Biological treatment of effluent containing textile dyes

I M C Gonçalves*, A Gomes, R Brás, M I A Ferra, M T P Amorim† and R S Porter‡

Chemistry Department, University of Beira Interior, 6200 Covilhã, Portugal

† *Textile Department, University of Minho, Guimarães, Portugal*

‡ *Clemson University, Clemson, USA*

Colour removal of textile dyes from effluent was evaluated using a laboratory 'upflow anaerobic sludge blanket' reactor. Several commercial dyes were selected to study the effect of dye structure on colour removal. The anaerobic reactor was fed with glucose, an easily biodegradable organic matter and selected individual dyes. Results show that some of the dyes are readily reduced under anaerobic conditions even at a high concentration of 700 mg/l. The average removal efficiency for acid dyes using this method was between 80 and 90% and that observed for the direct dye used was 81%. Laboratory experiments using the anaerobic reactor with disperse dyes, such as an anthraquinone-based dye, were unsuccessful even at low concentrations of 35 mg/l. Additional experiments were conducted to evaluate the toxicity of a selected disperse dye to an anaerobic environment. Results indicate that the purified dye is more toxic to the biomass than the commercial one.

INTRODUCTION

Pollution control of industrial effluent has become more stringent in the last few years and new methods for the removal of colour from such wastewater are continually being investigated. Throughout the world, regulations for industrial effluents are being updated and enforced, and the demand for more efficient wastewater treatment systems is increasing. Because industrial textile effluents contain several types of pollutants, such as dispersants, levelling agents, salts, carriers, acids, alkali and various dyes [1], they will be affected by the new regulations. Effluent from, for example, the dyeing and finishing of wool or from polyester fibre manufacturing, can contain a variety of components of varying concentrations, i.e. 50–5000 mg/l of COD (chemical oxygen demand); 200–300 mg/l BOD (biological oxygen demand); 50–500 mg/l suspended solids; 18–39 mg/l organic nitrogen; 0.3–15 mg/l total phosphorus; and 0.2–0.5 mg/l total chromium. Additionally, the effluents from such manufacturing processes are coloured due to the presence of soluble and insoluble dyes. Dyes are generally present in these effluents in concentrations of 10–50 mg/l. Considering a manufacturing production of 3 tonnes per day, the problem is significant. Colour is usually noticeable at concentrations above 1 mg/l and has been reported in effluent from textile manufacturing processes at concentrations exceeding 300 mg/l [1,2].

The residual colour present in textile effluent is dependent on the dyeing procedure used, in particular on factors such as the levels of shade, the application method and the liquor ratio. The reported quantity of dye lost in the discharged effluent is estimated to be around 5–20% for acid dyes, 10% for disperse dyes and 5–30% for direct dyes. Azo dyes represent the largest group of all synthetic dyes and represent 70% of all organic dyes used by the textile industry [3].

Dyes are, in general, not toxic to the environment. However, dark colours in water streams do reduce light penetration affecting the growth of plants and impacting on other forms of wildlife. Additionally colours cause an aesthetic problem to the surroundings.

Several methods have been studied to evaluate the removal of colour from industrial effluent, such as carbon adsorption, chemical precipitation and flocculation, oxidation with hydrogen peroxide (Fenton's reaction), UV techniques, ozonation and ion extraction, but each one has been found to exhibit certain limitations. Membrane technologies have also been applied with the main objective of recovering dyes and water. One of the problems associated with membrane technologies is the disposal of the concentrated stream generated during the process. These problems have been addressed by reusing the concentrate or treating it before disposal. For instance, an anaerobic process may be used for removal of high organic loads in some cases [1]. As the price of membranes become more affordable they will be applied more frequently to reuse and recycling processes for industrial waste streams.

Biological processes have also been used as a method of colour removal, but because most dyes are designed to resist light and oxidative degradation, they are naturally less amenable to conventional aerobic biological treatment [4].

