Biological treatment of wastewaters from a dye manufacturing company using a trickling filter

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Abstract

The aim of this work was to assess the effectiveness of a biological trickling filter for the treatment of wastewaters produced by a company manufacturing organic dyes and varnishes. The combined wastewater effluent was fed to a pilot-scale trickling filter in two feeding modes, continuously and as a sequencing batch reactor (SBR).

The biodegradability of the diluted wastewaters that were subjected to physicochemical treatment, using $Ca(OH)_2$ and $FeSO_4$, was initially studied using a continuously operated trickling filter. The system efficiency ranged up to 60–70% for a hydraulic loading of $1.1 \, m^3/m^2$ day and up to 80–85% for a hydraulic loading $0.6 \, m^3/m^2$ day. A stable chemical oxygen demand (COD) removal efficiency of 60–70% was achieved even in the case of undiluted wastewater at a hydraulic loading of $1.1 \, m^3/m^2$ day.

The effectiveness of biological treatment of a mixture of the company's main wastewater streams was also examined. The microorganisms developed in the trickling filter were able to efficiently remove COD levels up to 36,000 mg/L, under aerobic conditions at pH values between 5.5 and 8.0. Depending on the operating conditions of the system, about 30–60% of the total COD removal was attributed to air stripping caused by the air supply at the bottom of the filter, whereas the rest of the COD was clearly removed through biological action. The proposed biological treatment process based on a trickling filter, which was operated either continuously or even better in an SBR mode, appears as a promising pretreatment step for coping with dye manufacturing wastewaters in terms of removing a significant portion of the organic content.
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1. Introduction

Large amounts of dyes are annually produced and applied in many different industries, including the textile, cosmetic, paper, leather, pharmaceutical and food industries [1,2]. Azo dyes are the largest chemical class of dyes with the greatest colour variety, and have been used extensively especially for textile dyeing and paper printing. Approximately 10–15% of the dyes are released into the environment during manufacturing and usage [3].

Wastewaters from manufacturing factories are highly variable in composition: they contain a large number of different compounds, such as raw materials (e.g. anilines, solutes, etc.), intermediate products and even the dyes themselves. Their disposal is always a matter of great concern since they are considered as a quite dangerous source of environmental pollution.

Dye manufacturing wastewaters are normally characterized by high chemical and biological oxygen demands (COD and BOD), suspended solids and intense colour due to dye intermediates or residues and auxiliary chemicals from the process. Direct discharge of these effluents into municipal wastewater plants and/or the environment may cause the formation of toxic carcinogenic breakdown products [4] while certain metal complex dyes are of health concern [5]. Since dyes with complex aromatic structures are resistant to biodegradation by the typical microbial populations in activated sludge systems and may even be toxic to many of the microbial species present, discharge of the raw wastewater to the treatment plants may lead to their failure [6]. Wastewater of this kind, if not appropriately treated, might also pose a severe threat to receiving waters because it contain chemicals, which are toxic to aquatic life and in addition, may interfere with light penetration in sensitive water bodies. The dyes constitute also an aesthetic problem with great impact in the public opinion [7] and colour restricts the potential downstream use of the wastewater [8]. Given these concerns, dye manufacturing industries are required to reduce primarily the

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organic loading (chemical and biological oxygen demand) and the colour as well from their discharges.

Various combinations of conventional treatment processes, including physical and chemical methods (coagulation, adsorption on activated carbon, polymer and mineral sorbents, reverse osmosis, chemical oxidation, filtration and electrochemical treatments) as well as biological treatments have been used by dye manufacturing industries [6]. All these methods have different COD and colour removal capabilities, depending on the type of dyes present in the wastewater, limiting thus their application [9]. Increased capital costs and operating speed are often major concerns. Among these methods, coagulation and adsorption are the most commonly used; these, however, create large amounts of sludge, which presents additional disposal difficulties.

As reported by many researchers, advanced oxidation processes (AOPs) using, e.g. H_2O_2, UV, ozone, etc. have been employed to remove or degrade successfully some refractory organics and colour from various types of industrial wastewaters, such as leachates [10], textile wastewaters [11–13] and dyestuff-contaminated wastewater [14]. However, the characteristics of both textile and dyestuff contained wastewaters are quite different from that of dye manufacturing wastewaters and, moreover these processes are quite expensive to implement. So far, only few studies on the possible use of AOPs for treatment of dye manufacturing wastewater may be found in the literature [15].

