# Cosmetic wastewater treatment by upflow anaerobic sludge blanket reactor

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## ARTICLE INFO

## ABSTRACT

Anaerobic treatment of pre-settled cosmetic wastewater in batch and continuous experiments has been investigated. Biodegradability tests showed high COD and solid removal efficiencies (about 70%), being the hydrolysis of solids the limiting step of the process. Continuous treatment was carried out in an upflow anaerobic sludge blanket reactor. High COD and TSS removal efficiencies (up to 95% and 85%, respectively) were achieved over a wide range of organic load rate (from 1.8 to 9.2 g TCOD $L^{-1}$ $day^{-1}$). Methanogenesis inhibition was observed in batch assays, which can be predicted by means of a Haldane-based inhibition model. Both COD and solid removal were modelled by Monod and pseudo-first order models, respectively.

## 1. Introduction

Cosmetic wastewaters are characterized by relatively high values of chemical oxygen demand (COD), suspended solids, fats, oils and detergents [1,2]. These effluents are frequently treated by means of coagulation/flocculation with pressure-flotation to separate the resulting sludge in some cases [3,4]. Nevertheless, the more stringent regulations concerning industrial wastewaters makes necessary to implement new technologies for a more efficient treatment of this type of effluents. The application of activated carbon adsorption [5], ultrafiltration [6] and advanced oxidation processes, like Fenton [7] and catalytic wet peroxide oxidation [8,9] has been reported.

Due to the presence of non-readily biodegradable compounds of these wastewaters, conventional biological systems have not been thoroughly applied. However, some biological processes developed in the last two decades have the potential of efficiently treating industrial wastewaters at relatively low costs. Aerobic processes are intensive energy consumers. In contrast, anaerobic digestion produces a low quantity of waste sludge and it is capable to treat high organic load rates (OLR) and produce methane which can be used as an energy source for on site heating and electricity generation, partially counteracting the energy cost of anaerobic treatment plants [10].

Due to its low operating costs, flexibility and versatility, upflow anaerobic sludge blanket (UASB) reactors have been applied to a wide range of industrial effluents [11], such as slaughterhouse [12,13], food processing [14–16], piggery [17], olive mill residues [18], manure [19], pulp-bleaching [20] and brewery [21]. However, there is a lack of information in the literature on the applicability of UASB reactors to treat cosmetic effluents. The main difficulties for treating cosmetic wastewaters by biological processes derive from the presence of detergents, surfactants, hormones, cosmetics and pharmaceutical compounds [22].

Biodegradability tests and kinetic studies have been widely used in order to learn on the performance of anaerobic bioreactors for treating industrial wastewaters. The substrate consumption and methane production have been commonly modelled by means of inhibition [23,24] and non-inhibition models [15,17,25] depending on the wastewaters composition, which were used to implement the IWA Anaerobic Digestion Model 1 (ADM1) [26].

The aim of this study is to analyse the feasibility of the anaerobic treatment and the applicability of an UASB reactor for the treatment of cosmetic wastewaters. Kinetic tests concerning the organic substrate consumption, solids hydrolysis and methanogenic inhibition were also carried out.

## 2. Materials and methods

### 2.1. Wastewater

The wastewaters were collected from a cosmetic plant located near Madrid (Spain) and settled for 24 h in order to reduce the

