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Evaluation of an integrated anaerobic/aerobic SBR system for the treatment of wool dyeing effluents

Purification of wool dyeing effluent in a SBR

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Abstract

This work examined the performance of a sequencing batch reactor treating dyeing effluents from a factory that processes mainly wool and wool/polyester blends. Different operational conditions were evaluated, namely the influence of the anaerobic and the subsequent aerobic phase on the organic load removal, as well as the effect of the length of the aeration period (from 8 to 12 h) on process efficiency. A comparison between a fill stage in fast and slow modes was carried out. Results indicate that the cycle 2 conditions (fast fill and 12 h aeration time) improved the overall efficiency (85 ± 6% soluble COD and 95 ± 4% BOD_5 removal yields) with a predominant COD uptake occurring in the aerobic stage. Slow, linear COD removal was observed in the anaerobic phase, in contrast with an exponential COD decrease in the oxic phase. For SS a level under 100 mg/l was general achieved in the exit of the reactor. With respect to dye degradation, a noticeable decrease of the absorbance measured in the UV–visible range was observed. This could be explained by the reduction of the azo bonds of some of the present dyes in the anaerobic step, in which ORP values lower than −400 mV were attained. Some oxidation of anthraquinone sulphonate dyes and of the aromatic amines resulting from azo bond cleavage could also have been taken place, as well as bio-elimination mechanisms such as dye sorption.

Introduction

In wool and wool blend dyeing/finishing mills the input of chemicals and auxiliaries can be up to 1 kg/kg of processed textile, being the majority of the organic load rejected constituted of salts, detergents and organic acids (European IPPC Bureau 2002). Dyestuffs and other refractory organics (such as carriers, antifoam agents, easy-care finishing agents, biocides, antistatic, hydrophobic and oleophobic agents, softeners and spinning lubricants etc.) generally do not contribute in a significant way to the overall organic load. However, these substances are poorly biodegradable and tend to persist in the environment. Therefore their removal should deserve particular attention (Easton 1995; European IPPC Bureau 2002; Laing 1991). In order to ensure a high level of environmental protection, the European Commission through the Reference Document on Best Available Technologies for the Textile Industry, recommends close control of the input of auxiliary chemicals, savings in water consumption and increase in the reuse of recyclable/treated water (European IPPC Bureau 2002; Lourenço 2003). In wool dyeing baths,

acetic acid, levelling agents, carriers, salts and dyes are the main pollutants to be removed (European IPPC Bureau 2002; Parton 1988). These effluents present a COD/BOD_5 ratio of 3–4 for which bioreactors are a suitable treatment technology, even though some problems could arise from the presence of heavy metals (i.e., CrVI) and other xenobiotic compounds (European IPPC Bureau 2002; Laing 1991). Nowadays, several technologies have been proposed for the reduction of chromium emissions, such as optimisation (automation) of the batchwise dyeing process, lowering the level of metal-complex dyes applied or even substitution of the afterchrome dyes by metal-free reactive dyes (European IPPC Bureau 2002). However, residual colour levels still persist in dyebath effluents, mainly arising from azo and anthraquinone sulphonate dyes. In biological sequential batch reactors (SBR) with anaerobic and aerobic stages, a wide range of contaminants could be removed, or converted. The convertion of some types of azo (azo dyes represent almost 60–70% of the dyes commercially used nowadays), anthraquinone sulfonated and triarylmethane dyes in these system has been reported (Beckert et al. 2000; Hemmi et al. 1999; Jiang & Bishop 1994; Seignez et al. 1996). Azo dyes are generally resistant to aerobic degradation, but anaerobic conditions created in a separated stage of the SBR cycle are favourable to the reduction of azo bonds, resulting in decolourisation. The resulting aromatic amines present a harmful potential but some could be mineralised in oxic environments (aniline, carboxylated aromatic amines, chlorinated aromatic amines and benzidines), although the knowledge of their biodegradation mechanisms is still rather limited (Brown & Hamburger 1987; Brown & Laboureur 1983a, b; Lettinga 1997; Libra et al. 1997; Pagga & Brown 1986). Evermore SBR technology has been applied for the degradation of industrial recalcitrant compounds with notable success, due to the high versatility of the operational conditions which could be included in the cycle (Herzbrun et al. 1985; Irvine et al. 1997; Libra et al. 1997).

