Comparison between biological and chemical–physical treatment for colour removal

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Abstract The main aim of this research is to compare the efficiency of biological and chemical–physical treatments for the removal of organic azo dyes in the textile wastewater. Regarding the biological reduction of the wastewater colour the anaerobic/aerobic (ANA/AER) sequential step-treatment provides the best reductions in colour and COD. A lab-scale Sequencing Batch Reactor (SBR) fed with synthetic wastewater and mono-azo dye (at the initial concentration of 25 mg/l) was used achieving 84% colour reduction and 82% COD removal. Chemical–physical treatments were performed using the oxidative method with Fenton's reagent and adsorption on the activated carbon achieving respectively colour reduction over 90% (from the initial concentration of 250 mg/l) and 155 mg col/g GAC total adsorption capacity (from the initial concentration of 1 g/l).

Keywords Activated carbon; azo dyes; Fenton oxidation; sequencing batch reactor; textile waste

Introduction

The textile industry is characterised by its high water consumption and, consequently, its large amount of wastewater production. Unfortunately the wastewater quantity and characteristics strongly depend on the technique used for each single process (i.e. washing, bleaching, dyeing, etc) and raw material (i.e. wool, cotton, etc). According to the production method the wastewater production can be estimated within 40–300 m^3 per ton of finished substrate. Many dyes are difficult to decolourise due to their complex structure and synthetic origin (there are many structural varieties such as acidic, basic, disperse, diazo, azo, metal complexes dyes, etc). Over 90% of some 4000 dyes tested by the ETAD (Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry) have high toxicity.

Because these compounds retain their colour and structural integrity under exposure to sunlight, soil, bacteria and sweat, they also exhibit a high resistance to microbial degradation in wastewater treatment systems. No single treatment system is adequate for degrading the various dye structures. Currently, much research has been focused on biological and chemical–physical processes degrading azo dyes in wastewater. Regarding the biological processes, the anaerobic reduction of azo dyes to simpler compounds has been well researched (Chung *et al.*, 1978; Brown and Laboureur, 1983a; Razo-Flores *et al.*, 1997; Chinwetkitvanich *et al.*, 2000). These studies have demonstrated the ability of anaerobic microbes and sludges to effectively reduce azo dyes to their intermediate structures, thus destroying the apparent colour. But many of these intermediates are aromatic amines that are toxic and carcinogens. A further degradation of the dye compound is necessary if toxicity is to be eliminated or reduced (Levine, 1991; Brown and DeVito, 1993). This kind of treatment could be an aerobic degradation of azo dye wastes that occurs mainly by adsorption onto the cell walls (Pagga and Brown, 1983) and can be used to stabilise dye metabolites (Brown and Laboureur, 1983b). Because anaerobic bacteria are often able to reduce the azo linkages, but

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are generally unable to further stabilise the dye metabolites, it would seem advantageous to follow anaerobic treatment processes with an aerobic treatment step. Cyclic concentration gradients, to which biomass is exposed in a SBR reactor (Brown and Lester, 1979; Artan *et al.*, 1996), permit selection and enrichment of particular microbial species more capable to carry out the requested biological processes in the presence of inhibiting substances too. In this study, according to this particular process of selection/enrichment, a kinetic advantageous sequencing batch process is used in place of a continuously fed one.

Regarding the chemical–physical processes the most used are: the oxidative method, the adsorption on the activated carbon, the membrane treatment and other new processes as the treatment with the Cucurbituril (Robinson *et al.*, 2001). This study has been focused on the first two processes. The oxidative process is the most commonly used method to remove colour from liquid waste coming from textile industries. This is mainly due to its easy application and high efficiency; in particular it's a suitable method of treating wastewater resistant to biological treatment. The main oxidising agent is usually hydrogen peroxide (H_2O_2); it oxidises many organic compounds particularly where there are unsaturated carbon sites at which attack can take place (i.e. the aromatic ring cleavage of the dye molecules). However, attack is often enhanced by addition of a catalyst such as ferrous ion, the well-known Fenton's reagent. The mechanism of oxidation involves free radical attack and hydrogen atom abstraction. The O-O bond breaking in hydrogen peroxide to give hydroxyl radical occurs as the result of activation by Fe^{2-} ion:

$$Fe^{2+} + H_2O_2 \rightarrow (FeOH)^{2+} + OH^{\circ} \text{ and } (FeOH)^{2-} + H_2O_2 \rightarrow Fe^{2-} + HO^{\circ}_2 + H_2O$$