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**Nomenclature**

| | |
|---|---|
| $a$ | empirical proportionality factor between VSS and ICOD (g VSS g$^{-1}$ ICOD) |
| ADM1 | the IWA Anaerobic Digestion Model no. 1 |
| BICOD | biodegradable insoluble chemical oxygen demand (g ICOD L$^{-1}$) |
| BSCOD | biodegradable soluble chemical oxygen demand (g SCOD L$^{-1}$) |
| BVSS | biodegradable volatile suspended solids (g VSS L$^{-1}$) |
| COD | chemical oxygen demand (g COD L$^{-1}$) |
| $\varepsilon$ | energy |
| ICOD | insoluble chemical oxygen demand (g ICOD L$^{-1}$) |
| $k$ | first order apparent constant for COD consumption (g CH$_4$-COD L g$^{-1}$ X$_{VSS}$ g$^{-1}$ TCOD day$^{-1}$) |
| $K_h$ | hydrolysis constant (day$^{-1}$) |
| $K_i$ | methanogenic inhibition constant (g TCOD L$^{-1}$) |
| $K_s$ | half saturation constant or Monod constant (g SCOD L$^{-1}$) |
| $n$ | inhibition order (dimensionless) |
| NBICOD | non-biodegradable insoluble chemical oxygen demand (g ICOD L$^{-1}$) |
| NBSCOD | non-biodegradable soluble chemical oxygen demand (g SCOD L$^{-1}$) |
| NBVSS | non-biodegradable suspended solids (g VSS L$^{-1}$) |
| OLR | organic load rate (g TCOD L$^{-1}$ day$^{-1}$) |
| SCOD | soluble chemical oxygen demand (g SCOD L$^{-1}$) |
| SCOD$_{VSS}$ | portion of VSS transformed into SCOD (g SCOD L$^{-1}$) |
| SLR | sludge loading rate (g TCOD g$^{-1}$ X$_{VSS}$ day$^{-1}$) |
| SMA | specific methanogenic activity (g CH$_4$-COD g$^{-1}$ X$_{VSS}$ day$^{-1}$) |
| TCOD | total chemical oxygen demand (g TCOD L$^{-1}$) |
| TSS | total suspended solids (g TSS L$^{-1}$) |
| TSSLR | total suspended solids loading rate (g TSS L$^{-1}$ day$^{-1}$) |
| UASB | upflow anaerobic sludge blanket |
| $V_{max}$ | maximum SCOD consumption rate (g SCOD L$^{-1}$ day$^{-1}$) |
| VSS | volatile suspended solids (g VSS L$^{-1}$) |
| X$_{VSS}$ | biomass expressed as VSS (g X$_{VSS}$ L$^{-1}$) |

concentration of suspended solids and floatable fats and oils. The main characteristics of these wastewaters are summarized in Table 1.

The fed wastewater was supplemented with 1 mL L$^{-1}$ of the following micronutrients solution (mg L$^{-1}$): FeCl$_2$·H$_2$O (2000), H$_3$BO$_3$ (50), ZnCl$_2$ (50), CuCl$_2$·H$_2$O (38), MnCl$_2$·4H$_2$O (500), (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O (50), AlCl$_3$·6H$_2$O (90), CoCl$_2$·6H$_2$O (2000), NiCl$_2$·6H$_2$O (92), Na$_2$SeO·5H$_2$O (162), EDTA (1000), resazurin (0.2), sulfuric acid 36% (1 mL L$^{-1}$). Alkalinity was provided by adding 1 g NaHCO$_3$ g$^{-1}$ TCOD. A mixture of N$_2$:CO$_2$ (80:20) was previously bubbled to remove the dissolved oxygen.

**Table 1**
Characteristics of the raw and settled cosmetic wastewater.[a]

| Parameter | Wastewater | |
|---|---|---|
| | Raw | Settled |
| pH | 7.03–7.18 | |
| Conductivity (mS cm$^{-1}$) | 0.8–1.0 | |
| TCOD (g TCOD L$^{-1}$) | 7.9–11.8 | 3.8–8.1 |
| SCOD (g SCOD L$^{-1}$) | 5.2–7.8 | 2.5–4.6 |
| TSS (g TSS L$^{-1}$) | 1.57–1.80 | 0.51–1.07 |
| VSS (g VSS L$^{-1}$) | 1.30–1.55 | 0.45–1.02 |
| Fats and oils (g L$^{-1}$) | 1.42–2.00 | 0.52–1.21 |

[a] Number of samples analysed = 12.

### 2.2. SMA assay

Specific methanogenic activity (SMA) was measured by the displacing method described by James et al. [27]. SMA values were estimated using the Roediger model [28].

### 2.3. Biodegradability test

Anaerobic batch reactors (2 L) were inoculated with 1.5 g X$_{VSS}$ L$^{-1}$ of granular sludge. The reactors were filled up with 1.5 L of previously settled cosmetic wastewater and intermittently stirred (1 min each 5 min) to avoid the substrate external diffusion limitations. NaHCO$_3$ and micronutrients were added in the same way than in the continuous runs, using resazurin as redox indicator. The experiments were carried out by triplicate for 30 days. A blank study was accompanied under the same conditions but using granular sludge previously sterilized with 4% of formaldehyde for 24 h at 4 °C.

### 2.4. Inhibition tests

The inhibition assays were carried out following the SMA method described by James et al. [27], but using cosmetic wastewater as carbon source instead of volatile fatty acids. Settled wastewater was diluted with tap water at different ratios from 20% to 100% of settled wastewater. TCOD, SCOD, TSS, VSS and CH$_4$ were measured daily. The tests were carried out by duplicate.