The removal of water-soluble dyes by aerobic processes is a particular problem. Some of these dyes are adsorbed on the wastewater sludge. The degree of adsorption

depends on the number of sulphonic groups present, the specific structure and the molecular size of the dye [2,4]. Water-soluble reactive dyes are more readily adsorbed onto biomass (the anaerobic sludge) [2]. Fine particulate present in insoluble dyes, such as disperse dyes, are in general difficult to settle and, particularly anthraquinone dyes, are resistant to aerobic biodegradation [3].

Some dyes are less resistant to anaerobic biodegradation. For instance, although azo dyes are in general resistant to aerobic processes, they are readily degraded under anaerobic conditions [5–7]. A study presented by Brown and Laboureur assessed the anaerobic biodegradability of 22 water-soluble dyes and found that a substantial number were biodegradable [5].

When compared with conventional aerobic processes, the anaerobic treatment presents several advantages. Anaerobic processes are less expensive than aerobic ones and they can be carried out in simple and relatively inexpensive reactors like an 'upflow anaerobic sludge blanket' (UASB) reactor. Furthermore, according to the literature, anaerobic conditions can also be applied to the treatment of more complex industrial effluent containing compounds with multiple chloro, nitro and azo groups that are resistant to aerobic biodegradation [8]. Applications of anaerobic processes have increased significantly in the past few years mainly because of favourable reported laboratory results. Drawbacks have been slowly diminishing with the advance of this technology.

The objective of this study is to demonstrate the efficacy of a UASB reactor running anaerobically in the presence of azo dyes in commercial forms and high concentrations. The biological degradation of disperse dyes, such as anthraquinone-based dyes, is also reported. However, laboratory results showed that this kind of dye could affect the performance of the anaerobic reactor by causing inhibition of the anaerobic metabolism. Therefore fine particles of insoluble dyes, such as colloid solutions of disperse dyes that are difficult to settle, should be removed prior to treatment. These components are likely to be resistant to anaerobic biodegradation [5]. Studies are being performed in our laboratories to find out the toxicity of anthraquinone or other disperse dyes when submitted to anaerobic conditions in batch systems.

Dispersing agents are also able to inhibit anaerobic growth. In previously reported laboratory experiments it was difficult to determine the cause of reactor failure. It may have been due to the purified dye or to the dispersing agents [9]. Dispersing agents and dye concentrations in the waste stream are likely to be lower than of the anionic azo dyes because they have higher a adsorption degree (90–100%) on the fibre [1].

MATERIALS AND METHODS

Experimental apparatus

The UASB reactor consisted of a PVC column 100 cm in height and 140 mm in diameter. The reactor was equipped with several sample ports at 7, 14, 21, 28, 35, 42, 49, 59, 69, 79, 89 and 98 cm from the bottom, denoted as sample ports T_1, T_2, T_3, T_4, T_5, T_6, T_7, T_8, T_9, T_{10}, T_{11} and T_{12}, respectively. The reactor had a water-jacket to provide temperature control and was operated at 37 °C. In order to measure the volume of biogas[§] produced the outlet at the top of the reactor was connected to a gas washing flask which contained a solution of potassium hydroxide. The volume of biogas was monitored using a Triton-WRC flow meter and the feed to the reactor was controlled to give a hydraulic retention time of 12 h and an organic load of 3.5 kg/m^3 per day COD.

Some batch experiments were also carried out in this study. For these experiments the reactors had volumes of 1 l capacity and were inoculated with biomass taken from the UASB. A 20% (v/v) of innoculum was used.

Substrate and seed sludge

The reactor was fed with a synthetic medium consisting of glucose and sucrose as a carbon source. Micro- and macronutrients were added following the procedure described by Wiegant and Lettinga [10]. Dyes were dissolved in the synthetic waste at several concentrations and introduced into the reactor.

