

TEXTILES

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The present paper reviews literature on textile wastewater treatment and reuse published during the year 2003. Particularly, after a brief introduction, different alternative technologies employed for textile wastewater treatment and/or reuse are presented grouped into physical-chemical and biological processes.

Introduction

In recent years, corporate management strategies have been confronted with a number of environmental challenges. Firms who do not recognize the implications of environmental management strategy on the business operation will not gain comparative advantage in the market competition. A study was carried out addressing how to optimize a textile dyeing manufacturing process based on the best integration of waste minimization alternatives, the new environmental regulations and the limitation of production resources. The study covered not only the production costs and the incomes from product sale, but also the emission/effluent charge and water resources fees required by new environmental regulations (Wu and Chang, 2003).

Physical-Chemical processes

Coagulation and electrocoagulation

The mechanism of dye removal from textile wastewater using a poly-quaternary ammonium salt as a flocculant was proposed. It was shown that the cationic polymer

tends to react with anionic textile finishing chemicals and auxiliaries, forming intermolecular complexes which incorporate the dye ions or molecules and precipitate together (Zemaitaitiene et al., 2003). Treatment with lime alone proved to be very effective in removing color (70-90%) and part of the chemical oxygen demand (COD) (50-60%) from a textile wastewater, whereas the treatment with ferrous sulfate, regulating pH in the range 9.0 ± 0.5 using lime, was equally effective. Finally, the application of lime in the presence of increasing doses of ferrous sulfate was tested successfully and proved to be very costly, mainly due to the massive solids production (Georgiou et al., 2003).

It was shown that in the treatment of simulated textile wastewater, prepared from Remazol Red RB textile dye, using aluminum ions as coagulant-flocculant, the optimum conditions were low temperature (273 K), surfactant concentration of 0.10 g/L, electrolyte concentration of 0.10 g/L, dye concentration of 0.025 g/L, pH of 10.05. Under such conditions the mean settling velocity was 0.014 m/min whereas the mean sludge volume index was 140 mL/g (Gürses et al., 2003).

The color of Orange II in aqueous phase was effectively removed (over 98%) and also the COD was reduced (over 84%) by electrocoagulation, when iron was used as sacrificial anode and the concentration of the color was less than 200 mg/L. The optimum current density was found to be 34.62 A/m^2 (Daneshvar et al., 2003a). The use of iron and aluminum as sacrificial electrode materials in the treatment of textile wastewater was found to be pH-dependent. For pH below 6, COD and turbidity removal efficiencies of aluminum were higher than those for iron, while in neutral and alkaline conditions, iron was preferable. For the same turbidity or COD removal efficiencies, iron

required lower current density than aluminum and lower energy consumption per COD unit removed, while the electrode consumption was generally lower with aluminum (Kobyta et al., 2003).

Adsorption

The investigation on the ability of natural and modified sepiolite to uptake Everzol Black B, Everzol Yellow 3RS H/C and Everzol Red 3BS dyes showed that the maximum sorptive capacity of natural sepiolite was very low (around 0.1-1 mg/g) whereas, on the contrary, it was ten times higher for the modified sepiolite (Armagan et al., 2003). It was demonstrated through batch experiments that the sorption capacity of hydrotalcite for the removal of a reactive color, Cibacron Yellow LS-R, was relatively high for most experimental conditions. No single kinetic model could fully describe the sorption process at all times: at least three independent rate-controlling mechanisms appeared to compete with each other and dominate the different stages of sorption (Lazaridis et al., 2003). Surplus biological sludge from wastewater treatment plant was converted into activated carbon (SB AC) by thermal treatment in the presence of sulphuric acid, with a significant increase in surface area compared to the raw sludge, and then used more effectively than commercial activated carbon in removing acid and direct dyes from solution, due to its wider pore size distribution. For equilibrium pH values between 5 and 9, the adsorption capacity of SB AC for dyes was significantly modified due to the presence of ionizable surface functional groups (Martin et al., 2003).

Activated carbon produced from chemical activation and pyrolysis of sewage sludges was able to adsorb methylene blue and safranin from solution, in both batch and fixed bed systems. Nevertheless, methylene blue adsorption occurred faster than that of

saphranine, and it was preferably adsorbed when treating binary solutions in which both adsorbates were present together with activated carbon (Rozada et al., 2003). Activated carbon, prepared from agricultural solid wastes, silk cotton hull, coconut tree sawdust, sago waste, maize cob and banana pith, removed heavy metals and dyes from aqueous solution within very short time (Kadirvelu et al., 2003).