The adsorption techniques have gained favour recently due to their efficiency for the removal of pollutants too stable for conventional methods. The adsorption on the activated carbon is the most commonly used method and seems to be very effecting for adsorbing many dye types (Raghavacharya, 1997) according to the carbon and wastewater characteristics. Decolourising is a result of two mechanisms: adsorption and ion exchange (Slokar and Le Marechal, 1997) and it's influenced by many physical–chemical parameters.

The main aim of this study is to compare the efficiency of biological and chemical–physical treatments for the removal of organic azo dyes in the textile wastewater, using the SBR reactor as biological process, the Fenton oxidation and the adsorption on the activated carbon as chemical–physical processes.

Methods

The industrial textile dye Intazol FS-3B (MW = 1024.24), produced by Dystar, is an azo-dye identified as reactive red 195 in Colour Index (Figure 1).

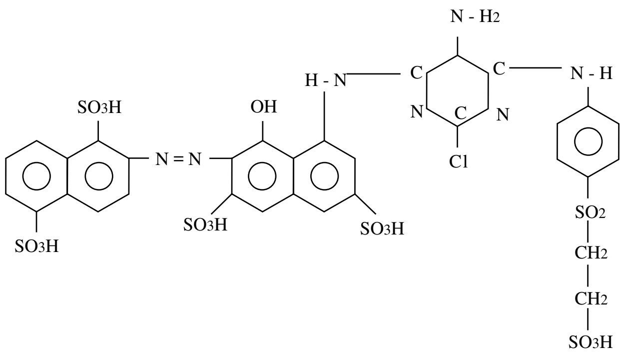

Figure 1 Reactive red intazol FS-3B chemical structure

Table 1 Physical properties of Sutcliffe Speakman Carbon DLC

Total surface area (m^2/g)	1400
Moisture (w %)	8.4
Density (g/ml)	0.32
Mesh	12–40
Iodine nr	1250
Methylene blue nr	307.16

Biological treatment

The experimentation has been carried out in a lab-scale SBR fed with synthetic wastewater containing: 600 mg COD/l, 40 mg N/l, 15 mg P/l and 25 mg/l of Reactive Red FS-3B. Activated sludge from the oxidation tank of a municipal wastewater treatment plant of Rome has been used as seed. Each twelve-hour cycle is divided into three main phases: the anoxic/anaerobic phase (9 hours), the aerobic phase (2 hours) and the settling phase (1 hour). During the anoxic/anaerobic phase the reactor is continuously stirred and feeding of wastewater to be treated occurs in the first 10 minutes. During the aerobic phase the reactor is stirred and aerated to keep dissolved oxygen concentration at 2 mg/l and draw occurs at the end of the phase. During the settling phase decant occurs at 55th minute. The initial volume is 3 l, the fill volume is 2 l and the reactor volume is 5 l. The hydraulic retention time is 20 h. The total sludge age of the reactor is 20 d and the average biomass concentration in the SBR is 2000 mg MLVSS/l. The temperature is kept constant at 35°C by a circulating water bath. A timer controls for each phase, time and duration of: draw, stirrer, feeding, aeration and decant. pH and ORP (Oxidation–Reduction Potential) are monitored throughout the process. Twice a week samples are collected from the reactor at the beginning and at the end of a cycle. Several samples are also collected within a typical operative cycle during the anoxic/anaerobic phase and during the aerobic phase in order to determine the colour and the COD removal rates.