The original seed sludge was collected from a municipal wastewater treatment plant. After the inoculation of the seed sludge, the reactor was acclimatised for three months. The sludge bed height was between 30 and 50% of the reactor height. Total biomass was calculated on the basis of the volatile suspended solids profile that resulted from the analyses of samples gathered from the sample ports.

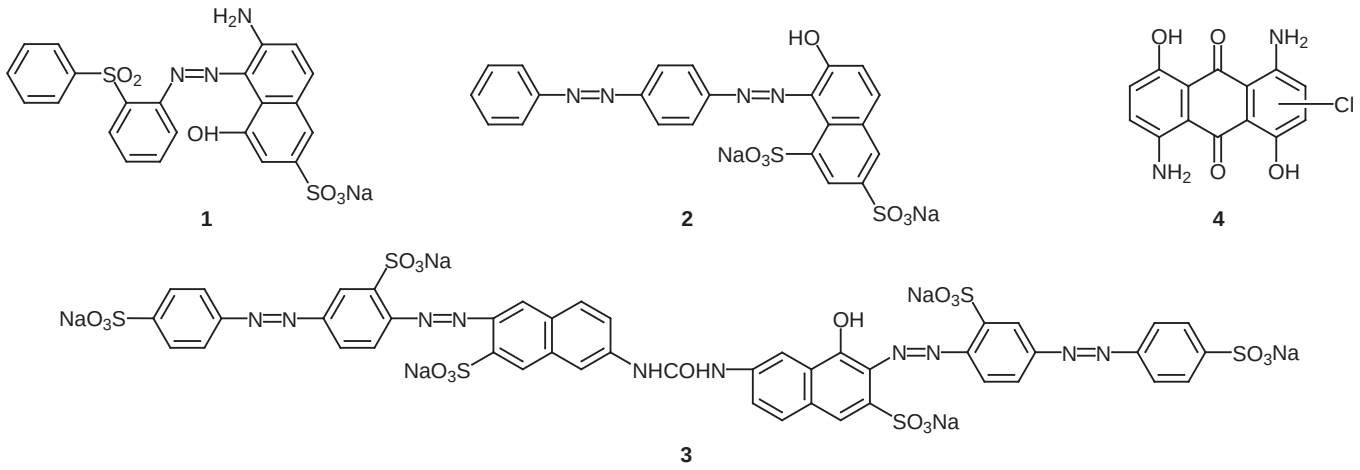
Dyes used in the study

Three commercial azo dyes were studied, CI Acid Red 42 (**1**), CI Acid Red 73 (**2**) and CI Direct Red 80 (**3**) which were obtained from Bayer and DyStar. The reactor was also monitored in the presence of CI Disperse Blue 56 (**4**), an anthraquinone-based dye, in which the content of disperse agent in the commercial dye is on average 65%. In order to study the influence of the disperse agent in the dye removal a purified form of the disperse dye was also used. The commercial and purified forms of the disperse dye were obtained from Ciba-Geigy.

Analytical procedures

The pH, the concentration of suspended solids and volatile suspended solids, and COD values were analysed according to standard methods [11]. The colour was measured in filtered samples using the maximum wavelength for each dye. Changes in dye structures were analysed by running ultraviolet–visible spectra and thin-layer chromatography tests. All the samples were analysed 2 h after collection so that colour changes in the filtered solutions could be minimised in the presence of oxygen and light. For the disperse dyes, which are

[§] Biogas is defined as the gas produced during anaerobic degradation of organic matter, mainly methane and carbon dioxide.



insoluble in water, samples were mixed with a fraction of dimethylformamide (DMF) in proportion of 2 parts of effluent samples to 3 parts of DMF. The resultant solution was then filtered and analysed.

Dye concentrations are listed in Table 1. The concentration range of the disperse dye **4** was much lower than that of the anionic azo dyes owing to its lower solubility and higher degree of fixation to the textile fibres. In order to evaluate the contribution of the dyes to the total COD of the solutions, the COD of the dye itself, dissolved in distilled water, was determined. The reactor was monitored and samples were taken from the sample ports in order to study the influence of the dyes in the presence of an easily biodegradable substrate.