Biological treatment processes, both suspended growth as well as trickling filters, are perhaps the most feasible and cost-effective processes for the removal or reduction of organic and inorganic compounds from industrial wastewaters. However, the utilization of biological treatment methods may be limited by the presence of recalcitrant and/or toxic organic compounds. Commercial dyestuffs all derive their colour from the relatively complex chromophore system, which they contain. A necessary criterion for their successful use is that they must be highly stable in light and also stable against microbial attack. Therefore, complete mineralisation of colour organic chemical compounds has not yet been achieved extensively under strictly aerobic conditions. Only some specific coloured organic chemical compounds, mainly azo dyes, have been transformed or degraded by specific microorganisms, including aerobic and anaerobic bacteria and fungi [16–23]. However, long growth cycles and moderate decolourization rates limit the performance of fungal systems [18]. In contrast, bacteria could reduce the colour intensity more satisfactorily, but individual bacterial strains cannot mineralise azo dyes completely [24,25], and the intermediate products are carcinogenic aromatic amines, which need to be further decomposed.

The present work aimed at the development of a treatment scheme for the wastewaters produced by a company manufacturing organic dyes and varnishes. A pilot-scale trickling filter was operated aerobically, either continuously or in a sequencing batch reactor (SBR) operation mode, in order to treat the combined effluent wastewater. The system performance was evaluated during this study through detailed examination of the most important operating parameters such as physicochemical pretreatment of the raw wastewater, mode of operation (continu-

ous and periodic), hydraulic and organic loading, cycle duration of the periodic operation, pH value and buffering capacity of the influent wastewater.

2. Materials and methods

2.1. Wastewater characterization

A detailed characterization was carried out on two grab samples of mixed stream wastewater taken at two different operation periods of the dye manufacturing company. An "average" sample was subsequently formed by combining the individual samples (1:1 ratio). The measured parameters included: pH, total suspended solids (TSS), total (TCOD) and dissolved chemical oxygen demand (DCOD), 5-day biological oxygen demand (BOD₅), total phosphorus on filtered and non-filtered samples, total Kjeldahl nitrogen (TKN) and concentrations of specific metals (Fe, Mn, Cu, Pb, Zn and Cr). All analyses were carried out as described in Standards Methods [31].

The basic characteristics of the four main wastewater streams (A, B, C and D) with the highest organic strength that contribute to the formation of the final mixed wastewater and account for approximately one-tenth of the total effluent wastewater flowrate ($500 \, m^3$/day) were also assessed. The rest of the wastewater includes low-strength and municipal-type wastewater streams. A mixed stream sample was composed of the four streams in equal volumes and used for subsequent experimentation. The potential for biological treatment of this mixed stream sample was assessed by feeding diluted or raw wastewater, without any pretreatment, to the trickling filter that had been previously fed and acclimated to the "average" mixed wastewater described above.

Specific characteristics of the four streams are described in the sequel. The main constituents of Stream A are: aniline oil, Dowanol PM (1-methoxy-2 propanol) and Dowanol DPM (2-MO-ME-EO propanol) in concentrations of 3.5%, 5.5% and 4.5% (w/w), respectively. The composition of Stream B is similar to Stream A containing mainly aniline oil (3.5%) and methyl-oxitol (8.5%). Stream C contains mainly isopropanol (17%, w/w) and its colour is deep green since two bands at 452 and 601 nm characterize the spectrum of this stream in the visible region. Stream D contains mainly methanol (around 7%, w/w) and small amounts of acetic acid (0.3%). Its colour is light brown with the spectrum of this stream in the visible region characterized by one band at 401 nm.

2.2. Physicochemical treatment of wastewater

The effect of physicochemical treatment of wastewater, prior to its feed to the trickling filter, was studied using addition of $Ca(OH)_2$ at a range of 2.5–10 mg/L (measured as final concentration) and 4.5 mL of $FeSO_4 \cdot 7H_2O$ 0.8% (w/w) solution per liter of wastewater.

2.3. Pilot scale trickling filter

A schematic diagram of the pilot scale trickling filter that was used in our study is shown in Fig. 1. The trickling filter consists of
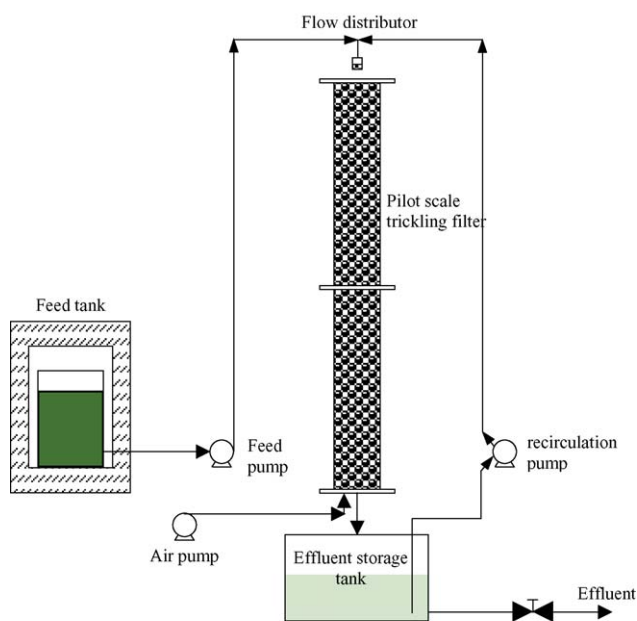
Fig. 1. Schematic diagram of experimental set up. Pilot-scale trickling filter.