The purpose of the present paper is to report on a feasibility study for the application of an anaerobic–aerobic SBR for the treatment of an industrial wool dyeing wastewater with azo and anthraquinone sulphonate dyes as the main dye types. The effect of altering the aeration time in the anaerobic–aerobic sequence on the organic load and dyes removal efficiencies was studied. The SBR performance was also tested with fast and slow filling modes. The kinetics of COD removal in the anaerobic and aerobic stages was also compared.

Materials and methods

SBR feed

The residual dye bath liquor discharged from a batch dyeing system in a factory processing mainly wool and wool/polyester blends was used as the base feed for the SBR. Typical chemicals and auxiliaries used in dye bath formulations include azo and anthraquinone sulphonate dyes, acetic acid, sodium acetate, sodium or ammonium sulphate, a levelling agent (Albegal Set, Bayer) and an antifoam agent (Respumit 40044, Bayer). Dyes are almost totally exhausted onto the fibre. On the contrary, auxiliaries are almost totally rejected in the wasted stream. Depending on the desired depth of shade, formulation concentrations are altered. On the basis of the significant variations observed in the COD/N/P ratio (from 62/3/1 to 420/3/1) of the effluent, nutrients were added when necessary (in the forms of NH_4Cl and NaH_2PO_4), in order to supply an equilibrated composition (COD/N/P = 250/5/1). The COD/BOD_5 value of 3, obtained in average, indicates that the effluent is amenable to biotreatment (European IPPC Bureau 2002). The pH of the industrial effluent was brought to 7.0 ± 0.5 with sodium bicarbonate. The measured characteristics of the dyeing effluent are summarised in Table 1.

Dyes present in the effluent

Dyes predominantly used in this period of time were two azo dyes (commercial name Jane Sandolane MF-RL (JS) and Rouge Sandolane MF-2BL (RS)) and a third that results from a mixing of an anthraquinone monosulphonate and an anthraquinone disulphonate dye (commercial name of Blue Sandolane MF-GL (BS)) used in wool/polyester/elastane dyeing. These dyes were supplied by BASF (Germany). Their chemical structures were not disclosed.

Table 1. Characteristics of the dyeing effluent fed to the SBR

Parameter	Number of samples	Maximum value	Minimum value	Average and standard deviation
COD (mg/l)	149	5037	779	2076 ± 717
BOD_5 (mg/l)	20	1128	449	896 ± 358
TSS (mg/l)	149	545	12	104 ± 83
VSS (mg/l)	149	365	10	83 ± 62
TKN (mg/l)	10	64.6	11.6	31 ± 18
P (mg/l)	10	21.4	0.6	12 ± 8
SO_4^{2-} (mg/l)	10	1968	1163	1649 ± 283
pH	250	5.5	3.5	4.5 ± 0.9

Laboratory scale reactor

The employed laboratory scale sequencing batch reactor (SBR) was constructed from a PVC cylinder (14 cm internal diameter, 65 cm liquid height) with a working volume of 9 l. The feed wastewater was introduced at the bottom and distributed under the bed of settled biomass through a T-shaped inlet. The reactor was equipped with a circular bubble diffuser at the bottom, for aeration, and with mechanical stirring, liquid draw and sludge wastage ports. Digital timer switches controlled the operation of the peristaltic pumps for the influent and effluent, as well as the air pump. A port at 20 cm height was used for installing a redox potential probe. The reactor was operated with a settled sludge volume of 3.5 l and at the laboratory temperature maintained close to 20 ± 2 °C. It was seeded with 25 gVSS/l of aerobic sludge originating from a pilot-scale reactor treating wool textile dyeing wastewater. The system reached a pseudo steady state in the operational conditions of cycle mode 1 (Table 2), after approximately 3 weeks, with COD removal levels of 80 ± 15%. The feeding rate was 5 l/d, giving a hydraulic retention time of 1.8 d with a loading rate ranging from 0.4 to 2.8 kgCOD/(m^3d). No sludge wastage was carried out during the experimental time. From the VSS levels measured in the effluent and in the collected samples the average sludge retention time values of Table 3 could be estimated. Table 3 also gives average values for other monitored parameters in the SBR for the operational modes of Table 2. The reactor was operated over a period of 25 months.