The equilibrium and the dynamics of the adsorption of Reactive Red 189 (RR 189) on chitosan beads ionic cross-linked by tripolyphosphate was investigated. A very high adsorption capacity to remove dye RR 189 was found; the Langmuir model agreed very well with the experimental data and its calculated maximum monolayer adsorption capacity was greater than 1800 g/kg at pH 3.0, and 30 °C (Chiou and Li, 2003).

The surface chemistry of a commercial activated carbon was selectively modified, without changing significantly its textural properties, by means of chemical treatments, using HNO₃, H₂O₂, NH₃, and thermal treatments under flow of H₂ or N₂. The resultant samples were characterized in terms of their surface chemistry and textural properties, and subsequently tested in the removal of different classes of dyes. The basic sample obtained by thermal treatment under H₂ flow at 700 °C was found to be the best material for the adsorption of most of the dyes tested (Pereira et al., 2003).

The thermally charred dolomite was demonstrated through batch experiments to have the potential to act as an adsorbent for the removal of Brilliant Red reactive dye from aqueous solution. The removal was heavily dependent on both the external mass transfer and intra-particle diffusion (Walker et al., 2003).

Metal hydroxide sludge, a waste from the electroplating industry, was an effective positively charged adsorbent with a high maximum adsorption capacity (48-62 mg/g) for

azo reactive dyes and a short contact time. The maximum color removal was reduced as the number of sulfonic groups on the dyes decreased (Netpradit et al., 2003).

The adsorption of Reactive Blue 114 (RB114), Reactive Yellow 64 (RY64), and Reactive Red 124 (RR124) by calcined alunite was studied by varying parameters such as the calcination temperature and time, particle size, pH, agitation time and dye concentration. Acidic pH was favorable for the adsorption of RB114 and alkaline pH was favorable to both RY64 and RR124. The equilibrium data fitted the Langmuir isotherm and the adsorption capacity was found to be 170.7, 236 and 153 mg/g for RB114, Ry64 and RR124, respectively (Özacar and Sengil, 2003).

Both basic (cationic) as well as acid (anionic) dyes could be sorbed onto brown coal fly ashes, with the adsorption process described by the multi-site Langmuir isotherm. The dye sorption was influenced significantly by the presence of organic solvents (methanol, acetone) and by pH, whereas the presence of inorganic salts exhibited only minor effect (Jano_ et al., 2003).

Three reactive dyes (Reactive Blue 19, Reactive Red 241 and Reactive Yellow 145) were rapidly adsorbed by the mycelium pellets of *Penicillium oxalicum*. The pellets exhibited high adsorption capacity (80-180 mg/g) for all of the three dyes over a wide pH range (2-10); the maximum adsorption was obtained at pH 2 (Zhang et al., 2003).

Decrystallized chitosan, produced from shrimp shells with a low degree of crystallinity (10%), was more efficient than normal chitosan and activated carbon for the decolorization of raw, mixed dye wastewater from a textile factory. Decolorization reached 90% within 10 min and could be carried out from pH 4.5 to 8.1 (Trung et al., 2003). The hydrogel systems poly(N-vinyl-2-pyrrolidone) and poly(N-vinyl-2-

pyrrolidone)/K₂S₂O₈ were employed for diffusion and swelling experiments in various textile dyes aqueous solutions (textile dyes such as Cibacron Blue (CB), F3GA, Methyl Orange (MO), Congo Red (CR)). The swelling percentage was found to increase in the following order: MO>CB>F3GA>CR at fixed dose 96kGy (Can et al., 2003).

Advanced oxidation

The decolorization of direct dye (Isma fast red 8B) by ozone in a batch bubble column reactor was found to be an efficient technique for textile dyeing wastewater treatment. The rate of dye oxidation increased with increasing ozone concentration in the gas phase and/or solution pH, and with decreasing the dye concentration. Furthermore, the decolorization breakdown products were found to be non toxic (Konsowa, 2003). Ozonation was demonstrated to be a potential technique for decolorization and biodegradability enhancement of wastewater containing reactive azo dyes, provided that the appropriate ozonation period is chosen. For instance, the short-term ozonation, with a 1/3 contact time of the total period, resulted in a significant increase of toxicity caused by first toxic by-products, whereas the long-term ozonation caused an appreciable enhancement of microbial biodegradability and a decrease of toxic intermediates (Wang et al., 2003). The potential advantages of membrane contactors for the ozone treatment of textile wastewater was experimentally demonstrated. Ceramic membranes (α -Al₂O₃) were chosen because of their ozone resistance and were covered with a thin metal oxide (TiO₂ and γ -Al₂O₃) to eliminate large defects (Ciardelli et al., 2003).