a Plexiglas tube with inner diameter of 9 cm and a total height of 180 cm. The supporting material for bacterial growth was silica gravel, with a mean diameter of 10.2 mm and a specific surface area of 709.5 m^2/m^3. The filter had a porosity of 0.36. At the top of the filter, a fixed flow distributor was installed in order to facilitate a uniform distribution of the wastewater fed to the filter's free surface. The waste was fed to the reactor after being stirred in a storage tank, which was kept in a refrigerator at 4 °C, in order to secure an almost constant wastewater composition. At the bottom of the filter an air pump was connected for supplying air to the system. Also, a 10 L storage tank was installed, in order to collect the effluent from the filter's draining system. The effluent from this tank was drawn to the sewage, whereas a recirculation stream could be fed to the top of the filter via a recirculation pump.

2.4. Trickling filter operation

Depending on the mode of filter operation (continuous or SBR mode) the outlet from the 10 L effluent storage tank was appropriately manipulated via a system of electromagnetic valves driven by digital timers. During the SBR operation mode of the filter, the system was operated in the typical sequence of *fill*, *react*, *settle* and *draw* phases. A *settle* phase was included to the time schedule, in order to facilitate the settlement of escaping solids (if any) in the filter's effluent inside the effluent storage tank. The operation cycle was 1 day, during which the *fill* phase lasted for 0.5 h followed by an aerated reaction phase of 23 h and a settling phase of 0.5 h. The *drawing* phase was almost instantaneous and was effected through the opening of an outlet valve.

The trickling filter was primarily inoculated with activated sludge taken from the aerobic basin of the sewage treatment plant of Patras (Greece) Industrial Zone. The pH of the physico-

chemically treated wastewater was adjusted to values between 7 and 8 using H_2SO_4 and NaOH solutions. As the treated wastewater was deficient in nitrogen and phosphorus, the appropriate amounts of N and P were added to the wastewater for supporting microorganism growth, and securing that both microbial growth and organic loading removal would be limited only by the wastewater carbon content. Nitrogen and phosphorus were supplied in the form of KH_2PO_4/K_2HPO_4 (to increase the wastewater buffer capacity) and $(NH_4)_2SO_4$ salts, in variable quantities depending on the feed wastewater COD (i.e. 8.45 mg P/L and 0.125 mg N/L for every 1000 mg feed COD/L).

2.5. Batch experiments

Besides the operation of the filter, small-scale experimentation took place using conical flasks of 5 L total volume. A mechanical stirrer was used to provide mixing to each of the flasks during the aeration period. An air pump provided the necessary oxygen supply to the flasks.

3. Results and discussion

The detailed characterization that was carried out on the two grab samples, taken at two different operation periods, and the "average" of mixed stream wastewater is shown on Table 1. The very low ratio of $BOD_5/TCOD$ of 0.045 (mixed sample) indicates that the wastewater is almost unamenable to biological treatment unless it is subjected to some type of pretreatment or unless properly acclimated biomass is used. In fact, according to Symons [32], the ratio of BOD_5/COD of the wastewater should be >0.6 if the wastewater is to be treated easily using biological treatment, while 0.4 is considered the minimum required value for biological treatment to be effective.

The effect of physicochemical treatment of wastewater (Table 2), prior to its feeding to the trickling filter, was studied using addition of 2.5–10 mg/L $Ca(OH)_2$ (final concentration) and 4.5 mL of $FeSO_4 \cdot 7H_2O$ 0.8% (w/w) solution per liter of "average" mixed stream wastewater shown in Table 1. This type of pretreatment resulted to an almost complete removal of TSS

Table 1
Mixed wastewater characteristics

Parameters	Sample #1	Sample #2	"Average" sample
TCOD (mg/L)	10970	16430	13320
DCOD (mg/L)	7410	13580	11830
BOD_5 (mg/L)	660	570	610
TSS (mg/L)	749	3243	2000
pH	4.40	1.71	2.22
Total unfiltered P (mg/L)	15.4	78.7	46.8
Total filtered P (mg/L)	12.6	79.4	46.1
TKN (mg/L)	N/D	N/D	685
Fe conc. (mg/L)	2.94	9.93	N/D
Mn conc. (mg/L)	0.23	0.52	N/D
Cu conc. (mg/L)	0.34	1.17	N/D
Pb conc. (mg/L)	0.80	1.23	N/D
Zn conc. (mg/L)	4.57	20.83	N/D
Cr conc. (mg/L)	0.15	0.30	N/D

