

TEXTILES

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The present paper reviews literature on textile wastewater treatment and reuse published during the year 2004. Particularly, after a general introduction, different alternative technologies employed for textile wastewater treatment and/or reuse are presented grouped into physico-chemical, biological and combined processes.

Introduction

The textile industry is economically very important in many States, but the effluents from the plants, particularly those involved with dyeing, contain high concentrations of color, NaCl, and other chemicals. These chemicals often cause problems for the municipal sewage treatment facilities in staying in compliance with their wastewater quality permits.

Increased regulatory pressures initiated aquatic toxicity testing of wastewater discharges from publicly owned treatment works. Details of a cleaner production framework developed to reduce the aquatic toxicity and environmental effects of textile chemicals in the south-eastern USA was provided. It offered evidence of how the application of the principles of dialogue and systems thinking provides a win-win situation for both the “textile production chain” and corporate stakeholders (Moore and Ausley, 2004).

Colorants and chemical auxiliaries in the fiber dyeing effluents could be reduced by (1) optimizing the acid dyeing conditions such as salt addition and pH control and (2) reuse of the spent dye bath that remained after the original dyeing process. Through laboratory scale trials, the acid dye exhaustion was successfully raised to over 90% by optimizing the dyeing conditions. The reuse of the spent acid dye bath also showed promising results with dye exhaustion ranging from 91 to 93% after four times of reuse (Fan et al., 2004). A detailed analysis on water use, process profile and wastewater characterization indicated a potential for 34% reduction in water consumption and for 23% of wastewater recovery for reuse in a wool finishing textile mill. Wastewater reuse required treatment and resulted in a remaining wastewater stream with stronger character and consequently more costly to treat (Erdogan et al., 2004).

A compilation of the newer achievements in the technologies developed for the removal of synthetic dyes from water and wastewater, classification and short description of the methods, critical evaluation of the technological processes and comparison of their advantages and disadvantages was presented (Forgacs et al., 2004).

Over the last years, regulations for sludge management have become more stringent; therefore, disposal of sludge, and particularly of that arising from industrial activities, by environmentally acceptable means poses a great challenge worldwide. Through several laboratory-scale experiments, it was demonstrated that vermicomposting can be considered as an alternative technology for the management of solid textile mill sludge mixed with cow and agricultural residues in appropriate quantities (Kaushik and Garg, 2004).

Physico-Chemical processes

Coagulation and electrocoagulation

Chemical coagulation was used to remove disperse and reactive dyes. The optimal coagulant conditions (pH and coagulant dose) were determined, and the dye removal effectiveness of disperse and reactive dye solutions was compared. In addition, the changes in the soluble chemical oxygen demand (SCOD)/total COD (TCOD) ratio were comparatively evaluated before and after application of the chemical coagulation. Compared to reactive dyes, disperse dyes had lower solubility, higher suspended solids concentrations and lower SCOD/TCOD ratios. It was concluded that disperse dye solutions were more easily decolorized by chemical coagulation than reactive dye solutions (Kim et al., 2004a). A Fe/Cu system reached over 88% of color removal efficiency from both methylene blue solution and the wastewater from a plant in a batch test. The removal efficiency increased rapidly with Fe/Cu dosage and reaction time. The results obtained in the continuous test showed that Fe/Cu systems supplied a long and stable removal of color, with an average of 63% efficiency under the condition of neutral range of pH (7.0-8.3) and 2 h of hydraulic residence time (HRT) (Ma et al., 2004). A jar test was conducted for simulating the chemical coagulation process with aluminum sulfate and polyaluminum chloride (PACl), after different activated sludge systems (with air or high-purity oxygen). The results showed that with sludge recirculation coagulation for color removal had up to 35% enhancement in comparison with no sludge recirculation. Meanwhile, the color removal was enhanced approximately 2-3 times by using aluminum sulfate as coagulant if compared to PACl, at the optimum ratio of return sludge (Liu and Liang, 2004). The treatment of Orange II dye in a flow-through

electrocoagulation (EC) cell using iron electrodes and sodium chloride as internal electrolyte could effectively remove approximately 99% of dye from the waste stream under optimum conditions. The removal efficiency was found to be dependent on the initial pH, the electrolyte concentration, the dye concentration, the applied current density, the flow rate and the recycling of the dye solution. The higher treatment efficiency was considered to be due to chemical coagulation involving maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and/or magnetite (Fe_3O_4) produced in the system as well as electrooxidation (Mollah et al., 2004).

Adsorption

The equilibrium adsorption of three basic dyes, namely Basic Blue 3, Basic Yellow 21 and Basic Red 22, onto peat was reported. The peat appeared to be very effective at removing such dyes from solution. The equilibrium results were modeled and evaluated by using five different isotherms and six different optimization and error functions, including a linear transformation model (Allen et al., 2004). Ca-montmorillonite (Ca-Mont) was exchanged with titanium cations and the adsorption equilibrium and kinetics of Basic Green 5 (BG5) and Basic Violet 10 (BV10) on these montmorillonite (Ti-Mont) were measured to examine the ion-exchange effects on the adsorption of basic dyes. The kinetics of BG5 and BV10 on Ca- and Ti-Mont followed the pseudo-second-order rate expression and Ti-Mont possessed a higher reaction rate as a result of its larger mean pore size. (Wang et al., 2004). Batch adsorption studies showed that dried activated sludge had considerable potential for the removal of basic dyes (Basic Red 18 and Basic Blue 9) from aqueous solution. Langmuir and Freundlich isotherms were fitted very well as a function of temperature and concentration ranges.

