Ozone efficiently decolorizes effluent; however the organic load is only partially decreased, and this is largely dependent on the type of dye (Soares et al. 2006; Faria et al. 2005; Sarayu et al. 2007). That is partly due to the formation of by-products during ozonation of the dye (such as organic acids, aldehydes, and ketones). Those final by-products are usually biodegradable (at least more biodegradable than the original dye). However, intermediate ozonation by-products can show high toxicity, also depending on the type of the treated dye (C. Wang et al. 2003; Muthukumar et al. 2005).

Archibald and Roy-Arcand (1997) have shown that ozone can be efficient at degrading typical dyes directly in paper machine whitewater. Ozonation of dyes in white water was however less efficient than in pure water.

Under model lab scale conditions ozone can degrade both rhodamine 6G (Menéndez et al. 2005) and rhodamine B (Yamashita and Akashi 2008). Ozonation of red-shaded biologically purified effluent suggested that ozone may degrade rhodamine based dye in industrial effluents (Öller et al. 1997). Good decolorization (close to 100%) of red-shaded DIP mill effluents have been obtained by applying 60 mg/L of O_3 (Pisicchio et al. 1997), also suggesting that ozone may degrade rhodamine and/or lithol rubine under industrial conditions.

Degradation kinetics of dyes by ozone appear to be quite fast; a comparison for ozonation of various dyes showed half-life times of about 1 min for rhodamine (Menéndez et al. 2005), 2 min for a selection of acid and direct dyes (Soares et al. 2006), and 4 to 6 min for an acid orange dye (Hsing et al. 2007). On the other hand, (Struga 2007) reports similar half-life times for various extractives (fatty and resin acids, lignans, triglycerides, and sterol esters), so that ozone will degrade them at the same rate as dyes.

Thus, in DIP process waters, ozone may react with various dissolved and colloidal substances. Dissolved organic matter such as fatty acids, their esters, and resin acids are usually very efficiently degraded by ozone (Roy-Arcand and Archibald 1996; Reynolds et al. 1989). Carbohydrates will be degraded to a lesser extent (Parthasarathy and Peterson 1990), with possible generation of anionic structures (Katai and Schuerch 1966). Synthetic surfactants will be degraded as well (Gieldowska-Bulska et al. 2004; Ikehata and El-Din 2004), which is anticipated to be beneficial for the flotation efficiency, but may release toxic by-products (Ledakowicz et al. 2005).).

Fenton's reagent (H_2O_2-Fe(II) salts) can efficiently remove color from effluents. (Kuo 1992) showed that decolorization of most commercial dyes of the acid, basic, and direct classes is usually very high (>95%); however rhodamine was not tested in this study. Redox reactions generate the hydroxyl radical, which attacks un-saturated dyes. Fenton's reagent works best in acidic media (pH<3.5), which is not compatible with alkaline DIP process water containing calcium carbonate filler. COD is also efficiently reduced in parallel. In optimized conditions, treatment of dyes with Fenton's reagent has been shown to be more efficient than ozone or electrochemical processes (Szpyrkowicz et al. 2001; Hsing et al. 2007). The main drawback is that this process generates a large quantity of sludge, as the ferric complexes tend to flocculate the dye molecules; those sludges require special handling. The floc formation and settling behavior depend on the nature of the dye (anionic/cationic) (Robinson et al. 2001).

Reductive chemicals

Treatment with strong reducing agents, such sodium borohydride or sodium dithionite, can significantly reduce color in dye effluent. These compounds chemically break the N=N double bond of azo dyes and produce lower molecular weight aromatic amines (potentially carcinogenic (Chung 1983)). Dithionite has been used successfully to decolorize white water in a yellow directory production (Dumont et al. 1994). The use of bisulfite-mediated borohydride reduction for the decolorization of wastewaters containing azo dyes (from a dye manufacturing plant) has had limited commercial success (Cook 1996). Other studies show that reducing agents (sodium dithionite, thio-urea peroxide, and sodium borohydride) were effective in eliminating color in textile plants, but produced a wastewater which was inhibitory to further biological (aerobic) treatment (McCurdy et al. 1991). Further addition of H_2O_2 partially remediated the problem. Treatment of large quantity of effluent with these methods is not economically attractive in the textile industry.