Table 1 Concentration ranges for the dyes used in this study

Dye	Concentration range, mg/l
1	40–80
2	40–700
3	40–80
4	30–35

RESULTS AND DISCUSSION

Figure 1 indicates the values obtained for COD in the feed of the reactor (influent) and in the solution that comes out of the reactor (effluent) for dyes **1**–**3**. The monoazo dye **1** was fed to the UASB reactor for 20 days in concentrations up to 80 mg/l. The direct polyazo dye **3** was also studied for 10 days in the same range of concentrations. The performance of the reactor, in terms of COD removal was not affected, giving an average of 82%. Removal of the dyes, measured at the maximum wavelength on the visible spectrum, was about 82% for **1** and 81% for **3**. The diazo dye **2** was tested in order to study the dye removal at higher concentrations. This dye was fed into the reactor for 30 days, at concentrations up to 700 mg/l. The COD removal was only affected for concentrations higher than 300 mg/l between days 95 and 98 and also days 132 and 138 (Figure 1). In this case the COD removal decreased from 84 to 66%, which can be explained by the increased

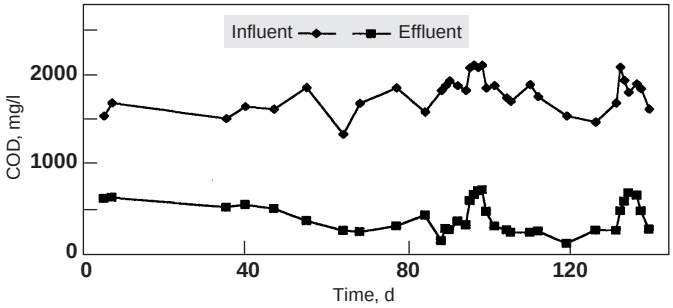


Figure 1 COD removal in the UASB reactor

of the contribution of the dye and its metabolites to the total COD value. From the samples taken at the sample ports of the reactor, the contribution of the dye to the total COD was only significant at this range of concentrations.

Dye decolourisation was also studied and from the results shown in Figure 2 it can be observed that the dye concentration decreased significantly inside the reactor. The percentage of dye removal, measured at the maximum wavelength (λ_{max}), was between 86 and 93%. Furthermore the removal of the colour occurs predominantly at the bottom of the reactor and is completed before sample port T_3, located 21 cm from the bottom. As the biomass is essentially distributed from 0 to 42 cm from the bottom, the total COD removal occurred mainly up to this height (Figure 2). Evidence of the removal of dye **2** can also be observed in Figure 3, with the absorption at λ_{max} being virtually zero after treatment in the reactor [Figure 3(b)]. The spectra show that the structure of the compound was altered, which is like to be by reduction of the azo groups and cleavage of the conjugated double bonds of the dye molecule.

It should be pointed out that the anaerobic consortia bacteria used in this study were not exposed to these kinds of xenobiotic compounds[¶] previously, however the azo dye molecules were altered. This means that anaerobic bacteria promptly reduced the dyes. According to the literature, this is a gratuitous process (anaerobic

[¶] Xenobiotic compounds are compounds which do not or rarely exist as natural products or contain structural elements that cannot be synthesised biochemically.

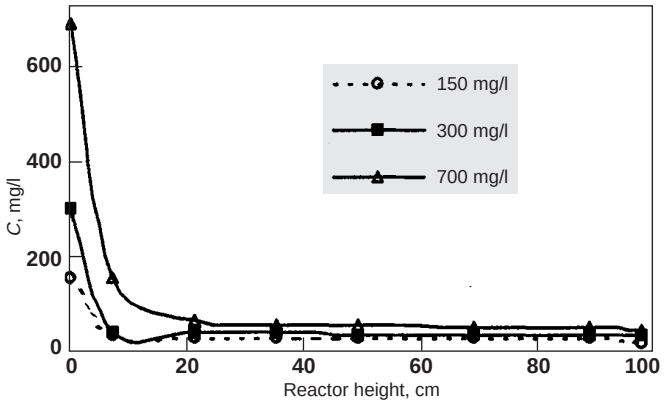


Figure 2 Decolourisation of the diazo dye **2** in the UASB reactor for concentrations up to 700 mg/l