The adsorption kinetics of dyes to dried activated sludge obeyed second order adsorption kinetics (Gulnaz et al., 2004). The influence of the surface chemical groups of activated carbon on the removal of different classes of dyes was evaluated. Oxidation in the liquid phase with 6 M HNO₃ and 10 M H₂O₂ (acid materials) and heat treatment at 700°C in H₂ or N₂ flow (basic materials) were carried out on the same starting material, in order to produce samples with different surface chemical properties but with no major differences in their textural properties. Equilibrium isotherms of selected dyes (an acid, a basic and a reactive dye) on the mentioned samples were obtained; in general, the Langmuir model provided the best fit for the adsorption data (Faria et al., 2004).

Dodecyltrimethylammonium bromide-modified bentonite (DTMA-bentonite) was prepared and tested as an adsorbent for Acid Blue 193 (AB193) removal from aqueous solution in comparison with Na-bentonite. Results showed that a pH value of 1.5 was favorable for the adsorption of AB193; the isothermal data could be well described by the Freundlich equation, while the kinetic data of adsorption were well fitted by the pseudo-second-order kinetic model. The adsorption capacity of DTMA-bentonite (740.5 mg/g) was found to be 11 times higher than that of Na-bentonite (67.1 mg/g) (Özcan et al., 2004a). Coarse size of metal hydroxide sludge (150-300 μm) was demonstrated to be usable as adsorbent in a fixed-bed column for reactive dye removal. The color was highly removed with a sufficient volume treated and the pH of the treated water was within the permitted range. The same sludge had also the potential to treat textile wastewater containing a reactive dye (Netpradit et al., 2004a). The efficiency of basic, direct and reactive dye removal from water by narrow-leaved cattail (NLC) powder treated with distilled water, 37% formaldehyde+0.2 N sulfuric acid, or 0.1 N sodium

hydroxide at various pH levels (3, 5, 7 and 9) was tested. The type of NLC treatment and pH of the dye solution had little effect on the removal of basic dyes, and efficiencies ranged from 97% to 99% over the range of pH used. The dye removal efficiency by the three NLC treatments ranged from 37% to 42% for direct dyes and from 22% to 54% for reactive dyes at pH 7. The pH of the dye solution had substantial effects on the removal efficiency of direct and reactive dyes (Inthorn et al., 2004). Bottom ash, from the thermal power plant, was used as a potential adsorbent for the removal of the toxic textile dye "malachite green" and preliminary information was gathered by batch adsorption studies. Then, a fixed-bed column was designed and necessary parameters were calculated by applying a mass transfer kinetic approach (Gupta et al., 2004). Adsorption of azo reactive dyes by metal hydroxide sludge was investigated using CI Reactive Red 2 (RR-2), CI Reactive Red 120 (RR-120), and CI Reactive Red 141 (RR-141). The adsorption isotherms, including the Langmuir constants and the Freundlich constant, for RR-2 decreased with increasing temperature, but this was reversed for RR-120 and RR-141. The adsorption of the less charged dyes (RR-2) was mainly physical, but that of the more charged dyes (RR-120 and RR-141) was chemical. The optimum system pH was 8.6 ± 0.3 . A higher dosage of sludge was required for real textile wastewater than for the synthetic dye solution (Netpradit et al., 2004b). Mahogany sawdust was used as carbon adsorbent for the removal of direct dyes from spent textile dyeing wastewater. Equilibrium data fitted well with the Langmuir model, while the rate of adsorption was found to conform to the pseudo-second-order kinetic with good correlation. The equilibrium adsorption capacity was found to be >300 mg dye per gram of the adsorbent, while the most ideal pH was equal to 3 or below (Malik, 2004). A novel

carbon-based adsorbent material, Nyex 100, was used to remove color, toxic and non-biodegradable organics from waters. Nyex 100 was characterized by a low porosity and high conductivity which favored its electrochemical regeneration. The adsorbent could be cycled through the process of adsorption and regeneration a number of times with little drop in adsorptive capacity. However, regeneration appeared to modify the preference for organic species adsorption. Besides, it was necessary to use large dose rates to achieve the discharge limits (Brown et al., 2004). Competitive adsorption between atrazine (AT) and dye compounds in natural aquatic sediments was investigated. Batch adsorption experiments were conducted at various Ca^{2+} concentrations, pH levels, temperatures and dye compounds. Both dyes (Congo Red, CR, and Methylene Blue, MB) reduced the adsorption of atrazine over the range of dye concentrations examined, and the competition between AT and MB was much stronger than that between AT and CR. Simultaneous adsorption and dye preloading inhibited the adsorption of atrazine (Tao and Tang, 2004). Activated carbons were prepared from bagasse through a low temperature (160°C) chemical carbonisation treatment and gasification with carbon dioxide at 900°C . Despite the high ash content of the precursor, this process allowed generation of high surface areas ($614\text{-}1433\text{ m}^2/\text{g}$) and microporous (median pore size from 0.45 to 1.2 nm) activated carbons. The micropore area provided favorable adsorption sites to acid blue dye (391 mg/g of carbon). The alkalinity of the carbon surface and total surface area had complementary effects in promoting the adsorption of the acid blue dye (Valix et al., 2004). Activated bleaching earth was used as clay adsorbent for an investigation of the adsorbability and adsorption kinetics of acid dyes (i.e., acid orange 51, acid blue 9, and acid orange 10) with three different

molecular sizes from aqueous solution at 25°C in a batch adsorber. The adsorbability of the acid dyes by activated bleaching earth followed the order: acid orange 51 > acid blue 9 > acid orange 10, parallel to molecular weights and molecular sizes of the acid dyes. The adsorption removals (below 3%) of acid blue 9 and orange 10 were far lower than that (24%) of acid orange 51 (Tsai et al., 2004). Spent brewery grains (SBG), a by-product of the brewing process, were tested as an adsorbent of acid orange 7 dye (AO7). High levels of color removal (>90%) were achieved with low contact time (less than 1 h contact) between adsorbent and dye. The maximum adsorption capacity was estimated to be 30.5 mg AO7/g SBG, at 30°C (Silva et al., 2004). The adsorption of Congo Red from solution on calcium-rich fly ash was between 93% and 98% under the conditions applied. Kinetic studies showed that the adsorption process obeyed the pseudo-second-order kinetic model, while the isotherm followed Freundlich and Dubinin-Radushkevich models. The adsorption was spontaneous and endothermic. Desorption was 20.18% in the presence of 0.1 N HCl and was 47.21% in the presence of CH₃COOH (0% v/v) (Acemioğlu, 2004).