Marlin et al. (2009) claim that a hot alkali stage (90°C, pH=12) can cause color stripping of dyed effluents, in the presence of cellulose. This color stripping effect may be explained by the reduction of the direct dyes by carbonyl functions liberated during cellulose degradation in strong alkaline conditions.

Photo-chemical treatments

This treatment involves creation of reactive hydroxyl radicals by means of UV illumination, which efficiently degrades dye molecules to CO_2 and H_2O. This can be achieved directly from H_2O_2 (Robinson et al. 2001). In some conditions the H_2O_2/UV light system can degrade rhodamine dye to some extent, but ionic contaminants such as chloride, carbonate, or sulphate hinder the dye degradation process (AlHamedi et al. 2009).

Besides, photo-catalytic oxidation with TiO_2 is an emerging and interesting option (Konstantinou and Albanis 2004). The UV photons excite TiO_2, which then reacts with water molecules or hydroxide ions to produce hydroxyl radicals. Dyes adsorbed at the surface of TiO_2 will then be degraded (Liu and Zhao 2000). This technology looks promising for treatment of textile dye effluents (Peralta-Zamora et al. 1999; Tanaka et al. 2000).

Interestingly, heterogeneous photo-catalytic treatment with TiO_2 particles has been shown to degrade rhodamine dye, which is recalcitrant to typical bleaching treatments. Jain et al. (2007) have reported effective destruction of rhodamine B with a TiO_2+UV illumination treatment (anatase powder, size =44 µm, 6gTiO_2/g rhodamine, at 30°C, UV illumination (254 nm) for 1 h). Better degradation efficiency was observed at alkaline pH. The presence of H_2O_2 as an electron acceptor was beneficial. The use of nano-TiO_2 crystallite can totally destroy rhodamine B in less than an hour (Asiltürk et al. 2006).

In addition, TiO_2 catalyst can be immobilized on a substrate, therefore eliminating the need to recover the TiO_2 in water streams. Good results have been obtained for degradation of rhodamine B with TiO_2 coated on non-woven paper substrates (Barka et al. 2008) or on polyester fabric (Böttcher et al. 2010).

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Photo-catalytic activity of TiO_2 against rhodamine B has been observed also under visible light illumination (F. Zhang et al. 1997), but with much lower degradation yield and slower kinetics (19% color removal over 24 h, with 52 g TiO_2/g dye, with specific surface = 55 m²/g). Under visible light illumination, the degradation mechanism is different. It is the dye itself that is excited by visible light, then it excites the TiO_2 when adsorbed at its surface, and then it finally undergoes degradation (Epling and Lin 2002). A synergistic effect of some heavy metal ions has been reported: the presence of Cr(VI) ions boosted the degradation of rhodamine B by TiO_2 under visible light illumination (Kyung et al. 2005).

However, use of TiO_2 is not economical for large-scale water treatment. Cheaper alternatives include treatment with ZnO as a photocatalyst. Kansal et al. (2007) showed that ZnO is actually more efficient than TiO_2 as a photocatalyst, and works even better with sunlight illumination (as it has a wider spectrum of absorption than TiO_2). Rhodamine 6G was efficiently destroyed with a ZnO/sunlight treatment (near 100% color stripping at pH=10, for 3h, with 20 g ZnO/g rhodamine, specific surface ZnO =5 m²/g). ZnO/sunlight treatment can also destroy rhodamine B under similar conditions, and lead to total mineralization of the dye (no by-products remaining) (Byrappa et al. 2006). Also, the ZnO catalyst powder can be recycled to the process several times (Byrappa et al. 2006).

The use of ZnO or TiO_2 as photocatalysts has been shown to be more efficient than ozonation for dye destruction (Peralta-Zamora et al. 1999).