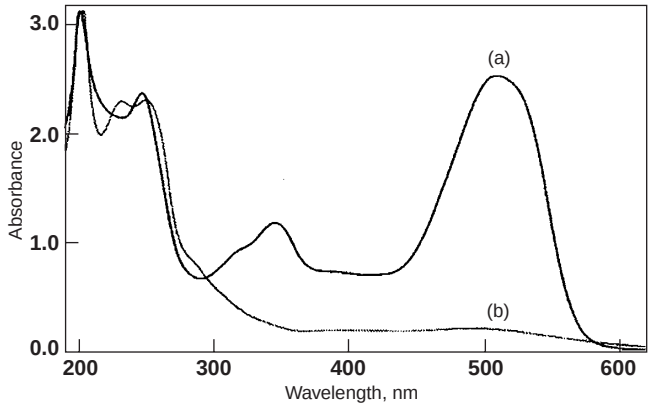


Figure 3 Absorbance spectra of the azo dye **2** (a) before and (b) after treatment in the UASB reactor

microorganisms do not use these compounds as the sole source of carbon and energy) carried out by extracellular enzymes [12]. Biogas production for this time period was an average of 345 l/kg of influent COD, and was not affected by the presence of the dye. After ceasing to feed the reactor with dye, its performance was followed and results showed a quick increase in the COD removal values.

In general it can be concluded that the presence of azo dyes affects the anaerobic treatment efficiency, in terms of COD, only for concentrations higher than 300 mg/l, which is not expected to exist in textile wastewater [1]. Results obtained from profiles of COD and dye concentration in the reactor indicated that the rate of decolourisation was faster than the rate of degradation of the organic matter used as the carbon source.

Some batch experiments were also carried out for dye concentrations up to 700 mg/l of dye **2** in order to study the influence of the azo dye in the removal of the readily degradable organic load. Results show that the dye contribution to the total COD (1.19 mg COD/mg of **2**) was kept almost constant even at 700 mg/l (Figure 4). The percentage of COD removal, after 72 h, decreased and averaged from 72% in the standard reactor with 0 mg/l of dye and up to 36% in the reactor with 700 mg/l of dye. Percentage of COD removal of the organic substrate used as the carbon source was not affected in a significant way. This can be concluded because if the dye contribution to the total COD values at different concentrations is subtracted from the total COD in each reactor, the results relative to the COD values are similar in the standard reactor. On the other hand, the anaerobic metabolites of azo dyes do not cause a significant decrease to the contribution to the total COD values. If the metabolites contribute to the total COD in lower values, the percentage of COD removal would increase, and this is not the case.

Colour removal was also analysed for dye **2**, as can be observed in Figure 5. The higher the concentration of dye, the longer the time required to meet the residual colour. These results are in agreement with those obtained in the UASB reactor, in which it was observed that the higher the concentration of dye, the higher the hydraulic retention time required to get a constant value of the residual colour (see Figure 2).

The study of the disperse dye **4**, an anthraquinone-based dye, was also carried out at concentrations up to 35 mg/l. The dye was fed to the UASB reactor for two weeks (between days 211 and 226). The biogas production decreased significantly, from 345 to 25 l/kg of influent COD on average (Figure 6) and the COD removal from 71 to 31%. Dye decolourisation was analysed by running spectra of the dye samples (Figure 7) obtained from the various ports of the reactor. As can be seen from this Figure, by the time the effluent has reached sample port T_8 the dye has been almost totally removed from the effluent.