Advanced oxidation

A comparison of various advanced oxidation processes (AOPs) (O₃, O₃/UV, H₂O₂/UV, O₃/H₂O₂/UV, Fe²⁺/H₂O₂) and chemical treatment methods using Al₂(SO₄)₃·18H₂O, FeCl₃ and FeSO₄ for COD and color removal from a polyester and acetate fiber dyeing effluent was undertaken. AOPs showed a superior performance compared to conventional chemical treatment. Although O₃/H₂O₂/UV combination among other AOPs studied in this paper was found to give the best result, use of Fe²⁺/H₂O₂ seemed to achieve a satisfactory COD and color removal performance and to

be an economically more viable choice (Azbar et al., 2004). UV/TiO₂, electro-Fenton (EF), wet-air oxidation (WAO), and UV/electro-Fenton (UV/EF) advanced oxidation processes were applied to degrade Reactive Red 120 (RR120) dye in aqueous solution. The decolorization efficiency was observed in the order WAO>UV/TiO₂ = UV/EF>EF while the order of WAO>UV/TiO₂>UV/EF>EF was determined in terms of total organic carbon (TOC) removal (mineralization). For all AOPs, it was found that the degradation products in the reaction mixture could be disposed safely to the environment after 90 min treatment (Kusvuran et al., 2004). Three different oxidation treatments were tested for the elimination of color downstream from a membrane bioreactor (MBR): ozonation, chlorination and hydrogen peroxide oxidation. For chlorination, even with 250 mg/L (active chlorine) only 80% color removal was achieved, which was considered unsatisfactory. For hydrogen peroxide, the color removal was even poorer (about 10%) at a concentration of 250 mg/L. In contrast, good results were obtained by ozonation. By using only 38 mg/L within 20 min, it was possible to achieve a satisfactory color removal of 93% (Brik et al., 2004). The decolorization of dye CI Reactive Blue 19 (RB-19) solution in a new gas-inducing reactor under continuous process was studied. Experiments indicated that the American Dye Manufactures Institute (ADMI) removal percentage (RADMI) decreased while the ozone utilization rate (UO₃) increased with increasing ADMI color value input rate or decreasing ozone input rate. The 70% ADMI removal efficiency was regarded as an indication of the competition of dye and its unknown intermediates for ozone. In addition, increase of the agitation speed improved the ADMI removal percentage as well as the UO₃ (Hsu et al., 2004). The hydroxyl radical (*OH) scavenging effects of carbonate (CO₃²⁻), bicarbonate (HCO₃⁻) and chloride

(Cl⁻) ions on the performance of an ultraviolet light-hydrogen peroxide (UV/H₂O₂) advanced oxidation process were investigated using a reactive azo dye, CI Reactive Red 141 as the model compound. In the absence of scavengers, complete color removal was possible in 15 min under the experimental conditions employed. The rate of color decay was significantly inhibited with increasing concentrations of bicarbonate and carbonate species, especially when the distribution of alkalinity favored the dominance of carbonate ions. Chloride inhibited only when it was between 100-1250 mM, and was ineffective at higher concentrations (Gultekin and Ince, 2004). The ozonation was effective for decolorization of an effluent, but it was ineffective for TOC reduction (Assalin et al., 2004). The acid black 1 solution was completely decolorized by using UV/H₂O₂, under optimal hydrogen peroxide dosage of 21.24 mmol/L and UV dosage of 1400 W, in less than 1.2 min. The decolorization rate followed pseudo-first order kinetics with respect to the dye concentration. It was found that the degradation rate increased until an optimum of hydrogen peroxide dosage, beyond which the reagent exerted an inhibitory effect (Shu et al., 2004). Investigation on the effect of mixing intensity and reagents addition strategy on Fenton's reagent degrading a common reactive diazo type dyestuff, Reactive Black 5, was carried out. The effect of mixing intensity on TOC removal was observed to be significant and complex. The degradation process was found to be enhanced with higher mixing intensity; however, a very high mixing level was responsible for the observed reduction in performance. The benefits of increasing mixing intensity appeared to be higher for lower reagents dosage (Aris and Sharratt, 2004). Degradation of 20 dyes in aqueous solutions by the Fenton process was performed. These dyes included 6 types: acidic, reactive, direct, cationic,

disperse and vat dyes. The former four types were decolorized and their TOC values were decreased significantly, while the color and TOC removals of the latter two types were lower. The catalytic abilities of four metal ions in the dark and under UV light irradiation were in the order of $\text{Fe}^{2+}/\text{UV} > \text{Cu}^{2+}/\text{UV} > \text{Mn}^{2+}/\text{UV} > \text{Ag}^+/\text{UV} > \text{Fe}^{2+} > \text{Cu}^{2+} > \text{Mn}^{2+} > \text{Ag}^+$. The color and TOC removals of dye solution by $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$ were higher than by $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ or $\text{H}_2\text{O}_2/\text{UV}$ processes (Xu et al., 2004). The comparative evaluation of Fenton oxidation and ferric coagulation in a large-scale Fenton process that treated dyeing wastewater revealed that ferric coagulation was the predominant mechanism for COD and color removal. A combined process of iron coagulation/precipitation with subsequent Fenton oxidation was more effective than a sole Fenton oxidation process and reduced the hydrogen peroxide dosage by over 40% (Bae et al., 2004). The catalytic effect of three iron exchanged ultra-stable Y zeolites (USY) for the degradation of CI Reactive Yellow 84 (RY84) using hydrogen peroxide as an oxidant, under very mild conditions (atmospheric pressure and 50°C) was evaluated through laboratory scale experiments. Important variables, the toxic potential of the dye degradation and oxidation end-products were examined. The best experimental conditions were determined to be pH=5, T=50°C, a catalyst concentration of 1 g/L and 20 mmol/L H_2O_2 . Under such conditions it was possible to remove 96.90% of color, 70.70% of COD and 34.52% of TOC using Fe-Y_{11.5} catalyst after 60 min of oxidation. After the same reaction time and under the same conditions, using Fe-Y₅ catalyst, 99.93% of color removal, more than 74.14% of COD and 64.21% of TOC removal were obtained (Neamțu et al., 2004a). The biodegradability of refractory organic matter in biotreated wastewater could be