A kinetic model for the decolorization of C. I. Reactive Black 5 by the combination of hydrogen peroxide and ultraviolet (UV) radiation was developed based on

experimental results and known chemical and photochemical reactions. The decolorization rate followed pseudo-first order kinetics with respect to the dye concentration and increased linearly with UV intensity and nonlinearly with increasing hydrogen peroxide concentration (El-Dein et al., 2003). The use of H₂O₂ alone was not able to bring about any color removal, whereas the use of UV treatment alone showed different results depending on the water samples treated: a significant color removal was obtained for the secondary effluent from a wastewater treatment plant treating mainly textile industrial water and for a synthetic wastewater made by adding direct azo dye to a demineralized water; conversely, very low efficiency was achieved for color removal from a synthetic wastewater made by adding direct azo dye to a well water. However, the combined UV-H₂O₂ process showed very good results regarding both color removal and degradation of organic compounds, for all of the water samples tested (Caretto et al., 2003).

The cobalt(II)/ascorbic acid/hydrogen peroxide system was used for decolorization of azo, acridine, anthraquinone, thiazine and triphenylmethane dyes. More than 90% decolorization was obtained with all dyes except Remazol Brilliant Blue R (75%); with other transition metals the system was less efficient (Verma et al. 2003).

Two commercial dyes viz., Red M5B and Blue MR, and H-acid, a dye intermediate, could be decolorized and mineralized by the Fenton's process with the rate of oxidation being influenced by the dose of Fe²⁺, H₂O₂, pH and contact time. The optimum conditions required for maximum degradation were: pH 3.0, Fe²⁺ concentration of 10-25 mg/L, and H₂O₂ dose of 400-500 mg/L (Swaminathan et al., 2003). The Fenton's reagent method was confirmed to be a suitable system for decolorization of

two direct dyes, Blue 54 and Red 31, and occurred through a two stage reaction: in the first stage, which took place before the first minute, the reaction rate was very rapid and was a $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ reaction; in the second stage, which took place after the first minute, the decomposition rate was slower and was a $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ reaction (Malik and Saha, 2003). The degradation of two azo reactive dyes, C.I. Reactive Yellow 84 and C.I. Reactive Red 120, by photo-Fenton and Fenton-like oxidation was investigated in a laboratory scale set-up with the most favorable system conditions for both dyes being: pH 3.0, $\text{H}_2\text{O}_2/\text{Fe(II)}$ 20/1 and UV or solar irradiation (Neamtu et al., 2003).

The simultaneous utilization of UV irradiation with Fenton's reagent increased the degradation rate of Direct Yellow-12 (DY12) which quickly reduced its intensity along with an appreciable decrease in COD value, indicating that the dissolved organics were oxidized. The results showed that the degradation was dependent upon pH, UV intensity, concentration of Fenton's reagent and dye (Rathi et al., 2003).

The heterogeneous catalytic degradation of Indigo Carmine (IC) dye with hydrogen peroxide catalyzed by supported transition metal complexes was successfully demonstrated. In addition to a fast color removal, catalytic oxidation led simultaneously to the degradation of the dye with almost complete mineralization of carbon, nitrogen and sulfur heteroatoms (Gemeay et al., 2003).

Wet air oxidation of a dye solution was performed to assess the efficacy of $\text{CoAlPO}_4\text{-5}$ and CeO_2 as catalysts in the reaction. Via adsorption and oxidation of dye, $\text{CoAlPO}_4\text{-5}$ effectively decreased color intensity and COD values in the dye solution. At a reaction temperature of 135 °C and an applied pressure of 1.0 MPa, color and COD removal were as high as 95% and 90%, respectively, after 2 h. The CeO_2 catalyst,

calcined from cerium chloride under high thermal impact (type A CeO₂) was very effective in removing color and COD from the solution. This catalyst demonstrated near 100% color removal at temperatures above 135 °C and the COD removal was above 95% at 165 °C (Chang et al., 2003).

Photodegradation

Acid Red 14 (AR14), commonly used as a textile dye, could be photocatalytically degraded using TiO₂ suspensions irradiated by a UV-C lamp (30W). The experiments showed also that TiO₂ and UV light had negligible effect when they were used on their own. The photodegradation of AR14 was enhanced by the addition of a proper amount of hydrogen peroxide, but it was inhibited by ethanol (Daneshvar et al., 2003b). The photocatalytic removal (decomposition+adsorption) of four azo dyes (Reactive Red 198, Acid Black 1, Acid Blue 7 and Direct Green 99) in water was investigated using Tytanpol A11 and Degussa P25 as photocatalysts. A11 photocatalyst had a lower activity in the reaction of photocatalytic decomposition of organic dyes than Degussa P25. The photocatalytic decomposition of the dyes took place on the photocatalyst surface at pH 2, while at pH 12 photocatalytic reaction proceeded via photogenerated hydroxyl radicals for both A11 and P25 (Zielinska et al., 2003).