Based on this experiment it can be concluded that the dye was removed by adsorption onto the biomass or just filtered by the sludge bed, and this resulted in the reactor

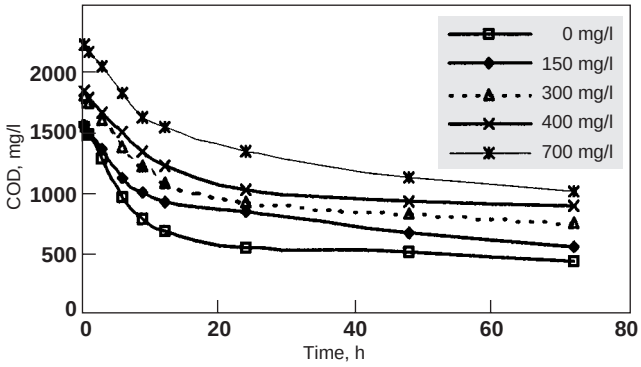


Figure 4 COD removal in batch systems at different dye concentrations for dye **2**

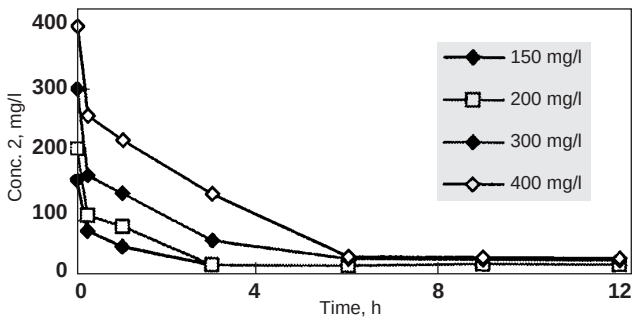


Figure 5 Anaerobic decolourisation tests of dye **2** in batch experiments

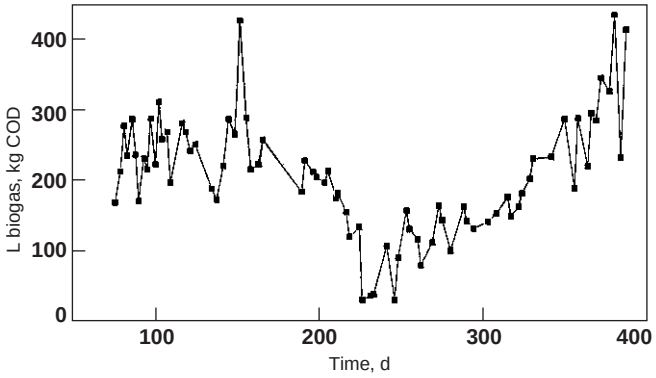


Figure 6 Biogas production during the study of disperse dye **4** in the UASB reactor

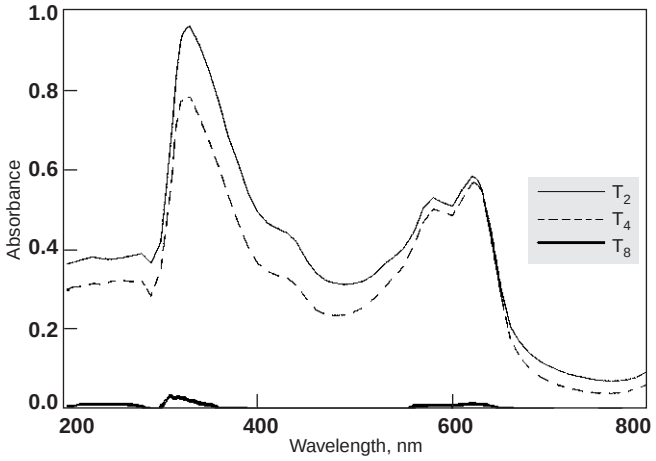


Figure 7 Spectra of the disperse dye **4** in the effluent gathered from samples ports T_2, T_4 and T_8 along the UASB reactor

to stop working. This could be observed, even after stopping feeding with the dye suspension, after 10 days the concentration at the second sample port (T_2) was much higher (about 170 mg/l) than the level in feed concentration (35 mg/l). In this case it was necessary to wait for a period of about five months for the reactor to reach steady state conditions again, as seen in Figure 6.