Table 2. Operational stages in the SBR cycle modes tested

Cycle phase	Cycle modes		
	1	2	3
Fill	48 min[a]	48 min[a]	8 h 48 min[b]
Anaerobic react	12 h[c]	8 h[c]	–
Aerobic react	8 h	12 h	12 h
Settle	2 h	2 h	2 h
Draw	48 min	48 min	48 min
Idle	24 min	24 min	24 min

[a] Static fill; [b] mixed fill; [c] mixed.

Table 3. Average values for some performance parameters monitored in the SBR

Parameter	Cycle modes		
	1	2	3
Sludge retention time (d)	235	320	218
Operation period (month)	10	12	3
Redox potential reached at the end of:			
anaerobic phase (mV)	−550	−470	−500
aerobic phase (mV)	+50	+65	+65
F/M (g COD/(g MLVSS day))	0.13	0.09	0.09
MLVSS (mg/l)	8648	13522	12837

The 24 h-cycle of operation was divided into five discrete phases or periods, i.e., fill, anaerobic–aerobic react, settle, draw and idle. Three different operational modes were tested as shown in Table 2.

Monitoring, sampling and analysis

The reactor performance was monitored through measurements of pH, suspended solids (SS), volatile suspended solids (VSS), biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), total Kjeldahl nitrogen (TKN), total phosphorus (P) and sulphate, according to Standard Methods (APHA et al. 1992). The oxidation–reduction potential (ORP) was measured with a platinum electrode with silver/silver chloride as a reference electrode, connected to a digital potentiometer (Metrohm, Switzerland). UV–visible spectra of filtered samples were acquired in a Lambda 6 spectrophotometer (Perkin Elmer,

USA). As three dyes were predominantly used in the experimental period, whenever possible particular attention was given to the absorbance at the maximum wavelength in the visible range of each, respectively 370, 500 and 630 nm for JS, RS and BS. As these values are close to those recommended by the European IPPC Bureau (2002), for determination of spectral absorption coefficients (which should be determined at 435, 500 and 620 nm, in order to cover the range of green–yellow, red and blue), they were used to calculate colour removal yields in the reactor. The SBR system sampling was done throughout the operational cycle, at the end of each stage. At the end of the static fill, the reactor content was slowly mixed for 1 min to unable the collection of representative samples. Samples of 10 ml were withdrawn and filtered through 1.2 μm pore glass microfiber membranes, for analysis of soluble components.

COD and BOD_5 removal results correspond to sampling in duplicate or triplicate and data are presented as the average and corresponding standard deviation values.

Results and discussion

Three different operational cycles were studied in the SBR fed with the industrial dyeing effluent. As anaerobic conditions are favourable for colour removal in all of them an anaerobic stage was included, followed by an aerated phase during which mineralisation of the resulting aromatic amines could take place (Brown & Hamburger 1987; Brown & Laboureur 1983a). In the first two cycle modes (Table 2) the influence of the length of the aerated stage on the reactor efficiency was evaluated. Results (Figure 1) show an increase in the total and soluble organic load degradation yield (soluble COD removal averaged 72 ± 10% in mode 1 and 85 ± 6% in mode 2). The slow, mixed fill imposed to the reactor keeping a constant aeration time of 12 h led to a deterioration of its performance, with the soluble COD removal yields lowering to 75 ± 7% (mode 3 of Figure 1). The later operational strategy can be used to attenuate eventual feed variations over the cycle, which is an advantageous procedure when potential inhibitor pollutants are present in the effluent or to overcome shock load conditions (Beckert et al. 2000; Herzbrun et al. 1985; Rhem et al. 1999). Both possibilities are likely to occur in the treatment of textile effluents (Laing 1991). Also, because sludge settleability largely determines the overall efficiency of an activated sludge system such as that is being tested, TSS and VSS levels were monitored in the exit of the system (Figure 2). For modes 1 and 2 no significant differences in the SS and VSS values measured in the treated effluent were observed. These were, in general, lower than 100 mg/l and the ratio of volatile to total suspended solids was between 80% and 90%, indicating that mainly biosolids were present in the treated effluent (Figure 2). However, a marked increase in suspended solids concentrations in the settled supernatant was observed for mode 3 (Figure 2). A possible