A continuous flow three-dimensional electrode-packed bed photocatalytic reactor was developed to investigate the feasibility of an electrochemically assisted photocatalytic process in the degradation of Reactive Brilliant Orange K-R dye in 0.5 mmol/L NaCl solution. It was found that the dye could be degraded more efficiently by this photoelectrochemical process than the degradation obtained by photocatalytic oxidation or by electrochemical oxidation alone, in terms of both decolorization and total

organic carbon (TOC) removal (Zhang et al., 2003). TiO₂/UV-based photocatalysis was able to oxidize triazine-containing azo dyes, Procion Red MX-5B and Reactive Brilliant Red K-2G, in aqueous solution, with partial mineralization of carbon, nitrogen and sulfur heteroatoms into CO₂, NH₄⁺, NO₃⁻ and SO₄²⁻, respectively. Cyanuric acid was the final organic product for both azo dyes, showing stable structure for photocatalysis (Hu et al., 2003a).

The photocatalytic degradation of aqueous solutions of Acid Orange 7 was examined with the use of a solar-irradiated TiO₂ catalyst. It was found that the dye adsorbed on TiO₂ and underwent a series of oxidation steps, which led to decolorization and formation of a number of intermediates, mainly aromatic and aliphatic acids. These molecules were further oxidized toward compounds of progressively lower molecular weight and, eventually, to CO₂ and inorganic ions, such as sulfate, nitrate and ammonium ions (Stylidi et al., 2003). The effect of acidity and inorganic ions, which are commonly found in industrial effluent, on the photocatalytic degradation of azo dyes, Procion Red MX-5B (MX-5B) and Cationic Blue X-GRL (CBX) was investigated in UV illuminated TiO₂ dispersions. The results indicated that CBX photodegradation was favored at the surface of TiO₂, while that of MX-5B occurred in aqueous phase. Besides, the inorganic anions affected the photodegradation of dyes by their adsorption onto the surface of TiO₂ and trapping positive hole and •OH (Hu et al., 2003b).

Electrochemical degradation

The performance of the electrolytic decolorization of dyestuff was evaluated with a bipolar packed bed cell (BPBC) using an aqueous solution of Reactive Brilliant Red X-3B as a model compound. The decolorizing load decreased with the increase of packed

layers, and was indifferent to solution pH but increased with cell voltage, water flow rate, dye initial concentration, and addition of NaCl. The specific energy consumption increased with the packed layers, the voltage, dye initial solution, solution conductivity and decreased with water flow rate (Fan et al., 2003).

Contact glow discharge electrolysis (CGDE) of two dyes, weak acid Brilliant Red B and weak acid Flavine G, was investigated under different concentrations, temperature and mediums. The degradation reaction of two dyes followed the first-order law and the addition of catalysts for hydrogen peroxide decomposition increased the degradation rate, with FeSO_4 being the most effective (Gao et al., 2003).

Sonochemical degradation

Degradation of the azo dye Acid Red B (ARB) on MnO_2 in the absence and presence of ultrasonic irradiation (sonication) demonstrated that counterions such as SO_4^{2-} and NO_3^- greatly inhibited the decolorization process; besides, the decolorization on MnO_2 was highly pH dependent, with increasing decolorization efficiencies at decreasing pH values. Since the efficiency was much higher in the presence of ultrasonic irradiation than using MnO_2 alone, it could be concluded that it is feasible to incorporate ultrasonic irradiation and MnO_2 for both decolorization and mineralization of the dye (Ge and Qu, 2003).

Membrane

Ultrafiltration (UF) purification of waters from bifunctional reactive dyes was carried out by polyacrylonitrile (PAN) membranes. The results showed the possibility for retaining reactive dyes by the UF-PAN membranes at a selectivity of 85-90% and sufficient productivity of 30-45 $\text{L/m}^2\cdot\text{h}$ (Petrov and Stoychev, 2003). An organic

nanofiltration membrane with molecular weight cut-off of 400 was used for the separation process to treat a dye mixture containing Reactive Black dye (Cibracon Black B) and Reactive Red dye (Cibracon Red RB). The experiments were conducted in an unstirred batch and rectangular cross flow cell. Separations with retentions up to 94 and 92% of the two dyes were achieved, respectively; besides, a sharp reduction in COD (up to 94%) was also observed (Chakraborty et al., 2003).