Table 2
Effect of physicochemical treatment of mixed wastewater using different doses of $Ca(OH)_2$

Test sample	1	2	3	4	5	6
Final concentration of $Ca(OH)_2$ (mg/L)	2.5	3.0	4.0	5.0	7.5	10.0
pH	11.00	11.08	12.00	12.47	12.50	12.50
Total P (mg/L)	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Ortho-P (mg/L)	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
TSS (mg/L)	50	49	46	47	60	22
TCOD (mg/L)	10590	10150	10990	10670	10220	10310
DCOD (mg/L)	9620	9400	9260	9860	9750	9600
TKN (mg/L)	N/D	N/D	N/D	N/D	N/D	670

Constant addition of 4.5 mL of $FeSO_4 \cdot 7H_2O$ 0.8% (w/w) solution per liter of wastewater to all samples

(final TSS concentration ranged between 22 and 50 mg/L as $Ca(OH)_2$ dosage was decreasing), complete removal of total and dissolved phosphorus, and about 20% removal of total and dissolved COD. The ratio of BOD_5/COD of the treated wastewater remained practically unchanged. The value of pH increased substantially with final values between 11.0 and 12.5 depending on the $Ca(OH)_2$ dosage. TKN concentration decreased slightly (670 mg/L).

Although the $Ca(OH)_2$ dosage increase from 2.5 to 10 mg/L did not improve the physicochemical treatment results obtained in our tests with the lower dosage (i.e. 2.5 mg/L), the higher $Ca(OH)_2$ dosage was eventually utilised for the treatment of the mixed wastewater. This selection was based on clearly practical reasons (the company supplied physicochemically pretreated mixed wastewater for the trickling filter operation), since this was the current practice followed by the company at that time.

Therefore, the trickling filter operation was initially fed with the pretreated "average" mixed wastewater diluted to a total COD concentration of 1000 mg/L. The wastewater was pretreated with 10 mg/L $Ca(OH)_2$ (final concentration) and 4.5 mL of $FeSO_4 \cdot 7H_2O$ 0.8% (w/w) solution added per liter of wastewater. The trickling filter was operated in a batch mode until no futrther COD removal was achieved and this lasted about 8 days of operation. The total COD of the treated wastewater was reduced by about 80% at that time, indicating the acclimation of appropriate biomass capable of degrading this type of wastewater. Microscopic observation of the acclimated biomass indicated that the prevailing microorganisms in the biofilm were mainly coccoidal and rod-shaped bacteria and very few ciliates. No filamentous bacteria were observed under all operating conditions.

The operation of the filter was then switched to continuous and its performance was monitored keeping the TCOD concentration in the feed constant. In order to investigate the effect of the hydraulic loading to the system, two different flowrate values were used in the feed, namely 7.2 and 3.5 L/day, hydraulic loading of 1.1 and 0.6 m^3/m^2 day, respectively. The system efficiency ranged up to 60–70% COD removal for the hydraulic loading of 1.1 m^3/m^2 day and up to 80–85% for the hydraulic loading of 0.6 m^3/m^2 day as can be calculated from the system performance (COD values) presented in Fig. 2.

The system performance was studied, in the sequel, using various wastewater dilutions (COD in the feed was increased to 2000, 4000, 7000 and 10.000 mg/L), for a constant hydraulic loading of 1.1 m^3/m^2 day, proving a stable apparent COD removal efficiency of 60–70% even in the case of the undiluted wastewater (Fig. 3).

The potential for biological treatment of a mixture of the company's main wastewater streams instead of the overall "aver-
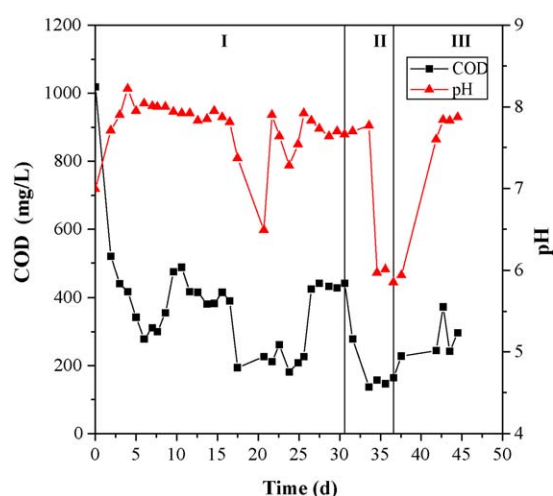