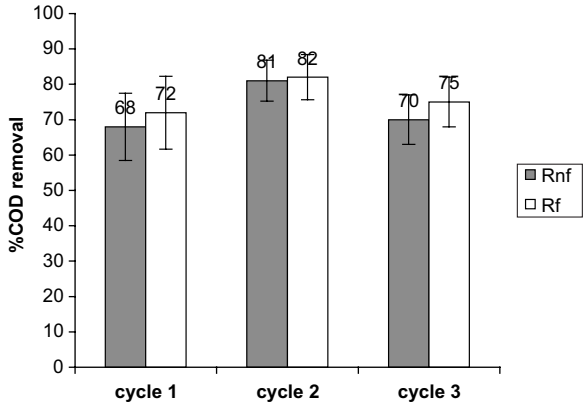

Figure 1. COD removal yields for filtered (Rf) and total (Rnf) samples obtained in the overall cycles of the three operational modes of the SBR. Averages and the corresponding standard deviation of 38, 93 and 12 daily samples in cycle modes 1, 2 and 3, respectively, are given.

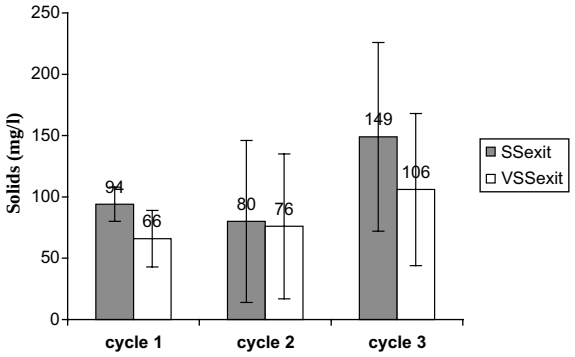

Figure 2. Suspended solids (SS) and volatile suspended solids (VSS) measured in the exit of the SBR in the three operational modes. Averages and the corresponding standard deviation of 38, 93 and 12 daily samples in cycle modes 1, 2 and 3, respectively, are given.

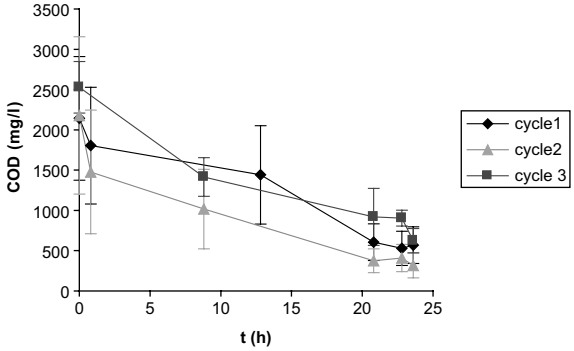

Figure 3. Soluble COD measured along cycle modes 1, 2 and 3 of the SBR for 7, 11 and 2 samples, respectively. Average and standard deviation of COD values of samples collected at the end of each cycle phase.

explanation for this behaviour is the enhancement of the bulking character of the sludge due to an attenuation of the feast-famine regime of cycle modes 1 and 2 originated in the SBR by the introduction of the slow fill (Winter 2000). Along with the increase in the VSS in the treated effluent, a decrease in the MLVSS was observed from cycle mode 2 to mode 3 (Table 3), supporting the idea that the biomass was partially being washed out of the reactor. On the other hand, the increase in MLVSS levels from mode 1 to mode 2 (Table 3) follow the change in the COD removal yields for those periods. The results also suggest that an increase in the aeration time leads to higher biomass yields, since the measured MLVSS increased by about 36%, while the COD removal yield was only approximately 13% higher. Higher MLVSS is also expected to ensure an improvement of dye removal process in the anaerobic stage. However, the high MLVSS levels reached in the reactor in modes 2 and 3 (12–13 g/l, Table 3) might have led to difficulties in floc formation, which, together with the change in the feed regime (in cycle mode 3), could have promoted the observed biomass loss in the settled effluent.