Depending on the nature of the attacked dye, several by-products may be formed, if the mineralization is not complete. As an advantage, no sludge is produced.

Electro-chemical destruction

Although some electrochemical processes involve the direct oxidation of dyes at anode surfaces, most processes actually generate active species that react with dye molecules and degrade them.

Electro-chemical treatment involves treating the effluent in an electrolytic cell (using Ti/Pt as anode and Stainless Steel 304 as cathode, with added sodium chloride as an electrolyte if necessary). The dye destruction is usually very good. That is explained by the strong oxidizing potential of the chemicals produced (chlorine, oxygen, hydroxyl radicals, and other oxidants) (Szpyrkowicz et al. 2000; Vlyssides et al. 2000), so that COD of effluent is largely reduced as well. This electrochemical technique has many advantages, as there is no consumption of chemicals and no generation of sludges. The cost of electricity is generally comparable to the price of chemicals from typical methods (0.5 EUR/kg dye). In some cases, organo-chlorinated by-products may be formed (Chatzisymeon et al. 2006). Electro-chemical destruction can be coupled with photo-catalysis with special TiO_2-coated electrodes (Pelegrini et al. 1999).

Physico-Chemical Treatments
Adsorption

Dyes may be removed from process water by adsorption on solid material. The sludges then need to be handled and treated, for further degradation and/or regeneration.

Dyes adsorption may occur by true sorption but also often by an ion exchange mechanism, so that pH of the effluent may affect adsorption rate (Robinson et al. 2001).

   The oldest and most efficient adsorbent is activated carbon. Because of its porous structure and large surface area, it can adsorb large amount of dyes (Al-Degs et al. 2000). However, treating large flows of waste water with activated carbon is not a cost effective method.

   Besides activated carbon, a number of low-cost adsorbents (including some agricultural residues, such as wheat straw or rice hulls) show good adsorption efficiency for industrial dyes (Gupta and Suhas 2009). Bagasse fly ash, a waste generated in sugar industries in India, has been converted into an inexpensive adsorbent material and utilized for the removal of two basic dyes, rhodamine B and methylene blue (Gupta et al. 2000). Also, coir pith carbon (a residue from coconut processing) can efficiently adsorb rhodamine B (Namasivayam et al. 2001). Neutral red (cationic dye) can be adsorbed on spent corncob substrate (used for mushroom cultivation in China) (Yu et al. 2011).

   Basic dyes may be adsorbed on activated sludge (Chu and Chen 2002; Gulnaz et al. 2004).

   Most dyes can be adsorbed on cellulosic ion exchangers (quaternized for better efficiency); however the exchanger then needs to be regenerated by various techniques (bisulfite-mediated borohydride reduction (Laszlo 1997) or anaerobic dye reduction (Laszlo 2000)).

   Bentonite (native or modified) is widely used in waste water treatment, as an adsorbent and in association with flocculation polymers (Beall 2003), as well as in dissolved air flotation treatment (Richardson and Grubb 2004). Interestingly, basic dyes in general may be adsorbed on montmorillonite particles (Hu et al. 2006; Wang et al. 2004); this was also efficient for both rhodamine G (Yagubov et al. 2010) and rhodamine B (Hou et al. 2010). Dye adsorption on bentonite may be combined with ultra-filtration for improved color removal, however decreasing the flux of permeate (Al-Bastaki and Banat 2004).

Membrane filtration

   A membrane filtration technique can efficiently remove most commercial dyes from effluents (Marmagne and Coste 1996; Fersi et al. 2005), while providing clean water that can be recycled to the process. However they are non-destructive methods, so that dyes are just concentrated in the residue, causing secondary pollution that must be handled, without possibilities to recycle it for further uses. Ultra-filtration removes most dyes, however low molecular weight dyes may pass through the membrane, so that nano-filtration may be required in some cases. Fouling of the membrane is a problem as well. The major drags for the use of UF and NF in the pulp and paper industry have been low fluxes and membrane fouling (Nuortila-Jokinen et al. 2003). Higher fluxes can be obtained with a cross-rotational filter (CR), together with less frequent need for membrane backwashing (Mänttäri and Nyström 2003).