Biological processes

White-rot fungi produce various isoforms of extracellular oxidases including laccase, manganese peroxidase and lignin peroxidase (LiP), which are involved in the degradation of lignin in their natural lignocellulosic substrates. This ligninolytic system is directly involved in the degradation of various xenobiotic compounds and dyes. A review was carried out in which the state of the art in the research and prospective use of white-rot fungi and their enzymes (lignin-modifying enzymes, LME) for the treatment of dye containing effluents, were summarized (Wesenberg et al., 2003).

Two yeasts, *Debaryomyces polymorphus* and *Candida tropicalis*, and two filamentous fungi, *Umbelopsis isabellina* and *Penicillium gastrivorus*, could completely decolorize 100 mg/L Reactive Black 5 within 16-48 h. Manganese-dependent peroxidase (MnP) activities between 60 and 424 U/L were detected in culture supernatants of three of these organisms, indicating that the color removal was by enzymatic biodegradation. Extensive decolorization by *D. polymorphus* and *C. tropicalis* was obtained with five other dyes and one anthraquinone dye (Yang et al., 2003).

White rot fungus *Irpex lacteus* was shown to be able to efficiently decolorize the anthraquinone-based Remazol Brilliant Blue R (RBBR) dye in submerged stationary, submerged agitated and cultures immobilized on polyurethane foam and pine wood, with a major role of MnP in biodegradation in stationary cultures (Kasinath et al., 2003). *Rhodobacter sphaeroides* AS1.1737 decolorized more than 90% of several azo dyes (200 mg/L) in 24 h. The optimal culture conditions were: anaerobic illumination, peptone as carbon source, temperature 35-40 °C and pH 7-8 (Song et al., 2003).

A microbial consortium having a high capacity for rapid decolorization of azo dye (C.I. Reactive Red 198, RED RBN) was immobilized by a phosphorylated polyvinyl alcohol (PVA) gel. The immobilized-cell beads exhibited a color removal capability of 75% even at a high concentration of RED RBN (500 mg/L) within 12 h using flask culture, mainly due to the biological process (Chen et al., 2003a).

The study on the treatment of dye industry effluent by mycelia of *Fomes lividus* showed that in batch mode 84.4% of colour was removed from the effluent on day 4 of incubation whereas in a continuous mode only 37.5% at maximum on day 5 (Selvam et al., 2003).

Rhodocyclus gelatinosus (XL-1) successfully decolorized the Reactive Brilliant Blue (KN-R) under anaerobic conditions, using peptone as growth substrate. MgSO₄ and MnSO₄ increased the activity of decolorization, whereas other metal compounds, (e.g. AgNO₃, CuSO₄, etc.), had inhibitory effects (Dong et al., 2003).

Among three strains of white-rot fungi isolated in Singapore, the local isolate *Trametes versicolor* CNPR 8107 was found to be effective in treating dye effluents, after

an initial lag period due to a low laccase production. Besides, CNPR 8107 did not require strict secondary metabolism to produce ligninolytic enzymes (Toh et al., 2003). It was possible to induce the dye decolorization activity of pellets of *Funalia trogii* by carefully selecting the optimal conditions. Additionally, pellets could be used several times and still maintained high decolorization activity especially at dye concentration of 13 mg/L and pellet concentration of 370 mg/50mL. Furthermore, it was possible to increase the stability of pellets with the addition of cheese whey even at high dye concentration (264 mg/L) (Yesilada et al., 2003). The basidiomycete strain Euc-1 decolourized the majority of the tested xenobiotic azo dyes and secreted a ligninolytic system of which laccase was the main produced enzyme (Dias et al., 2003). Six bacterial strains with the capability of degrading textile dyes were isolated from sludge samples and mud lakes. *Aeromonas hydrophilia* exhibited the greatest color removal from various dyes, particularly in anoxic or anaerobic culture. The most suitable pH and temperature were 5.5-10.0 and 20-35 °C, respectively. Nitrogen source such as yeast extract or peptone could enhance strongly the decolorization efficiency; in contrast, glucose reduced it because it was converted to organic acids that might decrease pH of the culture medium (Chen et al., 2003b).