COD profiles along the cycles of the three operational modes tested (Figure 3) indicate that, in average, faster COD removal is achieved in mode 2 and that the COD decrease is more pronounced in the aerated phase of the cycles. COD removal was also observed in the anaerobic stages, particularly in the fill periods when the biomass/feed mass ratio is temporarily high. In cycle mode 3, the fill and anaerobic react phases coincided (slow, mixed fill mode) and the COD removal rate resulted higher than in the subsequent aerobic phase. The feast-famine regime imposed by the sequential-batch operation of the system is known to select for microbial consortia with the ability to quickly uptake the available carbon substrates (Winter 2000). In the feed mode, the time gradient in F/M values would presumably promote rapid exhaustion of the step-fed substrate. Different attempts have been used to explain the COD uptake in the anaerobic stages of activated sludge units (Kuba et al. 1993; Lourenço 2003; Rhem et al. 1999). During the anaerobic fill and react stages an incorporation of the substrate in the biomass is probably occurring, in a mechanism similar to that used by several kinds of microorganisms, such as obligatorily aerobic poly-P bacteria. Under anaerobic conditions (stress) these bacteria are able to take up acetate (which is the predominant carbon source in residual wool dyeing baths) and store it as polyalkanoate reserve material. These storage products are further metabolised in subsequent aerobic stages along with phosphate uptake. Other carbon sources present in the dyeing effluent e.g., levelling agents, antifoam agents, could possibly be used by facultative anaerobic bacteria and converted to fermentation end products such as short chain organic acids, which can also be used in polyalkanoate synthesis (Rhem et al. 1999). The longer aeration period used in cycle modes 2 and 3 is also favourable for the metabolisation of the stored material, leading to

an increase in total COD removal and biomass yield (Table 3) (Kuba et al. 1993; Rhem et al. 1999). No significant organic load removal was measured during the settle, draw and idle stages. The idle phase, although short, probably could contributes to the improvement of the settling characteristics of the biomass (Herzbrun et al. 1985; Irvine et al. 1997).

Considering that cycle mode 2 conditions led to higher system efficiency, other parameters were analysed during this period of SBR operation, namely BOD_5, TKN, total P and sulphate. Results indicate that the BOD_5 removal yield averaged $95 \pm 4\%$. The COD/BOD_5 ratio increased in average from 2.4 in the feed to 16.3 in the treated effluent, showing that the residual organic matter is poorly biodegradable. A TKN uptake between 88% and 95% was attained, indicating that adequate cell growth was occurring. On the contrary, sulphate was not removed under the SBR cycle conditions and the slight decrease in its concentration could be attributed to its use as sulphur source for bacteria growth. Phosphorus removal yields were between 26% and 50%, averaging 45 mg per cycle, which is higher than the amount required for cell growth, calculated on the basis of the biological solids withdrawn from the system per cycle (12 mg P), considering that P constitutes approximately 3% of the cell dry mass (Rhem et al. 1999; Panswad et al. 2000). Thus it would seem that the presence of an easily biodegradable substrate (acetate) could have favoured grow of biomass with enhanced phosphorus removal capacity (Kuba et al. 1993; Rhem et al. 1999).

The COD removal was followed along the anaerobic and aerobic stages of cycle mode 2 and typical examples are given in Figure 4. The removal rates are significantly different, being apparently zero order for the anaerobic stage (Figure 4a) and a pseudo first order for the first 5 h of the aerobic stage (Figure 4b). The kinetic constant in the aerobic phase calculated for the first 5 h has a value of 0.14 h^{-1}. The latter part of the aerobic stage again shows apparent zero order kinetics. In this case the substrate availability could be a limiting factor of the COD degradation. Furthermore, the accumulation of inhibitory metabolites may have slowed down COD removal in the last hours of the aerobic phase. In anaerobic conditions it could be assumed that the organic load is mainly being uptaken and stored by the