   The membrane bio reactor (MBR) is an interesting technology combining the biological degradation (usually conventional activated sludge process) with membrane filtration (Judd 2011). MBR is efficient for wastewater treatment, and it has been successfully tested to treat textile dyed effluents (Brik et al. 2006), possibly using white

rot fungi (Hai et al. 2006). However membrane fouling limits the use of MBR technology (Le-Clech et al. 2006). To our knowledge, MBR systems have been installed in two papermills waste water treatment in France, but at least one of them had to be abandoned because of membrane fouling and scaling problems.

Electro-chemical coagulation

In electro-chemical coagulation, aluminum and iron sheets are used as consumable anodes to generate coagulants that adsorb and remove dyes (Yang and McGarrahan 2005). Aluminum coagulation involves adsorption only (there is no degradation of the dye), while ferrous ions generated in iron-based coagulation may further degrade the dye. The main drawback of this method is the generation of sludges to be handled (Robinson et al. 2001).

Flotation

Flotation can remove a large fraction of pigments, and dyes to a lower extent (Carré et al. 2000). However, rhodamine is not affected by flotation, so that its fraction increases compared to other colored materials, and this effect increases the red shade of pulp and process water. Micro-flotation of process water loaded with rhodamine (using appropriate chemistry: polyaluminumchloride + anionic polyacrylamide/acrylate, as rhodamine is cationically charged) makes it possible to remove a fraction of rhodamine; however the red shade was only slightly diminished (Muller-Mederer et al. 2002).

Flotation is currently not proposed as an effluent decolorization technique in the textile industry.

Biological Treatments

Anaerobic treatments

Azo dyes, which are the most widely used dyes in industries, are not effectively degraded by aerobic treatment (Forgacs et al. 2004), and may even be toxic to activated sludges. However, their color can be efficiently removed by an anaerobic step (Manu and Chaudhari 2003). Anaerobic degradation yields only azo reduction, so that mineralization does not occur. This often results in toxic and colorless aromatic amines (Maas and Chaudhari 2005), with mutagenesis and carcinogenesis potential (Chung 1983). The mechanisms of degradation (reduction) by anaerobic treatment and formed compounds are similar to those of reductive treatments such as dithionite. Since these by-products are resistant to anaerobic biodegradation, a further aerobic phase is therefore essential for complete biodegradation. Careful toxicity monitoring of these effluents is required (Alves de Lima et al. 2007). Moreover, rapid fluctuation in dye type and concentration in effluents can lead to severe inhibition of microbial activity.

Combined biological treatments (anaerobic, then aerobic), with some physico-chemical pre-treatments are the most economical ways to decolorize dyed effluents to date (Banat et al. 1996; Robinson et al. 2001). However, DIP process waters are generally not concentrated enough for a methanisation stage to be efficient.

White-rot fungi and enzymes

White-rot fungi have the ability to degrade lignin in wood and also several xenobiotics compounds, including synthetic dyes. Earlier work has been performed based on *Phanerochaete chrysosporium* and *Trametes versicolor* (Chander and Arora 2007). Other strains (such as *Dichomitus squalens, Irpex flavus, Daedalea flavida,* and *Polyporus sanguineus*, among others) have recently been identified to provide a better decolorization rate (Asgher et al. 2008). *Phanerochaete chrysosporium* produces an enzymatic system that can decolorize several industrial dyes (Kirby et al. 1995). The different isoenzymes of lignin peroxidase produced by *Phanerochaete chrysosporium* are able to decolorize several dyes with different chemical structures, including azo, triphenylmethane, heterocyclic, and polymeric dyes (Ollikka et al. 1993). Some azo dyes resistant to lignin peroxidase may be degraded by laccase systems, such as produced by other lignolytic fungi *Pyricularia oryzae* (Chivukula and Renganathan 1995), *Pleurotus ostreiformis* or *Trametes hispida* (Rodríguez et al. 1999). Laccase has been shown to efficiently decolorize inkjet prints (Nyman and Hakala 2011). Furthermore, laccase oxidation by fungi can result in the detoxification of azo dyes, as no aromatic amines are formed, the azo bond being degraded to molecular nitrogen. Detoxification effects have also been observed with lignin peroxidase from *Phanerochaete chrysosporium* (Spadaro et al. 1992; Kunz et al. 2001). The use of fungi in their natural environment is more effective against dyes than treating with purified enzyme solutions.