remarkably improved by advanced ozonation with the addition of hydrogen peroxide. The refractory chemicals contained in the scouring A and swelling agents could not be mineralized and their biodegradability was not improved by ozonation. However, the scouring agent B could be mineralized and its biodegradability enhanced by ozonation (Lim et al., 2004). Tetraamido-macrocyclic ligand (TAML[®]) catalyst (0.5 M, 0.23 mg/L of effluent) combined with hydrogen peroxide (6.5 mM, 0.19 g/L of effluent) were capable of permanently removing 46% of the color from bleach plant effluent in 1 h at 5,000 L effluent per day. Increasing concentrations to 2 M catalyst (0.9 mg/L of effluent) and 22 mM peroxide (0.75 g/L of effluent) resulted in 78% color removal. In addition, 29% of the chlorinated organic material (AOX) was removed. However, the COD was essentially unchanged (Wingate et al., 2004). The oxidation of Reactive Black 5 (RB5) and Reactive Orange 96 (RO96) with concentrations between 35 and 5,700 mg/L (RB5) and between 20 and 2,050 mg/L (RO96) was investigated in a laboratory scale bubble column. The reactor was modeled for two cases, a completely mixed and a plug flow gas phase. The oxidation rate was influenced by mass transfer for all dye concentrations used. For low dye concentrations, the mass transfer alone was decisive for the reaction rate showing no enhancement due to chemical reaction. However, in the region of high dye concentrations, the slope of the ozone concentration profile inside the liquid boundary layer increased with increasing dye concentrations as a result of a chemical oxidation (Choi and Wiesmann, 2004). The degradation of a reactive azo dye, Procion Marine H-EXL, by catalytic wet hydrogen peroxide oxidation (CWHPO) was evaluated with a laboratory scale apparatus. The results indicated that after only 10 min at T=50°C, 20 mmol/L H₂O₂ and 1 g/L FeY_{11.5}, the color removal was as high as 97% at

pH=3 and 53% at pH=5. More than 96% dye removal could be attained in 30 min at pH=5, T=50°C, 20 mmol/L H₂O₂ and 1 g/L FeY_{11.5} which corresponded to about 76% reduction of the initial COD and 37% removal of the initial TOC. No significant leaching of Fe ions was observed (Neamțu, et al., 2004b).

Photodegradation

Based on results from bench-scale flow-film reactors (FFR) and aerated cascade photoreactors, a solar catalytic pilot plant was built with an illuminated surface area of 50 m², for the treatment of 1 m³/h of wastewater. The solar catalytic technology was able to remove recalcitrant compounds and color (Bousselmi et al., 2004). ZnO and TiO₂ colloidal nanocrystals were successfully employed in thin film form for the photodegradation of methyl-red [2-(4-Dimethylamino –phenylazo)-benzoic acid) – CI13020]. The obtained results demonstrated a significant photocatalytic activity even in the presence of the organic capping layer on the nanocrystal surface. TiO₂ showed a higher efficiency than ZnO particles (Comparelli et al., 2004). Photocatalytically active nanocrystalline titania particles were prepared using a hydrothermal process, by controlling the particle size and crystallinity. Such particles showed a high photocatalytic activity for the decomposition of azo dyes dissolved in aqueous solution, with higher activity than that of conventional titania (Yun et al., 2004). The feasibility of heteropoly acid-mediated and isopropanol-induced photochemical degradation of dye-baths bearing disperse dyestuffs was demonstrated. The rate of decolorization strongly depended upon the heteropoly acid (photocatalyst) loading, nature of the organic solvent, i.e. the electron donor, and the presence of various dye assisting chemicals (Arslan-Alaton and Dogruel, 2004a). The photocatalytic degradation of azo dyes with

different functionalities was reviewed using TiO_2 as photocatalyst in aqueous solution under solar and UV irradiation. The kinetics of the photocatalytic oxidation followed a Langmuir-Hinshelwood model and depended on several factors such as dye concentration, mass of catalyst, wavelength, radiant flux and the addition of oxidants or the presence of naturally occurring substances (humic substances and/or inorganic ions) (Konstantinou and Albanis, 2004). The potential of a common semiconductor, ZnO, was explored as an effective catalyst for the photodegradation of two model dyes: Methylene Blue and Eosin Y. The effects of process parameters, like catalyst loading, initial dye concentration, airflow rate, UV-radiation intensity, and pH on the extent of photodegradation was investigated. Substantial reduction of COD, besides removal of color, was achieved. A rate equation for the degradation based on Langmuir-Hinshelwood was also proposed (Chakrabarti and Dutta, 2004). Photocatalytic degradation of a textile azo dye, Sirius Gelb GC, on TiO_2 or Ag- TiO_2 particles in the absence and presence of UV light was investigated. The optimum pH, which provided the best degradation ratio, was found to be 3.5. At the same pH, it was observed that silver loaded catalyst was more effective than the neat TiO_2 catalyst. The silver loading dramatically reduced the irradiation time from 20 min to 8 min. The catalytic behavior of both catalysts was also investigated in heavy salt media such as simulated wastewater and in a river water (Özcan et al., 2004b). Photocatalytic decolorization of an aqueous solution of Remazol Red RR in the presence of various semiconductor powder suspensions was studied in a quartz batch reactor with the use of artificial light sources (UV-C). ZnO and TiO_2 were found to be the most active photocatalysts; however, ZnO showed slightly higher efficiency. The decolorization efficiency increased with an