Fig. 2. Profiles of COD concentration and pH at the effluent of trickling filter operating in a continuous mode with constant feed COD of 1000 mg/L at a flowrate Q_{feed} of: (I) 7.2, (II) 3.5 and (III) 7.2 L/day.
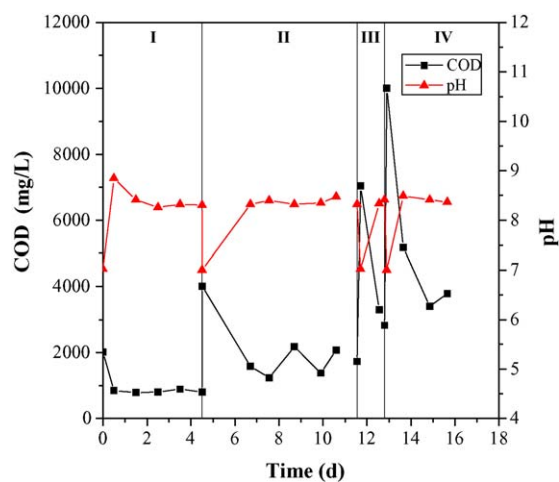

Fig. 3. Profiles of COD concentration and pH at the effluent of trickling filter operating in a continuous mode at constant Q_{feed} of 7.2 L/day and feed COD: (I) 2000, (II) 4000, (III) 7000 and (IV) 10,000 mg/L.

Table 3
Characteristics of main wastewater streams

Parameters	Stream A	Stream B	Stream C	Stream D	Mixed stream
TCOD (mg/L)	211570	255230	266960	74050	202330
DCOD (mg/L)	200490	240240	250670	69490	190830
TSS (mg/L)	174	184	90	82	170
pH	0.00	0.00	0.00	13.00	0.00

age" wastewater (which contains other low-strength streams and even municipal type wastewater contributions) was tested in the sequel. The idea was to assess the capability of a biological trickling filter to treat the main "industrial" waste streams, as a pretreatment step and then combine the effluent with the low-strength municipal-type wastewater giving a final wastewater that could be disposed of to the municipal sewer. Table 3 presents the basic characteristics of the four streams (A, B, C and D) with the highest organic strength accounting for about one-tenth of the company's effluent wastewater flowrate. A representative mixed stream sample was composed of the four streams in equal volumes and used for subsequent experimentation. As can be easily seen from Table 3, mainly the Streams A, B and C and less the Stream D carry extremely high concentrations of dissolved solutes and other dye manufacturing intermediates which contribute to the formation of primarily dissolved COD as also proved by the low TSS concentrations. Moreover, Streams A, B and C are extremely acidic whereas Stream D is, on the contrary, quite basic. The mixed stream wastewater, after being subjected to the appropriate adjustment of pH (since it remained extremely acidic even after mixing) and nutrients concentrations, was fed to the trickling filter, containing the acclimated biomass that had developed during its earlier operation, without any prior physicochemical pretreatment.

In order to increase the filter efficiency through continuous recirculation and in order to decrease channeling phenomena during the wastewater flow through the column, the system was operated in an SBR mode having an operation cycle of 1 day. The sequencing batch reactor technology has been usually implemented for nitrogen and phosphorus removal [26,27], and for agroindustrial (e.g. piggery) wastewater treatment [28,29] due to its good operational flexibility, simple operation and compact layout. Lab-scale SBR systems with sequenced anaerobic and aerobic phases were used by Lourenço et al. [30] for the study of colorant biodegradation in a simulated cotton textile effluent containing sulfonated azo and diazo reactive dyes.

Fig. 4 presents the filter performance, when it was fed with 1:20 diluted mixed stream wastewater (influent COD was 9700 mg/L). As shown in Fig. 4, the pH in the effluent of the tricking filter gradually decreased from 7 to about 5.5 after approximately 4 days of operation, with the apparent COD removal efficiency of the filter ranging around 65%. However, an increase in the effluent pH was observed on the 9th day of operation with a concomitant slight increase of the filter performance to about 74%, indicating that the biomass was able to cope effectively with the imposed change of the feed composition although the COD removal was slightly decreased during this transient
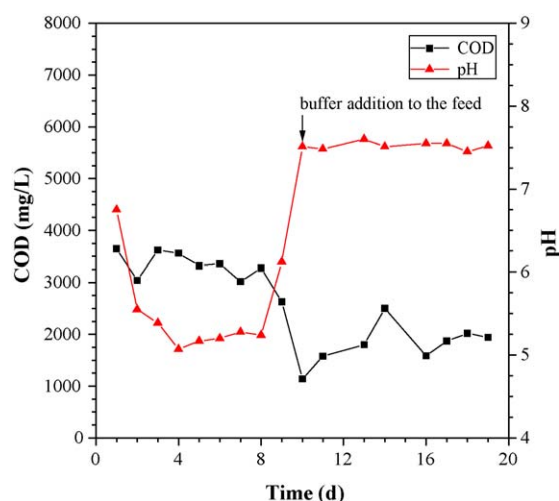

Fig. 4. Profiles of COD concentration and pH at the effluent of trickling filter during SBR type of operation ($Q_{feed} = 5.0$ L/day, feed COD = 9700 mg/L).

period. However, it is remarkable to note the robust behavior of the acclimated biomass, since the filter efficiency managed to stabilize to about the same levels as previously (shown in Fig. 3), while the effluent pH was 2.5 units lower.