CONCLUSIONS

The color of DIP process water arises from printing inks pigment and dyes, together with dyes used for tinting and shading paper. Most of these dyes and pigments can be efficiently degraded by conventional bleaching treatment, especially by dithionite bleaching. The main problem arises from the occasional but persistent red shade of process water, caused by lithol rubine pigment and rhodamine dye. While lithol rubine can be degraded by dithionite bleaching, rhodamine on the other hand is recalcitrant to conventional bleaching. Comparison of the main decolorization technologies for process water is summarized in Table 1.

Ozone treatment of process water appears to be the most promising treatment to efficiently decolorize DIP process water, as it can degrade most dyes (including rhodamine). Besides, applying ozone on water (instead of pulp) would limit side reactions with mechanical pulp (observed in DIP bleaching applications). However, this will not degrade rhodamine adsorbed on fibers. Possible side reactions with dissolved matter may increase ozone consumption. As a bonus, ozonation of DIP process water would contribute to pulp sterilization and limit ageing problems of DIP in storage tower. Ozone treatment requires only moderate capital investment (compared to chlorine dioxide for instance), and can be produced on demand, depending on process water shade. Ozone may also be bought "over the fence", at no capital cost but higher prices. The technico-economical balance of implementing an ozonation treatment of DIP process waters must take into account all these various aspects.

Electro-chemical coagulation techniques are also well proven processes to remove dye from effluents, which may be used in process water. The major drawback is the generation of sludges, and possible destabilization of process water, if applied directly in DIP circuits.

An exciting way to degrade dyes in process water would be photo-catalysis (with TiO_2/UV or ZnO/visible light as cheaper alternative). This technique can totally mineralize dyes, without addition of chemicals and without generation of sludge (only water and carbon dioxide). Immobilization of the catalyst on fabrics offers promising ways to treat water flows. The feasibility of an industrial implementation of such a photo-catalytic treatment for processing large scale flows remains to be validated.

Finally, an interesting low cost alternative combining several treatment methods has been suggested by (Robinson et al. 2001). It involves adsorption of dye from the effluent on a low cost adsorbent (selected from various agricultural residues for instance). Then this sludge can be degraded and mineralized by white-rot fungi, in solid state fermentation. The residue of this process can then be safely used as natural soil fertilizers.

Table 1. Comparison of Main Decolorization Technologies for Process Water

Technology	Pros	Cons
Ozonation	• Degrades all dyes (including rhodamine) • Sterilization • Proven technology • Quick reaction time • On-demand production and treatment	• Reaction by-products (toxic ?) • Little selectivity (reaction with other soluble substances) • Cost
Electro-chemical coagulation	• Efficient decolorization • Proven technology	• Sludge generation • Destabilization of process waters
Photo catalysis	• Degrades all dyes (including rhodamine) • Total mineralization of dyes (no by-product) • No sludge generation • No chemical addition	• Difficult recovery of catalyst (if not immobilized) • Cost • Emerging technology
Bio sorbents	• Valorization of bio-waste as adsorbent • Low cost	• Sludge generation • No degradation of dyes • Emerging technology
White rot fungi	• Efficient decolorization • Total mineralization of dyes (no by-product) • Low cost	• Sensitive to water quality changes • Long reaction time • Still emerging technology

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