Chemical–physical treatment

The hydrogen peroxide (title 25.5%), produced by Ashland Italy S.p.a., and the Ferrous Sulphate hepta-hydrate $FeSO_4.7H_2O$ (analytical grade reagent from Merck) have been used in order to realise the Fenton oxidation. The commercially available adsorbent used for the

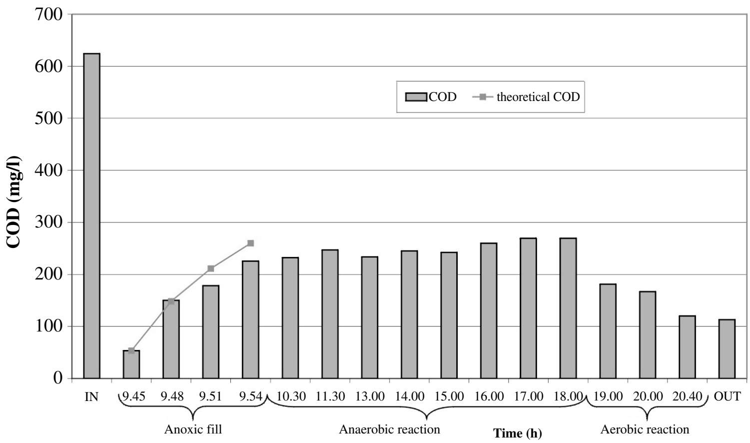

Figure 2 COD time-profile within a typical SBR cycle

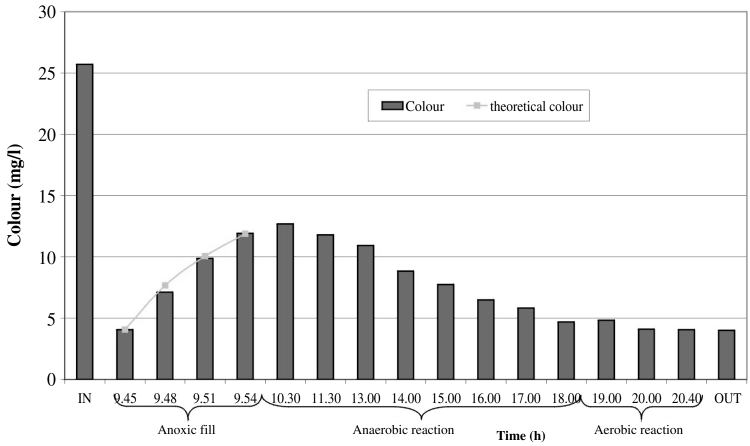

Figure 3 Colour time-profile within a typical SBR cycle

adsorption process was Sutcliffe Speakman Carbon DLC produced by B.M.D. S.r.l. (Italy), that is a mineral based granular activated carbon with high activation degree (Table 1). The adsorbent has been washed in deionised water and sieved into discrete particle size ranges before contacting with the adsorbate solution. It's particularly suited to adsorb the water's pollutant characterised by relevant molecular dimension. Its meso-porous structure allows to utilise it in the decolourising process. The kinetic and the equilibrium isotherms were determined by contacting a known mass of adsorbent with dye solutions at T = K while the breakthrough curve were obtained by a packed column (BV = 28.4 ml) that was fed at constant flow rate.

Analysis methods

During the experimentation, lab analyses have been carried out according to the *Standard Methods for the Examination of Water and Wastewater* (1995). Samples are filtered at 1.2 μm to determine total and volatile solids (by gravimetric method) and at 0.45 μm to determine COD and colour. The colour concentration has been determined by using the UV-visible DMS 200 twin beam spectrophotometer produced by Varian at a wavelength of 543 nm. The