increase in pH, while it was inversely related to the dye concentration (Akyol et al., 2004). Photodegradation efficiency of Acid Red 14 was small when photolysis was carried out in the absence of ZnO and it was also negligible in the absence of UV light. The addition of a proper amount of hydrogen improved the decolorization, while its excess could have quenched the formation of hydroxyl radicals (OH). Besides, ethanol seemed to inhibit the photodegradation of the dye (Daneshvar et al., 2004). The efficiency of photooxidation of Yellow Procion H-4R, Bright Blue Remazol (blue reagent-19), Red Procion H-E7B and a mixture of the two last dyes was compared using hydrogen peroxide (30%) as a bleaching reagent, solar and ultraviolet radiation, common glass borosilicate, quartz assay tubes and no solid catalysts. The color of blue dye and a mixture of blue and red dyes were almost completely removed after 3 h, either by solar or ultraviolet radiation. The best results of color removal (93%) for the red and yellow dyestuffs were obtained only after 6 h, using quartz tubes, hydrogen peroxide and ultraviolet radiation (Costa et al., 2004). The photocatalytic degradation of Orange II was demonstrated to be feasible. The optimum pH was found to be 7.00. The presence of Mn^{2+} did not alter its degradation pathways, but it reduced the dye degradation efficiency because Mn^{2+} was adsorbed on the surface of TiO_2 . A modified Langmuir-Hinshelwood model was able to describe the TiO_2 -mediated photocatalytic kinetics of Orange II appropriately with and without the presence of Mn^{2+} in solution (Mu et al., 2004).

Membrane

A membrane process was proposed for the recycling and reuse of energy, water and chemical. The process consisted of microfiltration pre-treatment of used finishing

baths, followed by a dual nanofiltration (NF) unit. The first of the NF unit used a loose nanofiltration membrane that retained most of the organic fraction but not the dissolved salts. The second unit used a tight nanofiltration membrane, which produced a permeate fraction that could be directly reused, and a concentrate brine that was fed to a membrane crystallizer. In this unit, salts were recovered and recycled for use in new dye baths. The concentrate stream from the first NF unit was fed to a membrane distillation unit, where the high temperature was advantageously used for further concentration. The remaining fraction could not be reused, but had a significant energetic value, and could be utilized for compensation of energy losses and preheating of process water (Van der Bruggen et al., 2004). Micellar enhanced ultrafiltration (MEUF) was used to remove acid dye from aqueous solution. Cetyl (hexadecyl) pyridinium chloride (CPC) and eosin were taken as cationic surfactant and acid dye, respectively. The retention of dye without surfactant was only 10% at a typical feed dye concentration of $10 \times 10^{-3} \text{ kg/m}^3$, whereas under the same operating pressure (276 kPa), retention increased up to 73.4% by using surfactant micelles. Free surfactant molecules present in the permeate were then removed by a two-step chemical treatment procedure (Purkait et al., 2004). Thermally stable nanofiltration membranes were used to recover hot water from rinsing effluents from acid and reactive dye operations. Two types of flat-sheet membranes, MPF-34 (MWCO 200) and MPF-36 (MWCO 1000), were tested at 60°C and 10 bar. Experiments carried out with the synthetic feeds containing acid dye and acetic acid showed that both membranes were able to retain more than 99% of the dye. MPF-34 suffered from substantial flux decline due to the dye and acid in the feeds, but still provided higher fluxes than MPF-36. Furthermore, the reactive dye

rejection of MPF-36 was acceptable, while the fluxes were exceptionally high. MPF-36 was also tested with the wastewater from the industrial processes; it could recover hot water by removing more than 98% of acid dye and 90% of reactive dyes (Sungpet et al., 2004).

Various

The degradation of an anionic azo dyes Acid Red 14 (AR14) by an electrokinetic-electrooxidation process (EK-EO process) was experimentally investigated. It was found that under an electric field AR14 could migrate into the anode compartment and be efficiently mineralized. After 360 min electrolysis of 100 mg/L AR14 solutions at 4.5 mA/cm², complete decolorization was observed in both the cathode and anode compartments. About 60% of TOC electromigrated from the cathode compartment to the anode compartment, and more than 25 mg/L TOC was abated in the anode compartment (Wang et al., 2004). Power ultrasound of 850 kHz at 60, 90 and 120 W was used for the degradation of industrial azo dyes Acid Orange 5 and 52, Direct Blue 71, Reactive Black 5 and Reactive Orange 16 and 107. The results obtained showed that power ultrasound was able to mineralize azo dyes to non-toxic end products, which was confirmed by respiratory inhibition test of *Pseudomonas putida*. All investigated dyes were decolorized and degraded within 3-15 h at 90 W and within 1-4 at 120 W, respectively (Rehorek et al., 2004). A recent non-thermal plasma technique (i.e., a gliding arc discharge which generates reactive species at atmospheric pressure) was tested for pollution abatement of dyes dispersed in synthetic solutions and industrial effluents. The degradation processes achieved by the oxidising species formed in the

plasma was almost complete and followed pseudo-first-order laws (Abdelmalek et al., 2004).