A mixed culture isolated from a domestic wastewater treatment plant was found to remove the colour of the azo dye, methyl red, efficiently, with total degradation and decolorization occurring within 18 h. The mixed culture could degrade 700 mg/L of methyl red in the presence of 200 mg/L of glucose, and only 100 mg/L in the absence of glucose. The pH of the medium decreased continuously during degradation; when it reached 3.5 further degradation was not possible (Vijaya and Sandhya, 2003).

The use of riboflavin, the redox active moiety of commonly occurring enzyme cofactors, as a redox mediator to accelerate the reduction of the azo dye, mordant yellow 10 (MY10) by anaerobic granular sludge was evaluated. The results showed that at a molar riboflavin/dye ratio of 1/60, the total rate constant increased by 61% (Field and Brady, 2003). Lower levels of protein (approximately 38-42 mg/VSS) and higher levels of DNA content (approximately 11-17 mg/gVSS) were measured in the textile (cotton knit fabrics) floc extracellular polymer substances (EPS). Besides, larger contact angles (between 37 and 42°), low negatively charged surface values (between -0.11 and -0.25 meq/gVSS) and high amounts of bound water (between 20 and 24 g/gTSS) were determined in textile activated sludge samples (Sponza, 2003).

An anaerobic (upflow sludge blanket reactor)/aerobic (completely stirred tank reactor) sequential system was used to treat a synthetic wastewater with minerals and co-substrate together with Congo Red dye (Direct red 28). At a hydraulic retention time (HRT) of 0.486 days and a maximum organic loading rate of 6.656 kg COD/m³•d, 77% of COD and 95% color was removed. Besides, the total aromatic amines (TAA) produced under anaerobic conditions were ultimately removed in the aerobic stage, resulting in a reduced toxicity of the aerobic effluents (Isik and Sponza, 2003a).

Reduction rates of two azo dyes (Acid Orange 7 and Reactive Red 2) were compared in batch assays over a range of sulfide concentrations in the presence of living or inactivated anaerobic granular sludge. Biological dye reduction followed zero order kinetics and chemical reduction followed second order kinetics as a function of sulfide and dye concentrations. Both biological and chemical mechanisms of dye reduction

were greatly stimulated by the addition of the redox-mediating compound, anthraquinone-disulfonate (van der Zee et al., 2003).

In an attempt to promote the aerobic biodegradation of the aromatic amines produced during the anaerobic stage of a Sequencing Batch Reactor, three different approaches were tested: the increase of the relative duration of the aerobic phase, the increase of the hydraulic retention time through the decrease of the daily fill flow and finally the increase of the dye/carbon source concentration ratio through the decrease of the fed volumetric organic load. However, no effective biodegradation of these metabolites was observed during the experimental period (Lourenco et al., 2003).

The degradation of an azo dye mixture by an aerobic bacterial consortium was studied in a rotating biological reactor (RBC), made by an old gramophone records onto which laterite stone of particle size 850 μm to 1.44 mm were fixed using an epoxy resin. The RBC had a high efficiency for dye degradation even at a high dye concentration (100 mg/L) and high flow rate (36 L/h), at alkaline pH and salinity conditions normally encountered in the textile effluents; besides, toxicity was also appreciably reduced (Abraham et al., 2003).

The degradation of starch products, used as sizing agents and then released in the wastewater (making up about 50% of the organic load in wastewater from textile wet-processing), was studied in a series of batch experiments with and without surfactants.

It was shown that the desizing process (pretreatment, e.g by amylase) increased biodegradability of the sizing agent, as long as no surfactant was present. However, improvement was significant with native starch only, while all hydrolyzed products were degraded with a comparable rate and to similar extent. The final mineralization was

equal or only slightly lower in the presence of sodium n-decyl sulfate, as surfactant, but the degradation kinetics were negatively affected (Feitkenhauer, 2003).

Anaerobic treatment of real cotton textile wastewater in a fluidized bed reactor (FBR) was possible with the supplementation of an external carbon source in the form of glucose (about 2 g/L). The corresponding maximum COD, biochemical oxygen demand (BOD₅) and color removal were around 82%, 94% and 59%, respectively, for HRT of around 24 h and organic loading rate of 3 kgCOD/m³•d. Further increase in external carbon source added to real textile wastewater did not improve the color removal efficiency (Sen and Demirer, 2003).

Biological decolorization of textile dyestuff Reactive Orange 16 was investigated in a fed-batch reactor by using facultative anaerobic bacterial consortium called PDW. The experimental results indicated that over 90% efficiency could be obtained with up to 350 mg/L dyestuff concentration and 200 mL/h feeding rate, using yeast extract as the sole carbon source (Kapdan and Oztekin, 2003).