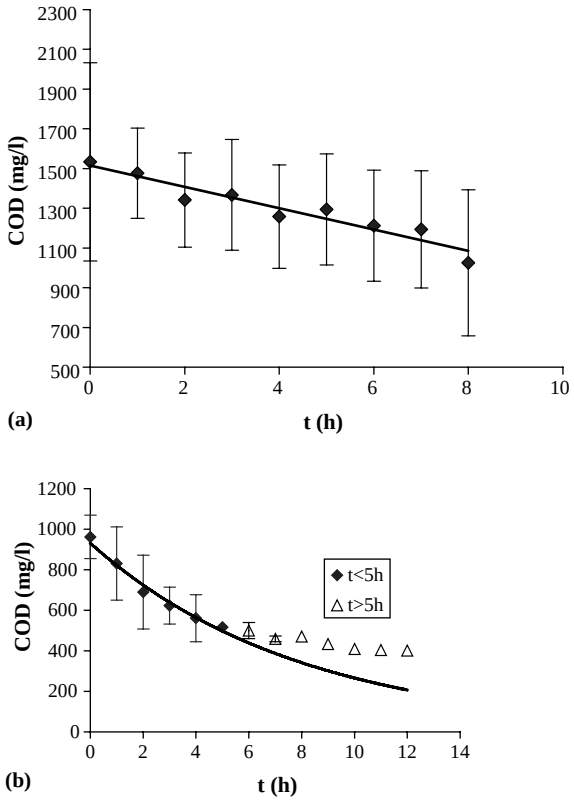

Figure 4. COD versus time in the anaerobic (a) and aerobic (b) phases of cycle mode 2 (average and the corresponding standard deviation of 11 samples).

cells and the fermentative conversion is not significantly contributing to the measured decrease in COD. The apparent zero order kinetics indicate a saturation of the uptake mechanisms by the high concentrations of available substrate in the anaerobic stage.

Dye colour removal in cycle modes 1, 2 and 3 was followed by UV–visible spectrophotometry. As the residual dye concentration in the industrial effluent fed to the SBR was generally low leading to low absorbance levels in the visible region, spectra in the whole range were acquired, in order to analyse eventual modifications. Furthermore, as different dye combinations were used in dye bath formulations throughout this study, the fed effluent presented different shades (green–yellow, red, yellow and blue), thus different spectra were obtained, as exemplified in Figure 5. A noticeable decrease in the absorbance over the whole spectral range is observed when samples gathered from the feed and the outlet were compared in all cycle

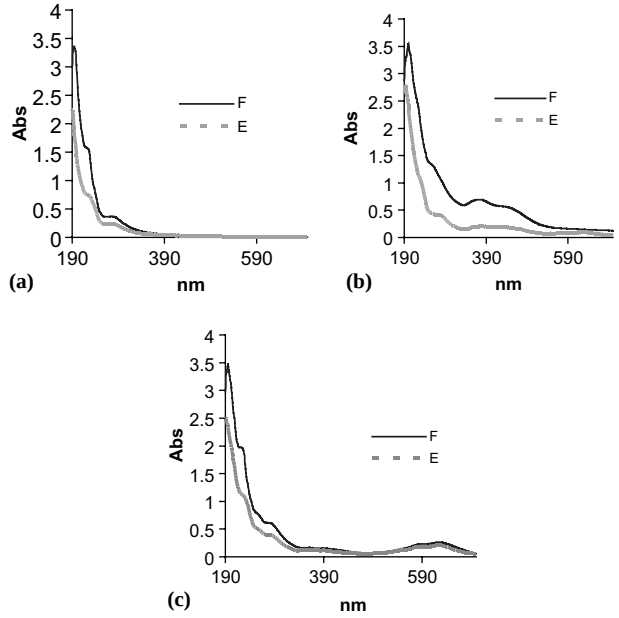

Figure 5. Examples of spectra obtained for filtered samples of the feed (F) and exit (E) of the SBR. Spectra are shown for different noticeable feed shades: red (a) green–yellow (b) or blue (c).