Biological processes

Bacterial processes

The abiotic and biotic fate of Acid Orange 7 (AO7) was investigated under a variety of operating conditions (aerobic nitrification, anoxic denitrification and anaerobic digestion), and in biofilm and activated sludge treatment processes. The adsorption of AO7 onto biofilm matrix and activated sludge flocs was found to fit Langmuir equation; however, there was significant difference in the adsorption capacities of the two biological processes tested. AO7 was recalcitrant under aerobic conditions in both biological systems, while it was readily decolorized under anaerobic conditions. Although some decolorization of AO7 was observed under anoxic conditions, however nitrate presence exerted an inhibitory effect on such process (Li and Bishop, 2004). An experimental activity was carried to verify the efficiency of a pilot-scale Membrane Bio-Reactor (MBR) technology for the treatment of municipal wastewater, in which textile industry effluent predominated. During the five months experimental period, the pilot-scale MBR proved to be very effective in removing both conventional parameters as COD, ammonium nitrogen and suspended solids, and also compounds typical of a textile effluents, i.e. surfactants and dyes (Lubello and Gori, 2004). Decolorization and inhibition kinetics of CI Direct Black 38 (DB38) at concentrations varying between 200 and 3,200 mg/L were investigated with partially granulated anaerobic mixed culture using glucose (3,000 mg/L COD) as carbon source and electron donor during batch

incubation. The first order kinetic model was found to be the most appropriate model. Increases in dye concentrations from 0 to 3,200 mg/L reduced the degradation rate constant. Decolorization was achieved effectively under the test conditions, but ultimate mineralization of azo dyes was not observed. Aromatic amine accumulation was observed proportionally at a higher DB38 concentration. A competitive kinetic model that described co-metabolism of increasing DB38 dye concentrations with glucose as co-substrate was developed based on the experimental data (Sponza and İşik, 2004). A facultative biofilm reactor (FBR) with an aerobic reactor (AR) was used to treat wastewater contaminated by anthraquinone acid dye (acid blue BRLL). The facultative biofilm process was more effective for decolorization than the anaerobic stage of an anaerobic-aerobic process. Most color removal occurred in the facultative reactor and the biochemical oxygen demand (BOD)/COD of the FBR effluent was increased significantly (Li and Xi, 2004). Azo dye reduction at 55°C by thermophilic anaerobic granular sludge was investigated distinguishing between the biotic and abiotic mechanisms. The impact of the redox mediator anthraquinone-2,6-disulfonate (AQDS) on color removal and co-substrate oxidation was also studied. Metabolic activities of the thermophilic inoculum induced a fast azo dye reduction and indicated a biotic predominance in the process. The addition of co-substrate enhanced the decolorisation rates (dos Santos et al., 2004a). Decolorization and inhibition kinetic characteristics of two azo dyes, namely Reactive Black 5 (RB5) and Direct Brown 2 (DB2), were investigated with partially granulated anaerobic mixed culture using glucose (3,000 mg/L COD) as carbon source and electron donor during batch incubation. Decolorization and substrate removal were achieved effectively under the test

conditions but ultimate removal of azo dyes and substrate were not observed at high dye concentrations. Aromatic amines and volatile fatty acids accumulation were determined proportionally at higher azo dye concentrations (Işik and Sponza, 2004a). Batch anaerobic and sequential anaerobic upflow sludge blanket (UASB)/aerobic continuous stirred tank reactor (CSTR) were used to determine the color and COD removals under anaerobic/aerobic conditions. Two azo dyes, namely Reactive Black 5 (RB5) and Congo Red (CR), and glucose as carbon source were used for synthetic wastewater. Decolorization was achieved effectively under the test conditions but ultimate decolorization of azo dyes was not observed at all dye concentrations in a batch assay (Işik and Sponza, 2004b). Selective enrichment of microbial populations capable of degrading/decolourizing Acid Violet-17 (AV-17) was carried out. A consortium of five bacterial isolates was used to develop an up-flow immobilized cell bioreactor for the treatment of AV-17. The bioreactor was able to achieve 91% decolorization and 94.3% and 95.7% removal of BOD and COD, respectively (Sharma et al., 2004). The impact of redox mediators on color removal of azo dye model compounds and textile wastewater by thermophilic anaerobic granular sludge (55°C) was investigated in batch assays. Additionally, a comparative study between mesophilic (30°C) and termophilic (55°C) color removal was performed with textile wastewater, either in the presence or absence of a redox mediator. The study clearly evidenced the advantage of color removal at 55°C compared with 30°C, when dealing with azo colored wastewaters. The impact of the redox mediators anthraquinone-2,6-disulfonate (AQDS), anthraquinone-2-sulfonate (AQS) and riboflavin was evident with all dyes, increasing decolorisation rates up to 8-folds compared with the mediator-free incubations (dos

Santos et al., 2004b). Reductive decolorization of two anthraquinone reactive dyes (Reactive Blue 4, RB4; Reactive Blue 19, RB19) under methanogenic conditions was performed using a mixed, methanogenic culture. Decolorization of the two dyes was investigated to evaluate the rate and extent of color removal as well as to assess possible toxic effects of the dyes and their decolorization products on the methanogenic culture as a function of initial dye concentration ranging from 50 to 300 mg/L. A dextrin/peptone mixture was used as the carbon and electron source. A high rate and extent of color removal was achieved ranging from 4.3 to 29.9 mg/L h and 73-91% for RB4, and 13.0-74.4 mg/L h and 90-95% for RB19 (Lee and Pavlostathis, 2004a). Eight highly-effective decolorization strains were isolated by enrichment using Direct Fast Scarlet 4BS as the sole source of carbon end energy. The optimal microbial consortium was selected by optimizing a combination of decolorization experiments with these eight freely suspended strains, whose decolorization activity was higher than individual strains due to synergistic reaction with each other. The optimal microbial consortium was also immobilized using polyvinyl alcohol (PVA) as the carrier. The study optimized the immobilization and operational conditions, investigated the effect of the environmental factors (temperature, pH and dissolved oxygen) and initial dye concentration on the rate of decolorization by the immobilized microbial consortium (Fang et al., 2004). The degradation of a synthetic wastewater containing the colorant disperse blue 79 (DB79) as a model compound and a real textile wastewater containing reactive azo dyes was achieved in a sequencing batch reactor (SBR) operated through anaerobic/aerobic cycles. It was observed that the DB79 was biotransformed to amines in the anaerobic stage, which were subsequently mineralized in the aerobic stage