By taking samples from the sample port T_2 the concentration of the dye in the sludge bed was monitored. Results show that only after 150 days (about 5 months), the dye was completely removed from the sludge bed, which is in agreement with the results obtained for the biogas production (see Figure 6).

In order to find out if it was the dye itself or the dispersing agent that was toxic to the biomass, batch experiments were carried out with the commercial and the purified form of the disperse dye. Results show that although the commercial disperse dye **4** had a higher practical solubility (which is due to the disperse agent), the efficiency of COD removal was almost the same in both (85% of COD removal after 31 h for the purified form and 87% for the commercial dye).

The results of this work show that anaerobic processes can be useful as part of an integrated system for wastewater treatment where several chemical, physical and biological processes are used together to produce clean effluent suitable for discharge to the environment. The difference in the behaviour of the reactors when the disperse dye was used may be explained by the fact that in a continuous reactor the disperse dye has a tendency to form aggregates and was trapped in the sludge bed and reached a very high concentration which was toxic to the biomass. In batch experiments the total dye that accumulated was much lower than the value reached in the continuous reactor.

CONCLUSIONS

This study highlighted a number of facts. Firstly azo dyes, even with several azo groups in their structure, are readily decolourised by anaerobic biomass. In addition the removal of the extra organic load, which was easily degradable, was not affected by the type of dye used, even at very high concentrations (up to 1500 mg/l of dye **2**). Finally, the anthraquinone-based disperse dye **4** could be accumulated in the sludge bed of the reactor and inhibit the metabolic process after a short periods of continuous feeding (10 days) even at relatively low concentrations (35 mg/l). The influence of dispersing agent on the commercial dye did not seem to affect the removal of the organic load at this concentration in any significant way, in the batch systems.

Anaerobic digestion should be implemented to remove anionic azo dyes and the subsequent colour produced by them. In this process these compounds are readily reduced to aromatic amines which can be later degraded by an aerobic treatment [8,12]. Anthraquinone dyes can be removed in a short period of time, 2 or 3 days, at a very low concentration (35 mg/l) in order to avoid the inhibition of the biomass in the reactor or else should be removed previously by coagulation/flocculation. However, this may not be a problem soon as, according to the literature [13], these dyes may in the future by replaced by more environmentally friendly ones.

REFERENCES

1. P Cooper, *Colour in Dyehouse Effluent* (SDC: Bradford, 1995).
2. I G Laing, *Rev. Prog. Coloration*, **21** (1991) 56.
3. R A Moll, *Melliand Engl.*, **72** (1991) E343.
4. J J Porter and E H Snider, *J. Wat. Pollution Control Federation*, **48** (1976) 2198.
5. D Brown and P Laboureur, *Chemosphere*, **12** (1983) 397.
6. U Pagga and D Brown, *Chemosphere*, **15** (1986) 479.
7. D Brown and B Hamburger, *Chemosphere*, **16** (1987) 1539.
8. G Lettinga , J Field , J van Lier , G Zeeman and L W Hulshoff, *Wat. Sci. Tech.*, **35** (1997) 5.
9. P Ritcher, *Melliand Engl.*, **74** (1993) E314.
10. W M Wiegant and G Lettinga, *Biotech. Bioeng.*, **17** (1985) 1603.
11. A D Eaton, L S Clesceri and A E Greenberg, *Standard Methods for the Examination of Water and Wastewater*, 19th Edn (Washington: APHA, AWWA, WPCF) 1995.
12. H J Knackmuss, *Degradation of Xenobiotics*, Advanced Course on Environmental Biotechnology, Delft, The Netherlands, June (1997).
13. M Bide, *Text. Chem. Colorist*, **24** (1992) 17.