A six phase anaerobic/aerobic sequencing laboratory scale batch reactor was developed to treat a synthetic textile effluent, made by polyvinyl alcohols (PVOH) from desizing and an azo dye (Remazol Black). The reactor removed 66% of the applied organic carbon (food/microorganisms equal to 0.15) compared to 76% from a control reactor without dye. Color removal was 94%, but dye metabolites caused reactor instability and aromatic amines were not completely mineralized during the aerobic phase (Shaw et al., 2003).

The degradation of two azo dyes, Congo Red (CR) and Direct Black 38 (DB 38) was investigated using two facultative microorganisms (*Escherichia coli* and

Pseudomonas sp.) under anaerobic, aerobic and microaerophilic conditions. The colour of the CR and DB 38 was removed up to 98 and 72%, respectively, by *E. coli* at the end of anaerobic incubation, while no decolorization occurred throughout the aerobic incubation. Under microaerophilic conditions, the azo dyes CR and DB 38 were decolorized up to 39 and 75% by *E. coli*, respectively. In studies with *Pseudomonas* sp., the color of the CR and DB 38 was removed up to 100 and 83%, respectively, after 5 days of anaerobic incubation, while 76 and 74% color removal efficiencies were observed under microaerophilic conditions (Isik and Sponza, 2003b).

Decolorization studies of simulated wastewater containing vat dye (C.I. vat blue 1: indigo) and azo dyes (Reactive blue H3R and Reactive red HE 7B) were carried out using mixed bacterial cultures under anaerobic conditions in laboratory scale semicontinuous reactors with long HRT. COD removal up to 95, 90 and 92% was achieved in the control (no dye), blue and red dye containing reactors, while color removal of 98-99% could be obtained for both the azo dyes. In the indigo dye containing reactor, COD and color removal up to 90 and 95%, respectively, was observed (Manu and Chaudhari, 2003).

The presence of high total dissolved solids (TDS) negatively influenced the biological stability of an activated sludge process treating textile effluents, since it reduced oxygen transfer efficiency in the aeration tank and hence affected metabolism. Therefore, the activated sludge process was more sensitive to hydraulic shock loads and prone to process upset (Pophali et al., 2003).

The feasibility of thermophilic (55 °C) anaerobic treatment applied to colour removal of a triazine contained reactive azo dye was investigated in two 0.531 expanded granular

sludge blanket (EGSB) reactors in parallel at HRT of 10 h. Reactive Red 2 (RR2) and anthraquinone-2,6-disulfonate (AQDS) were selected as model compounds for azo dye and redox mediator, respectively. The reactors achieved excellent colour removal efficiencies with high stability, even at high loading rates of RR2. Although AQDS addition at catalytic concentrations improved the decolourisation rate, the impact of AQDS on colour removal was less apparent than expected. The decolourisation rates were co-substrate dependent, in which the volatile fatty acids (VFA) mixture was the least efficient one, while either hydrogen or formate, and also glucose had a significant impact (dos Santos et al., 2003). The biological decolorization of an industrial spent reactive dyebath and its three dye components (Reactive Blue 19 [RB 19], Reactive Blue [RB 21] and Reactive red 198 [RR 198]) under methanogenic conditions was studied. Overall, a high rate and extent of color removal (over 10 mg/L•h and 88%, respectively) were observed in methanogenic cultures amended with either RB 19 (an anthraquinone dye) or spent dyebath at an initial concentration of 300 mg/L (expressed as RB 19 equivalent) and 30 g/L of NaCl. However, inhibition of acidogenesis and, to a larger degree, of methanogenesis was observed in both RB 19 and spent dyebath amended cultures. On the contrary, RB 21 (a phthalocyanine dye) and RR 198 (an azo dye) tested at an initial concentration of 300 mg/L did not result in any significant inhibition (Fontenot et al., 2003).

The toxicity of C. I. Reactive Black 5 and three Procion dyes, as found in textile effluents, was determined using the bioluminescent bacterium *Vibrio fischeri*. Hydrolysed Reactive Black had a slightly greater toxicity than the parent form. Decolourisation of hydrolysed Reactive Black 5 in a synthetic effluent carried out in a

baffled bioreactor with anaerobic and aerobic compartments, resulted in an increased toxicity. Toxicity was not detectable when decolourised Reactive Black 5 was metabolised under aerobic conditions (Gottlieb et al., 2003).

Combined processes

In order to enhance the decolorization efficiency of photosynthetic bacteria, a laboratory scale photo-reactor with thin film photocatalysis was used to control excessive algal growth and for improving the efficiency of optical irradiation. The system showed improvement of the continuous dye biodegradation efficiency; moreover, although photocatalytic reactions of TiO_2 could inhibit the growth of isolated photosynthetic bacteria, the negative effects of photocatalysis on photosynthetic bacterial growth and decolorization activity was negligible under UV+fluorescence lamp irradiation (Hong and Otaki, 2003).