(Melgoza et al., 2004). Two laboratory scale UASB reactors were used for the treatment of wastewater generated from the acid-dye process of mixed-species raw silk. The COD removal was in the range of 74.1-85.3%. The apparent color removal was similar to the COD removal (Karnchanawong and Sawangpanyangkura, 2004). A two stage anaerobic/aerobic process was used to decolorize and partially mineralize a reactive vinyl sulfone diazo dye (CI Reactive Black 5, RB5) in a synthetic wastewater. An overall color removal of approximately 65% was found for both fully and partially hydrolyzed dye. Partial mineralization of the fully hydrolyzed RB5 was achieved in the two stage rotating disc reactors. While the anchor group metabolite was mineralized, an oxidized form of the center metabolite remained in the aerobic stage effluent, causing the effluent to be colored although no RB5 was present (Libra et al., 2004). The performance of a pilot scale upflow anaerobic sludge blanket reactor treating simulated cotton textile wastewater was examined to understand the effect of salt concentration on COD and color removal efficiencies. The salt (NaCl) concentration increased from 0 to 128 g/L, while the HRT and the organic loading were kept constant giving HRT of 20 h and a 3.86 of volumetric loading rates. The COD removal efficiency decreased from 80 to 18% as methanogenic bacteria were inhibited by increasing salt concentration in the feed. However, color removal was not affected with increasing salt concentration as high as 128 g/L in the feed (Işık, M., 2004).

Polyacrylonitrile (PAN) is one of the major synthetic fibers commonly used in the mass production of clothing. PAN wastewater contains high concentrations of organic nitrogen and TKN/COD ratios in the range 0.15-0.26. In order to enhance biodegradation of nitrogenous compounds in PAN wastewater, a combined three-stage process of

thermophilic anaerobic/anoxic denitrification/aerobic nitrification fluidized bed reactors was employed. The results obtained showed that the concentration of effluent COD and organic nitrogen in the three-stage process was 175 mg/L and 13 mg/L, respectively (Cheng et al., 2004).

Ex situ nuclear magnetic resonance (NMR) spectroscopy and electrospray ionization (ESI)-ion trap mass spectrometry performed directly on incubation medium were used to follow kinetics of sulfonated azo dye Orange II enzymatic degradation. Nine transformation products were identified using these complementary analyses performed ex situ without any prior treatment (López et al., 2004).

Fungal processes

The ability of 19 isolates of 13 different fungal species to decolorize the reactive dye Blue-BF-R was investigated. All isolates evaluated on solid medium decolorized the dye (dos Santos et al., 2004). Detailed and extensive studies were made and a process was developed for the treatment of dye containing wastewaters by white rot fungi and their enzyme systems (Murugesan and Kalaichelvan, 2004). The decolorizing capacity of 26 white rot fungi from Argentina was investigated. Extracellular production of ligninolytic enzymes by micelium growing on solid malt extract/glucose medium supplemented with different dyes, dye decolorization and the relationship between these two processes were studied. Only ten strains decolorized all the dyes; all ten strains produced laccase, lignin peroxidase and manganese peroxidase on solid medium. A new fungus was identified: *Coriolus versicolor* f., *antarcticus*, potentially a candidate for use in biodecolorization processes (Levin et al., 2004). Decolorisation of Remazol Brilliant Blue R, an azo textile dyestuff, by crude filtrate of *Funalia trogii* ATCC

200800 growing in solid-state fermentation (SSF) medium containing wheat bran and soybean hull was studied. Optimum pH and temperature for laccase and horseradish like peroxidase (HRP) production in SSF medium were determined at 5 and 30°C, respectively. Maximum enzyme synthesis was found in ten days old cultures. The optimum pH and temperature for enzymatic decolorisation were determined at 3.0 and 50°C, respectively (Deveci et al., 2004). White-rot fungi, namely *Coriolus versicolor* and *Schizophyllum commune*, were studied for the biodecolorization of textile dyeing effluent in shaker-flask experiments. The results showed that *C. versicolor* was able to achieve 68% color removal after 5 days of treatment while that of *S. commune* was 88% in 9 days. Both fungi achieved the above results in non-sterile condition with diammonium hydrogen phosphate as the nutrient supplement (Lee et al., 2004). The ability of the white-rot fungus *Lentinula (Lentinus) edodes* to decolorize several synthetic dyes was investigated using solid state cultures with corn cob as substrate. Cultures containing amido black, congo red, trypan blue, methyl green, remazol brilliant blue R, methyl violet, ethyl violet and Poly R478 at 200 ppm, were completely decolorized after 18 days of incubation. Partial decolorization was observed in the cultures containing 200 ppm of brilliant cresyl blue and methylene blue (Boer et al. 2004). Alginate beads, polyurethane foam, nylon sponge and stainless steel sponge were tested as carrier materials for the white-rot fungus *Trametes hirsuta* for laccase production under submerged fermentation conditions. Stainless steel sponge was the best carrier material leading to the highest laccase activities. In a 1-L bioreactor containing *T. hirsuta* immobilised on stainless steel sponge laccase activities of about 2,200 U/L were obtained when the culture medium was supplemented with 1 mM