In the aim to stabilize and even possibly increase the filter performance, since the pH increase seemed to positively affect the COD removal efficiency, an addition of a phosphate salts buffer (KH_2PO_4/K_2HPO_4) in the feed of the system was implemented after the 10th day of operation. This addition kept indeed the effluent pH at rather constant values (around 8), while the apparent COD removal efficiency increased above 80%. Similar results have been presented by Ahn et al. [6], where a fixed bed reactor was used to treat a mixed stream wastewater from a dyestuff manufacturing company that had been previously subjected to Fenton oxidation and activated carbon adsorption. This type of treatment resulted to a decrease of an initial COD of 17,000 mg/L to around 3800 mg/L in the influent of the fixed bed reactor and 580 mg/L in the effluent (85% COD removal).

In order to delineate the effect of the pH and also investigate the effect of cycle duration on the system performance, the filter was subsequently operated at 24 and 48 h cycles. The filter was fed in both runs with the same type (regarding organics composition) of mixed stream wastewater, as before. However, in terms of buffer capacity, the feed for the 24-h cycle was the same as the one fed to the system for the days 1–9 of the previous runs (without buffer addition) and the feed for the 48-h cycle operation included the phosphate salts buffer. The filter performance is presented in Fig. 5 for both runs. Although the pH difference was about 1.5 units at the end of the 24-h cycle, the COD removal was exactly the same for both runs, proving again the biofilm robustness and the ability to operate effectively under pH conditions of a wide spectrum. Although the obtained apparent COD removal efficiency at the end of the 24-h cycle was about 70%, the cycle that lasted 48 h resulted to almost 95% COD removal. Therefore, cycle duration proved to be a more critical parameter than pH in affecting filter performance.

The effect of organic strength to the apparent COD removal efficiency was examined by running simultaneous batch experi-
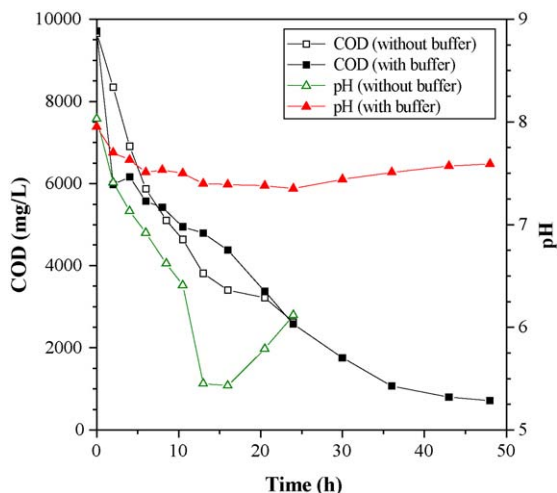
Fig. 5. Effect of cycle duration on system performance. Profiles of COD concentration and pH during 24 and 48 h SBR cycle batch operation. Feed COD = 9700 mg/L.

ments, using acclimatized biomass from the trickling filter. The biomass behavior against mixed stream wastewater with initial organic strength of 9500 mg COD/L, 18,200 mg COD/L and 36,500 mg COD/L was monitored and the results are shown in Fig. 6(a–c). Although pH was not a very crucial parameter, the mixed liquor pH was adjusted to 8 with phosphate salts buffer, in order to provide constant pH conditions in all batches. It is remarkable to notice that even in the third case, with the highest initial COD, the COD removal efficiency was above 80% and the biomass yield was very low. The estimated biomass yield factor ranged from 0.02 to 0.08 mg VSS/mg COD, based on total COD removal, for the runs of 36,500 mg COD/L and 9500 mg COD/L, respectively.

Since mixed stream wastewater contained a large amount of volatile compounds a major concern was if the high apparent COD removal observed in the contacted batch experiments could be entirely attributed to biological degradation of organic compounds. In order to differentiate between abiotic and biotic COD removal, a batch experiment was therefore carried out where diluted mixed stream wastewater with an initial organic strength of 153,000 mg COD/L, which is close to the range of full strength mixed stream wastewater, was split into two conical flasks. One of the flasks was inoculated with acclimatized biomass from the trickling filter at an initial concentration of about 1350 mg VSS/L, whereas the second flask was used as control (same operating conditions but without biomass). The observed COD removal profiles from the two batches are shown in Fig. 7. As can be concluded, from the total 66% apparent COD removal observed under mixed (biotic and abiotic) conditions about 63% could be attributed to air stripping!