The ability of activated carbon cloths (ACC) to treat coloured wastewater was assessed by coupling adsorption with ultrafiltration. First, both processes were operated step after step. The membrane filtration step (3000 Da molecular weight cut-off) allowed a great removal of turbidity (over 98%), whereas adsorption onto ACC provided decolourization of the stream with an adsorption capacity in continuous flow reactor of 180 mg/g of the acid Orange 7. Secondly, UF and adsorption onto ACC were operated continuously. When the breakthrough was reached, a total volume of 101 L was successfully decolorized, with a permeate flow rate higher than $20 \text{ L/m}^2 \cdot \text{h}$ (Métiver-Pignon et al., 2003).

Immobilization of laccase by *Trametes versicolor* on silica chemically modified with imidazol groups, amberlite Ira-400, glass-ceramic chemically modified and montmorillonite modified, for decolorization of textile reactive dyes (Remazol Brilliant Blue R, Remazol Black B, Reactive Orange 122 and Reactive Red 251) was afforded. In the first stage of the process, the decolorization was mainly due to adsorption of the dyes onto the support surface. However, when working in a successive dye addition system, the adsorption capacity of the supports decreased (saturation) and the enzymatic decolorization process was clearly evidenced. The use of a brief photochemical pretreatment permitted a significant increase on the efficiency of the enzymatic decolorization (Peralta-Zamora et al., 2003).

The effectiveness of biological pretreatment involving appropriate microorganisms and suitable support media, followed by chemical coagulation and electrochemical oxidation, was evaluated. COD and color were reduced by 95.4% and 98.5% by the combined process, respectively (Kim et al., 2003).

A bisulfite-catalyzed sodium borohydride reduction followed by activated sludge technique was used in order to remove the color at ambient temperature and pressure. Both synthetic wastewater, made by several groups of dyes, such as direct, basic and reactive, and actual wastewater collected from two different textile industries, were used. The combined process was able to decrease color, BOD, COD and total suspended solids (TSS) by 74-88%, 76-83% and 92-97%, respectively. Besides, color removal occurred without causing any disposal problem (Ghoreishi and Haghighi, 2003).

Reuse

In the textile industry, many different processes are used and almost all of them generate wastewater. The resulting effluents differ greatly in composition, due to differences in processes, used fabrics and machinery. Although effluents are usually treated as a mixed stream, however for water and chemicals reuse purposes it is preferably to keep process streams apart and treat them separately. To such a purpose, characterisation of effluents is of great importance. An overview of the composition of the textile wastewaters generated from different processes was provided, along with the methods used for their characterisation (Bisschops and Spanjers, 2003).

The feasibility of the combination of physico-chemical treatment with nanofiltration to reuse wastewater of printing, dyeing and finishing textile industry was studied.

Particularly, for the physico-chemical treatment two coagulants (one containing Al^{3+} and another containing Fe^{2+}) were compared by carrying out jar-tests; after that, nanofiltration was applied to the effluent from the physico-chemical process. The results showed that the COD and conductivity of the nanofiltration permeates were lower than 100 mg/L and 1000 $\mu\text{S}/\text{cm}$, respectively (Bes-Pià et al., 2003a).

The suitability of combinations of different processes to improve final water quality for its reuse was evaluated. Nanofiltration and chemical oxidation using ozone and ozone/UV radiation on the effluent from activated sludge process were compared. Both processes produced effluent with very low COD; however, with nanofiltration there was reject stream generation, while oxidation did not reduce the water conductivity and therefore did not allow the treated water to be reused (Bes-Pià et al., 2003b).

Combination of H₂O₂/UV pre-oxidation and reverse osmosis (RO) membrane separation post-treatment could improve the textile effluent quality and meet the water quality criteria for its reuse in the textile industry (Kang et al., 2003).

The application of membrane technologies to textile wastewater advanced treatment, downstream of a biological activated sludge process, aimed at water reuse in textile technology process was evaluated in a pilot-scale plant. The plant scheme was made by a sand filtration as a pretreatment, a microfiltration or ultrafiltration membrane process, and a final separation treatment performed by means of a nanofiltration or a RO membrane. The results obtained and the preliminary economic analysis indicated the possibility of technological transfer of the membrane processes to an industrial scale for textile wastewater reclamation (Marcucci et al., 2003).

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