copper sulfate. The textile dye Indigo Carmine was almost totally degraded in 3 days by *T. hirsuta* in this bioreactor, while Lanaset Marine was degraded in two successive batches (Couto et al., 2004). The decolorization of dyes with different molecular structures by *Cunninghamella elegans* was evaluated under several media conditions. The decolorization profile was highly dependent upon the incubation time, the molecular structure of the dye and the presence or absence of co-substrates. The presence of sucrose or both sucrose and peptone significantly increased the decolorization of the solution; however, the presence of only the nitrogen source suppressed it. It was observed that biodegradation occurred in addition to the biosorption of the dyes; besides, toxic metabolites were produced (Ambrósio and Campos-Takaki, 2004). The biodegradation of Grey Lanaset, which consists of a mixture of metal complexed dye, was studied in a bioreactor which retained pellets of the fungus *Trametes versicolor*, and was operated under conditions of laccase production. Although the decolorization efficiency was very high (90%), no direct relationship to extracellular enzyme was apparent. Moreover, the extracellular enzyme was found to be unable to degrade the dye in vitro (Blánquez et al., 2004).

Combined processes

Biotreated textile wastewater ($COD_0=248$ mg/L; $TOC_0=58$ mg/L; $A_{620}=0.007$ 1/cm; $A_{525}=0.181$ 1/cm; $A_{436}=0.198$ 1/cm) was subjected to advanced treatment with ozonation and granular activated carbon (GAC) adsorption in serial and simultaneous applications. Ozonation appeared to be more effective for decolorization, whereas GAC adsorption yielded higher COD removal rates. It was also found that GAC addition at

pH=7 and 9 enhanced significantly the COD abatement rate of the ozonation process and that the sequential application of ozonation followed by GAC adsorption resulted in the highest treatment performances both in terms of color and COD reduction, under the operating conditions tested. Simultaneous application of GAC and ozone at acidic and alkaline pH seriously inhibited COD abatement rates (Arslan-Alaton and Seremet, 2004b). Comparative degradation of azo dyes by 520 kHz ultrasonic irradiation and in combination with ozone and/or ultraviolet light (UV) was investigated using a probe dye CI Acid Orange 7. At equivalent initial dye concentrations and contact times, the individual effects of UV irradiation, ultrasound and ozone were “no effect”, “bleaching”, and “bleaching/organic carbon degradation”, respectively. However, UV irradiation was found to induce a catalytic effect when applied in combination with either ultrasound or ozone schemes; the overall degradation process was most rapid under simultaneous operation of the three in the presence of a continuous flow of a gas mixture made of argon and oxygen (Tezcanli-Güyer and Ince, 2004). Combination of Fenton process and chemical coagulation was applied for the decolorization of some of the most commonly used disperse and reactive dyestuffs. Fenton oxidation in combination with Fe^{3+} showed to effectively remove COD and dye. In particular, the disperse dye solutions were more easily decolorized by chemical coagulation than reactive dye solutions. Conversely, reactive dye solutions had a higher applicability to the Fenton oxidation than disperse dye solutions due to their higher solubility, lower suspended solids and higher SCOD/TCOD ratios (Kim et al., 2004b). The suitability of a combined process made by adsorption on bentonite and ultrafiltration (UF) for the removal of color caused by methylene blue (MB) dye was investigated. Permeate flux increased linearly

with increasing pressure while the permeate concentration remained almost constant. The addition of bentonite significantly increased the rejection coefficient of MB but decreased the permeate flux (Al-Bastaki and Banat, 2004). The potential of biological treatment as a single process as well as in association with chemical oxidation to treat a textile wastewater was studied. The experimental activity incorporated three schemes: biological treatment only (stage 1), chemical oxidation prior to biological treatment (stage 2), and biological treatment followed by chemical oxidation (stage 3). Biodegradation was accomplished employing three identical sequencing batch reactors (SBRs), while chemical treatment involved the addition of Fenton's reagent in the range of 25-300 mg/L, in a batch-type operation. Both combined alternatives resulted in enhanced color reduction, in comparison to stage 1. Overall, stage 2 appeared to be the best option regarding the treatment of the textile wastewater used (Fongsatikul et al., 2004). A biologically treated textile wastewater was subjected to ozonation as a pre-treatment stage to nanofiltration (NF), with the aim of preventing membranes from fouling and of oxidising organic matter that could damage the membrane material. With ozonation, wastewater COD was reduced to three different levels (160, 135 and 82 mg/L). NF of the sample with the lowest organic matter concentration had the lowest flux decline during the process. Salt retention was very similar for the three feeding streams (Bes-Piá et al., 2004).

Reuse

An industrial process was developed for the treatment of used reactive dye baths which consisted of the combination of pre-filtration, neutralization, nanofiltration and

reverse osmosis, focusing on membrane processes. It permitted not only the recycling of pure water, but also the recovery of the salts used for dyeing and the separation of the unfixed dyes and dyeing chemicals in the forms of a highly concentrated, low-volume liquor which could easily be subsequently treated by usual processes. The water and the salts recovered were reused for a new dyeing at the inlet of the process (Allègre et al., 2004). A combined biological-chemical process for the purification and recycling of residual dye-house effluents containing azo dyes was developed. The process separated the effluents according to source into two streams, both of which were subjected to anaerobic and aerobic treatment steps and biomass separation. One stream was also membrane filtered and treated with ozone, which made possible the recycling of 60% of the total discharge. The combined process increased the quality of the treated streams for recycling purposes and the dye capacity of the textile mill, and minimized operational costs. Furthermore, the municipal water treatment plant to which the textile plant discharged its waste did not need to enhance its capacity (Krull and Döpkins, 2004). The feasibility of biological decolorization of spent reactive azo dyebaths using a halophilic mixed culture and the direct reuse of the renovated dyebath as process water in the dyeing process was experimentally demonstrated (Lee and Pavlostathis, 2004b).

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