Since the organic loading of the control batch experiment that was carried out was quite high, another control experiment was conducted using the trickling filter operating without biomass under the same conditions as before, namely, in SBR mode with 24-h cycle duration and diluted mixed wastewater in the feed (COD = 9700 mg/L). According to the performance presented in Fig. 8 only 30% of the observed COD removal was due to
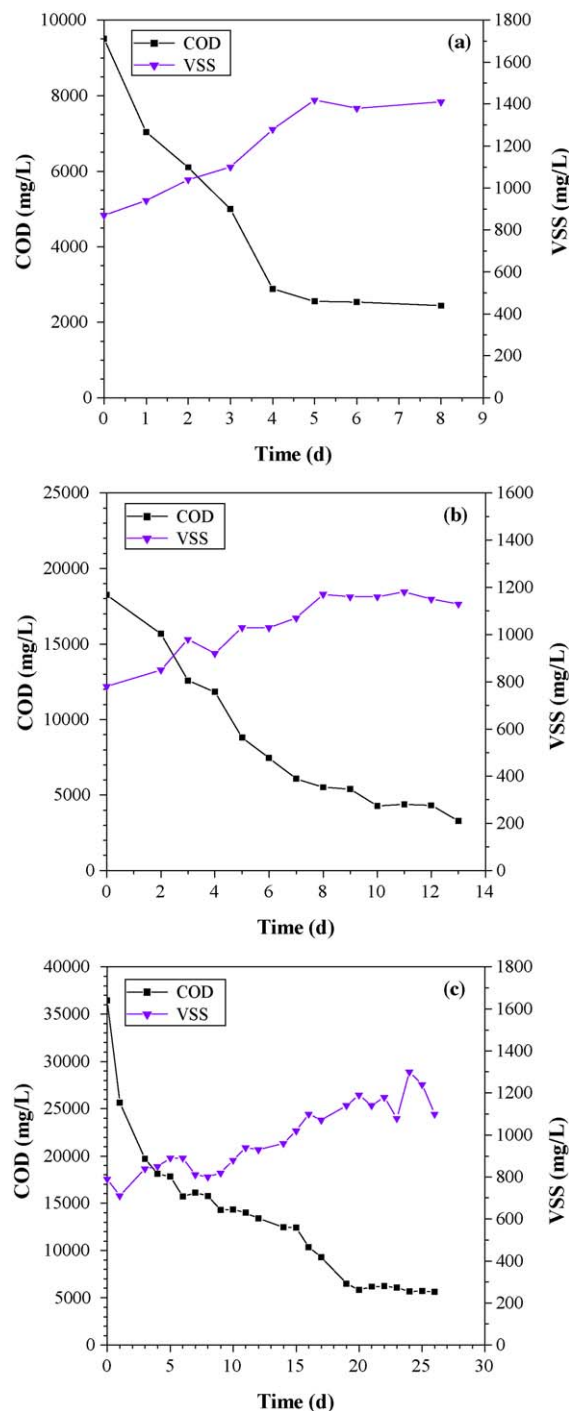

Fig. 6. Effect of wastewater organic strength on biomass performance during batch growth. Initial COD: (a) 9500 mg/L (b) 18,200 mg/L and (c) 36,500 mg/L.

air stripping under these operating conditions. In any case, for safety reasons and depending on the operating conditions of the system, about 30–60% of the total apparent COD removal can be attributed to air stripping, caused by the air supply at the bottom of the filter, whereas the rest of COD removed is clearly due to biological action.