modes, particularly for the UV region. Spectral profiles along the reaction time indicated a marked decrease of absorbance in the anaerobic stage, whenever RS and JS (both azo dyes) were present in higher proportions (Figure 5a and b). Absorption coefficients measured at 370, 500 and 630 nm in the feed and exit of the SBR, were used to determine colour removal yields whenever possible, which were respectively of 67, 65 and 40% for dark coloured samples (obtained with dark shades in dyeing bath). However, it should be enforced that for the most part of the samples the residual colour was not significant, as can be seen in Figure 5a in which absorbance in the visible range is too low to be quantified. Azo dyes are decolourised under low redox potential (ORP) conditions (i.e., values lower than – 350 mg/l) (Brown & Laboureur 1983a) through the reduction of the azo bond. In the studied SBR operational modes, lower values were consistently attained (Table 3). Although an anaerobic environment favours azo bond cleavage, the resulting metabolites (aromatic amines) remain largely undegraded. It has been reported (Brown & Laboureur 1983a) that aromatic compounds can be biodegraded by oxidative processes, which can occur in the aerated stage of the SBR. The success of this mechanism is however dependent on the structure and type of substituent groups of the aromatic rings (Brown & Laboureur 1983a; Tan 2001). In the aerobic stage a noticeable decrease in absorbance was also observed and a colourless treated effluent was indeed achieved. However, more detailed analysis, such as the detection of dye metabolites, would be necessary to distinguish the extension of the dye degradation and bioelimination (sorption) mechanisms. An example of the filtered liquor spectra obtained along an operational cycle of the SBR is shown in Figure 6.

The presence of sulphate used as an electrolyte in dye bath could play a key role in azo bond cleavage. The fraction eventually reduced to sulphide during the anaerobic stages could be enough to improve colour reduction by electron transfer to the azo bond (Libra et al. 1997; Van der Zee et al. 2000). However, due to the low dye concentrations fed, in comparison with those of sulphate, this mechanism could not be effectively assessed. Furthermore sulphide is subsequently oxidised in the aerobic phase, leading to a very small overall sulphate removal yield, as previously noted.

For dye BS containing feed (in higher proportion than the others two dyes) the absorbance reduction was more marked in the aerobic phase

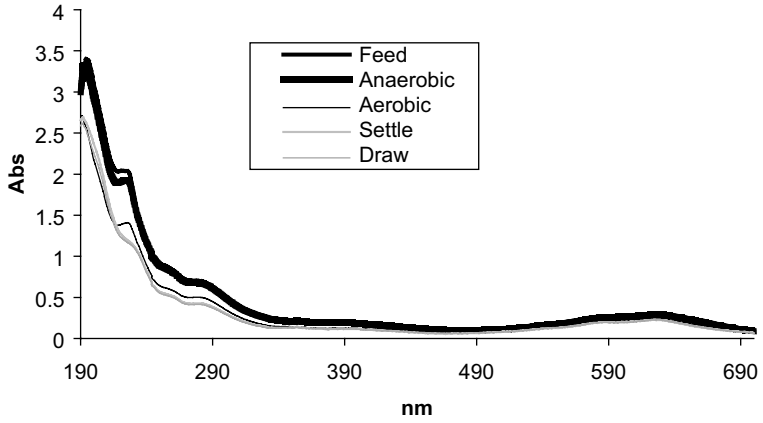

Figure 6. Typical spectra obtained in filtered samples at the end of each phase of cycle mode 2.

(Figure 6). This is in agreement with reported by Seignez et al. (1996), which indicate the possible degradation of anthraquinone sulphonate dyes in aerobic environments. However, adsorption onto sludge flocs again could not be ruled out.

Conclusions

An SBR operated with anaerobic and aerobic cycle stages could be considered a suitable technology for organic load removal from wool dyeing effluents. Soluble COD and BOD_5 degradation efficiencies of 85 ± 6% and 95 ± 4%, respectively, were achieved. The residual suspended solids levels were in general acceptable (lower than 100 mg/l), and could be attributed to the operation with no biomass wastage, which led to high MLVSS concentrations.

Although nutrients were occasionally added to the feed, their removal (TKN and total P) was consistently good, in contrast to sulphate, which was not removed with the cycle conditions selected. Colour removal was achieved, azo dyes (RS and JS) being possible decolourised through azo bond reduction and bioelimination mechanisms (Lourenço 2003; Seshadri et al. 1994; Tan 2001). For sulphonate anthraquinone dyes (BS) bioelimination and a partial oxidation in the aerated stage could have been responsible for colour removal. This aspect requires, however, further investigation (Seignez et al. 1996).

For the three different operational conditions tested in the present work, results suggest a tendency for a better performance in mode 2. This is probably due to the longer aerated react stage imposed (12 h) leading to more efficient cell growth and COD combined with a fast fill, that provided the feast-famine conditions which favoured sludge settleability.