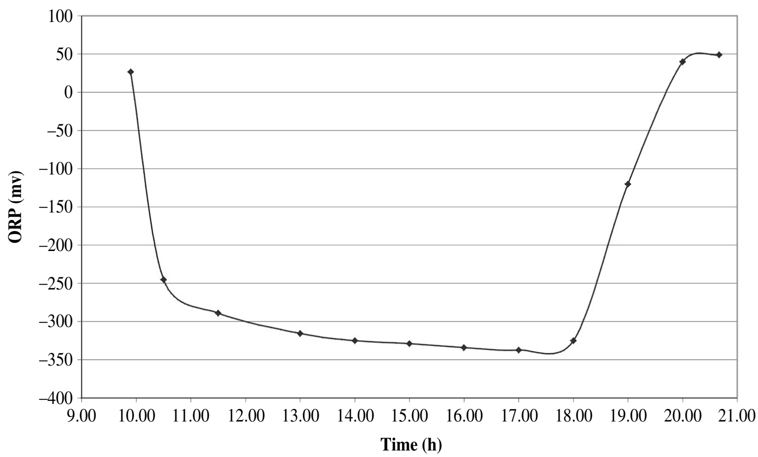

Figure 4 ORP time-profile within a typical SBR cycle

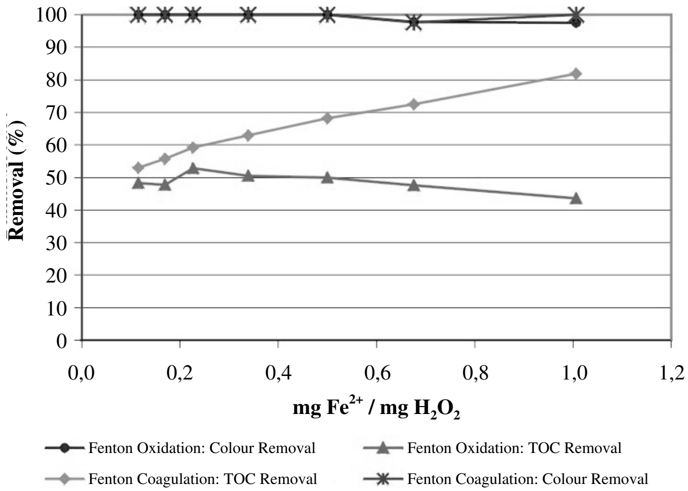

Figure 5 Colour and TOC removal efficiency of the Intazol red solution after Fenton oxidation and coagulation respectively (colour concentration = 250 mg/l, temperature = 20°C, pH = 2.5)

TOC measurements have been carried out by injecting 50 μL of the sample into high temperature analyser DC–190 (Rosemount Analytical Inc.).

Results and discussion

Biological treatment

Preliminary study on several cycles with only aerobic phase was performed in order to establish a quick acclimation of the biomass to the Intazol Red colour (25 mg/l).

During this period the COD average removal rate was 60% and colour removal rate decreased up to 4% (results here not shown). This low colour removal efficiency is probably due to the colour adsorption onto the cell walls and demonstrates that the aerobic micro-organisms are not able to degrade the colour molecule. Hence, an anoxic/anaerobic phase has been introduced at the beginning of the SBR cycle in order to reduce the azo dye to its intermediate structures, thus destroying the apparent colour.

Figures 2 and 3 show the results obtained within a typical operative cycle respectively as COD and colour time-profiles during the anoxic/anaerobic phase and during the aerobic phase. Theoretical values refer to the concentration that would have been measured in absence of any reaction, i.e. due to dilution only.

Figure 2 shows a constant COD value during the anaerobic phase and a quick consumption of the COD during the aerobic phase due to the heterotrophying biomass utilisation. Besides, the high COD concentration during the anaerobic phase represents the necessary co-substrate for the colour removal process. The average COD removal efficiency of the SBR is about 82%.

Table 2 Langmuir and Freundlich model parameters for GAC DLC with Intazol red solution

	Langmuir		Freundlich	
T (°C)	1/A	R^2	k	R^2
20	0.0126	0.988	188.67	0.993
30	0.0111	0.994	184.93	0.971
40	0.0106	0.959	62.17	0.999

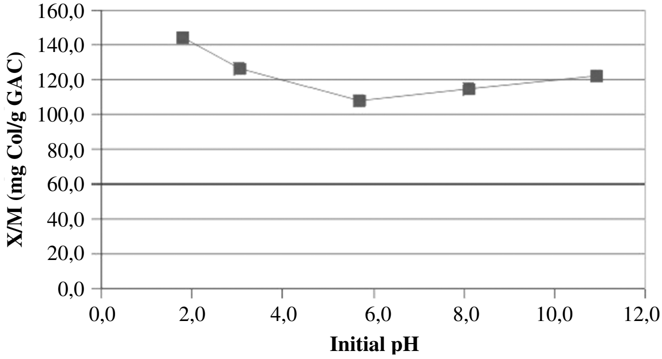

Figure 6 pH influence on equilibrium adsorption capacity (1g Intazol Red/l, 100 mg GAC DLC (12 × 40), Temperature = 20°C)

Figure 3 shows that the colour removal occurs during the anaerobic phase because the anaerobic bacteria are able to reduce the azo linkages while, during the aerobic phase, the colour concentration is almost constant and similar to the effluent value. The average colour removal efficiency of the SBR is about 84 %.