Based on the above results, the biological treatment of either the final mixed wastewater after physicochemical treatment with 2.5 mg/L $Ca(OH)_2$ (final concentration) and 4.5 mL of
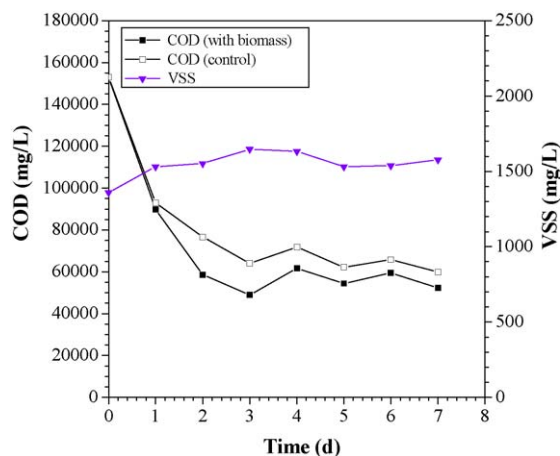
Fig. 7. Effect of air stripping on apparent COD removal under batch conditions. Initial COD of diluted mixed stream wastewater: 153,000 mg/L.
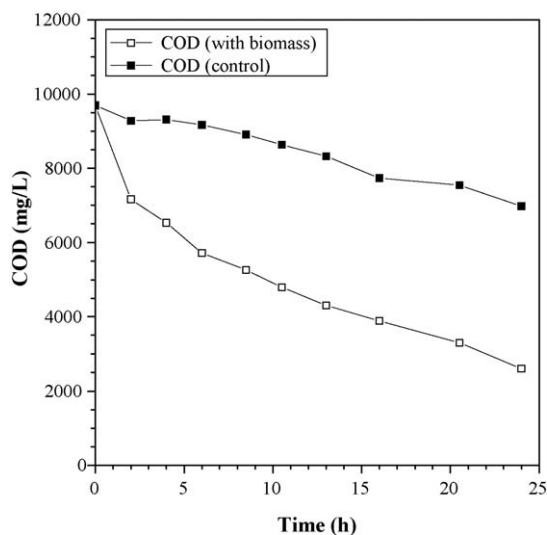

Fig. 8. Abiotic COD removal during SBR type of operation of the trickling filter (control experiment). Feed COD = 9700 mg/L.

$FeSO_4 \cdot 7H_2O$ 0.8% (w/w) solution added per liter of wastewater or the mixed stream wastewater diluted to a level of about 40,000 mg/L TCOD with other wastewater streams (characterized by very low organic loading and high flowrate) could be a first step in an integrated wastewater management scheme, where all biodegradable compounds are being removed. In order to reach more stringent quality criteria the produced effluent from the biological treatment plant can be treated further with, e.g. advanced oxidation processes, using peroxide Fenton's oxidation for example either alone [6] or assisted with UV-light [33], in which the high oxidizing potential of species like hydroxyl radicals is utilized [34].

4. Conclusions

The ability to use a biological treatment plant and more specifically a trickling filter for the removal of biodegradable compounds from the wastewater produced from an organic dyes and varnishes manufacturing company was addressed in this work. A pilot scale trickling filter was operated either continuously or as a sequencing batch reactor in order to treat: (a) the combined wastewater at the company's outlet and (b) a mixture of the four main wastewater streams containing the main organic loading.

The filter sustained appropriately acclimated aerobic biomass in both cases that was proved able to remove efficiently the organic loading even under extreme operating conditions, i.e. initial feed COD of around 40,000 mg/L and pH in the range between 5.5 and 8.0.

The system apparent COD removal efficiency ranged up to 60–70% for a hydraulic loading of 1.1 m^3/m^2 day and up to 80–85% for a hydraulic loading 0.6 m^3/m^2 day when treating mixed effluent wastewater. However, a stable COD removal efficiency of 60–70% was achieved even in the case of undiluted mixed effluent wastewater at a hydraulic loading of 1.1 m^3/m^2 day. When diluted mixed stream wastewater was fed to the system, the pilot unit operated in an SBR mode was able to remove about 70% of the initial COD at the end of a 24-h cycle, whereas it achieved an almost 95% COD removal in a 48-h cycle. However, depending on the operating conditions of the system, about 30–60% of the total COD removal was due to air stripping caused by the air supply at the bottom of the filter, whereas the rest of the COD was clearly removed through biological action. The gaseous outlet from the trickling filter should therefore be further treated either physicochemically (e.g. passing through a catalytic converter, an activated carbon filter, etc.) or even biologically using a biofilter with appropriately selected biomass.

The concluded results from this study provide therefore sound evidences against the common perception, often stated by various researchers: that although conventional biological treatment, exemplified in activated sludge or trickling filter plants, is a suitable process for the removal of the bulk of the organic load, it is not as effective in dealing with wastewaters generated in organic synthesis operations, as those of dyes [18,35].

According to these results, the proposed biological treatment process based on a trickling filter operating either continuously or even better in an SBR mode appears as a promising pretreatment step for coping with dye manufacturing wastewaters in terms of removing a great amount of the (potentially) biodegradable compounds. Such a step is generally required when integrated schemes of wastewater treatment are developed for industrial type wastewaters that contain remarkable amounts of biodegradable compounds. In these cases, advanced oxidation processes face strict limitations, both technical and economical, in their application to the whole site wastewater flow, whereas they are quite effective in converting rather recalcitrant compounds into intermediates amenable to biological oxidation (via recirculation to the inlet of the biological unit) or even better completely mineralizing these compounds when applied in the outlet of a biological treatment facility as a final polishing step.

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