In the treated effluent from the SBR residual COD levels with recalcitrant pollutants (COD/BOD_5 ratio of 16) are still present. Further tests are thus necessary (possible involving complementary technologies) to ensure the elimination of these residual compounds, in order to meet the requirements of EC legislation.

References

APHA, AWWA & WPCF (1992) Standard Methods for the Examination of Water and Wastewater, 19th edn. Rhodes Trussel, Washington

Beckert M, Ohmann U & Platzer B (2000) Long-time experience for wastewater treatment according to the SBR-process. Melliand English 1–2, E20–E22

Brown D & Hamburger B (1987) The degradation of dyestuffs: Part III – Investigation of them ultimate degradability. Chemosphere 16(7): 1539–1553

Brown D & Laboureur P (1983a) The aerobic biodegradability of primary aromatic amines. Chemosphere 12(3): 405–414

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

Easton JR (1995) The dye maker's view. In: Cooper P (Ed) Colour in Dyehouse Effluent. Society of Dyes and Colourists

European IPPC Bureau (2002) Integrated Pollution Prevention and Control (IPPC), Reference Document on Best Available Techniques for the Textiles Industry. European Commission, Institute for Prospective Technological Studies, Seville

Hemmi M, Krull R & Hempel DC (1999). Sequencing batch reactor technology for the purification of concentrated dyehouse liquors. Can. J. Chem. Eng. 77: 948–954

Herzbrun PA, Irvine RL & Malinowski KC (1985) Biological treatment of hazardous wastes in the SBR. J. Water Pollut. Control Federation 57: 1163–1167

Irvine RL, Wilderer PA & Flemming HC (1997). Controlled unsteady state processes and technologies – an overview. Water Sci. Technol. 35(1), 1–10

Jiang H & Bishop PL (1994) Aerobic biodegradation of azo dyes in biofilms. Water Sci. Technol. 29(10–11): 525–530

Kuba T, Smolders G, Loosdrecht MCM & Heijnen JJ (1993) Biological phosphorus removal from wastewater by anaerobic-anoxic sequencing batch reactor. Water Sci. Technol. 27(5–6), 241–252

Laing IG (1991) The impact of effluent regulations on the dyeing industry. Rev. Prog. Coloration 21: 56–71

Lettinga G, Field J, van Lier J, Zeeman G & Hulshoff Pol LW (1997) Advanced anaerobic wastewater treatment in the near future. Water Sci. Technol. 35(10): 5–12

Libra J, Yoo ES, Borchert M & Wiesmann U (1997) Mechanisms of biological decolorization: their engineering application. Biologische Abwasserreinigung 9: 245–266

Lourenço NDM (2003) Azo dye biodegradation in sequencing batch reactors, Ph.D. Thesis, Universidade Técnica de Lisboa, Instituto Superior Técnico, Lisboa, Portugal

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

Panswad T, Techovanich A & Antai J (2000) Comparison of dye wastewater treatment by normal and anoxic + anaerobic/aerobic SBR activated sludge processes. Water Sci. Technol. 43(2): 355–362

Parton K (1988) The dyeing of wool: past, present and future. J. Soc. Dyers Colourists 114(January): 8–10

Rhem H-J, Reed G, Pühler & Stadler P (1999). Biotechnology, Environmental Processes, 11a, 2nd edn, Wiley-VCH

Seignez C, Adler N, Suard JC & Péringer P (1996) Aerobic and anaerobic biodegradability of 1-Anthraquinone sulphonate. Appl. Microbial Technol. 45: 719–722

Seshadri S, Bishop PL & Agha AM (1994) Anaerobic/aerobic treatment of selected azo dyes in wastewater. Waste Manage. 14(2): 127–137

Tan NCG (2001) Integrated and Sequencial Anaerobic/Aeróbic Biodegradation of Azo Dyes. Thesis Wageningen University Research Center, Wageningen, The Netherlands

Van der Zee FP, Lettinga G & Field JA (2000) The role of (aceto)catalysis in the mechanism of anaerobic azo reduction. Water Sci. Technol. 42(5–6): 301–308

Winter J (2000) Environmental processes I: wastewater treatment. In: Rehm H-J, Reed G, Pühler & Stadler P (Eds) Biotechnology, Vol. 11a, 2nd edn. Wiley-VCH