Figure 4 shows the ORP time-profile. The ORP decreased quickly up to −250 mV during the anoxic phase due to the nitrate depletion and reached −350 mV during the anaerobic phase (required ORP value for high colour removal, Dubin and Wright, 1975).

Chemical–physical treatment

Oxidative method. The optimum operative conditions for removing the Intazol Red colour at concentration of 250 mg/l, at pH = 2.5 and at room temperature, seems to be starting from Fe/H_2O_2 ratio of 0.2. In Figure 5 the performances in terms of both colour and TOC removal are reported and in particular the results obtained show that, by using Fenton's reagent, increasing the H_2O_2 quantity the organic material, such as degradation products, is still present in the solution. Therefore the high Fe content of the solution can be utilised to promote the coagulation/flocculation process simply by pH adjustment until pH 8.5 with alkali (NaOH). By this supplementary operation some organic degradation products can be adsorbed into the flocs and then removed. As reported in Figure 5, in particular the TOC removal efficiency increases (>80%) as the Iron content increases.

Adsorption method. Laboratory tests have been performed on the carbon with the Intazol Red colour at concentration of 1 g/l in order to determine the kinetic, the pH effect and the

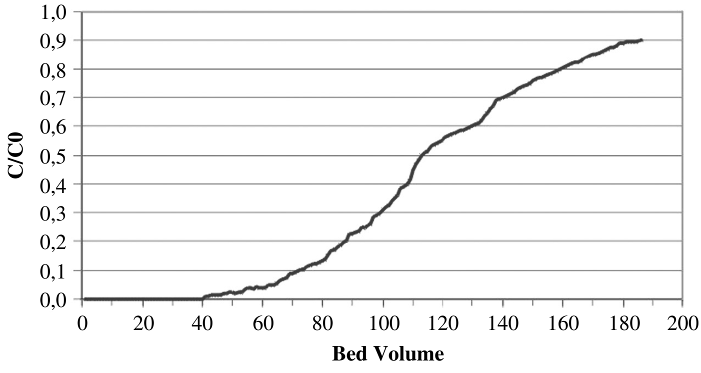

Figure 7 The breakthrough curve of the GAC DLC with the Intazol red solution

adsorption isotherm. The shape of the kinetic curve seems to be mainly due to the diffusion model according to previous works (Allen *et al*., 1988). Considering the adsorption isotherm, the Freundlich adsorption model fits a little better than the Langmuir model in particular according to the temperature increasing (Table 2). The temperature doesn't give favourable conditions probably because the carbon surface acquires a "basic" character at high temperatures (Puri, 1970).

The pH of the solution being treated may affect the response of the solute adsorption in particular for acidic and basic dye (unpublished data) but for the Intazol Red colour (reactive dye) Figure 6 shows higher adsorption values at pH < 6.

Probably this behaviour is due to a favourable combination of the negative charge of the carbon surface and the cationic species formation of dye (Al Dajs *et al*., 2000). Moreover we can attribute to the activated carbon an amphoteric property considering the constant adsorption rate at high pH.

The breakthrough curve (Figure 7) shows that the column leaks colour early and confirms that a long time until complete breakthrough has been achieved. In particular at 3% of breakthrough, 53 ml Bed Volume occurs. The calculated length of the wave front (Mass Transfer Zone) is 72.04% of the column length and the total adsorption capacity is 155.01 mg col/g GAC.

Conclusions

This study has suggested that it's possible to treat wastewater containing organic azo dyes using both biological systems as the SBR reactors and chemical–physical processes as the Fenton oxidation and the adsorption on the activated carbon. In particular a lab-scale SBR fed with synthetic wastewater and Intazol Red FS-3B azo dye (at the initial concentration of 25 mg/l) achieved 84% colour reduction and 82% COD removal. The Fenton oxidation achieved more than 90% colour reduction (from the initial concentration of 250 mg/l Intazol Red) and up to 80% TOC removal efficiency with coagulation. The total adsorption capacity of the adsorption process was 155 mg col/g GAC (from the initial concentration of 1 g/l Intazol Red). However, chemical treatment is often cost and application limited, while physical removal can lead to extra solid wastes and increased overhead. Biological treatment has been effective in reducing dyehouse effluents, and when used properly has a lower operating cost than other treatment processes. Our results lead to the conclusion that a much better efficiency and cost effectiveness can be achieved using the following sequence of treatments: biological treatment should be applied first in order to remove organic azo dyes and surfactants, then the Fenton oxidation in order to remove recalcitrance compounds and finally the adsorption on GAC for residual wastewater.

References

Al Dajs, Y., Khraishen, M.A.M., Allen, S.J. and Ahmad, M.N. (2000). Effect of carbon surface chemistry on the removal of reactive dyes from textile effluent. *Wat. Res.*, **34**, 927–935.

Allen, S.J., Mc Kay, G. and Khader, K.Y. (1988). The adsorption of acid dye onto peat from aqueous solution-solid diffusion model. *Journal Colloid Interface Science*, **126**, 517–524.

Artan, N., Akkaya, M. and Artan, S.R. (1996). Experiences with the SBR treatment of industrial wastewaters. In *Proc. of the First IAWQ Specialized Conference on Sequencing Batch Reactor Technology*, Munich, Germany, 18–20.

Brown, D. and Laboureur, P. (1983a). The degradation of dyestuffs: Part I. Primary biodegradation under anaerobic conditions. *Chemosphere*, **12**(3), 397–404.

Brown, D. and Laboureur, P. (1983b). The aerobic biodegradability of primary aromatic amines. *Chemosphere*, **12**(3), 405–414.

Brown, M.J. and Lester, J.N. (1979). Metal removal in activated sludge: the role of bacterial extracellular polymers. *Water Research*, **13**(9), 817–837.

Brown, M.A. and DeVito, S.C. (1993). Predicting azo dye toxicity. *Critical Reviews In Environmental Science and Technology*, **23**(3), 249–324.

Chinwetkitvanich, S., Tuntoolvest, M. and Panswad, T. (2000). Anaerobic decolorization of reactive dyebath effluents by a two-stage UASB system with Tapioca as a co-substrate. *Water Research*, **34**(8), 2223–2232.

Chung, K., Fulk, G.E. and Egan, M. (1978). Reduction of azo dyes by intestinal anaerobes. *Applied and Environmental Microbiology*, **35**(3), 558–562.

Dubin, P. and Wright, K.L. (1975). Reduction of azo food dyes in cultures of *Proteus vulgaris*. *Xenobiotica*, **5**, 563–571.

Levine, W.G. (1991). Metabolism of azo dyes: implications for detoxification and activation. *Drug Metabolism Reviews*, **23**(3–4), 253–309.

Pagga, U. and Brown, D. (1986). The degradation of dyestuffs: Part II. Behaviour of dyestuffs in aerobic biodegradation tests. *Chemosphere*, **15**(4), 479–491.

Puri, B.R. (1970). *Chemistry and Physics of Carbon*. Marcel Dekker, New York.

Raghavacharya, C. (1997). Colour removal from industrial effluents: a comparative review of available technologies. *Chem. Eng. World*, **32**, 53–54.

Razo-Flores, E., Luijten, M., Donlon, B., Lettinga, G. and Field, J. (1997). Biodegradation of selected azo dyes under methanogenic conditions. *Water Science & Technology*, **36**(6–7), 65–72.

Robinson, T., McMullan, G., Marchant, R. and Nigam, P. (2001). Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresource Technology*, **77**, 247–255.

Slokar, Y.M. and Le Marechal, A.M. (1997). Methods of decolouration of textile wastewaters. *Dyes Pigments*, **37**, 335–356.

Standard Methods for the Examination of Water and Wastewater (1995). 19th edn, American Public Health Association/American Water Works Association/Water Environment Federation, Washington D.C., USA.