### 2.5. Experimental setup for continuous runs

Experiments in continuous mode were carried out using a 5.2 L UASB reactor with an internal diameter to height ratio of 1:7.2. The reactor was equipped with a gas–liquid–solid separator installed 15 cm below the outlet point. The influent was pumped continuously from the bottom of the reactor by means of a peristaltic pump (Gilson Minipulse3) and the effluent was withdrawn from the top. CO$_2$ was removed from biogas using a Mariotte flask with a 4 M NaOH solution trap, and CH$_4$ was measured with a wet gas-meter (Schlumberger). The hydraulic retention time was 24 h and the working temperature 30 ± 1 °C. The reactor was inoculated with 100 g X$_{VSS}$ of granular sludge from a full scale UASB reactor treating a brewery wastewater and was operated for 148 days. The sludge was characterized by a VSS to TSS ratio of 0.80, an average granule diameter of 1–2 mm and a SMA of 0.74 g CH$_4$-COD g$^{-1}$ X$_{VSS}$ day$^{-1}$. An acclimation period of 96 days was used for reactor start-up until steady-state was reached. In order to emulate the disturbances observed in the main characteristics of the cosmetic wastewater at the full-scale treatment plant the OLR was changed describing different operational periods. Each period was considered over when at least 80% of COD removal was maintained during 3 consecutive days at each set of operating conditions.

### 2.6. Kinetic analysis

Two biodegradation tests were carried out during 50 days in batch mode. Previously settled wastewater was used and both insoluble and soluble organic matters were monitored. The same facilities as described in biodegradability tests were used, but they were inoculated with completely adapted granular sludge withdrawn from the UASB reactor at the end of the continuous assays.

### 2.7. Analytical methods

Analyses of TCOD, SCOD, TSS and VSS were performed according to the APHA Standard Methods [29].
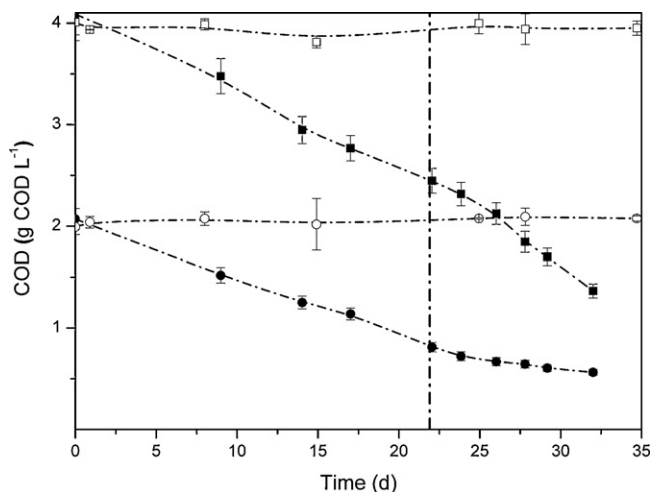
**Fig. 1.** Time evolution of TCOD (squares) and SCOD (circles) in biodegradability (solid symbols) and adsorption assays (empty symbols), respectively.



**Fig. 2.** UASB reactor performance. OLR (bars), TCOD removal efficiencies (circles) and methanogenic efficiency (continuous line).

Organic acids and alcohols were quantified by HPLC coupled with a refraction index (HPLC/RI) detector using sulfonated polystyrene resin in the protonated form (67H type) as the stationary phase (Varian Metacarb 67H 300 mm – 6.5 mm) and sulfuric acid (0.25 mM in milliQ water) as the mobile phase at flow rate of 0.8 mL min$^{-1}$. Column temperature was 65 °C. Bicarbonate accumulated in the NaOH trap was measured by ionic chromatography (Metrohm 790 Personal IC equipped with a 6.1005.200 Metrosep Organic Acids column). A 0.5 mM sulfuric acid solution in milliQ water was used as solvent at a constant flow of 0.5 mL min$^{-1}$.

The identification of species in the initial and treated effluents was performed by gas chromatography/ion trap mass spectrometry (GC/MS, CP-3800/Saturn 2200, Varian) with an autosampler injector (CP-8200, Varian) and solid-phase microextraction (Carbowax/Divinylbenzene, Yellow-Green). A Factor Four VF-5ms capillary column (30 m long, 0.25 mm diameter) was used as stationary phase. The carrier gas (helium) flow rate in the GC/MS was 1 mL min$^{-1}$. The sample injection was carried out with split-less at 220 °C. The temperature programme used during the GC/MS analyses ramped as follows: 40 °C for 15 min and 15 °C min$^{-1}$ until 250 °C. The identifications were assessed with the aid of the database library NIST.

## 3. Results and discussion

### 3.1. Biodegradability test

Fig. 1 shows the experimental results of TCOD and SCOD degradation. After 32 days fairly high TCOD and SCOD removal efficiencies were achieved (67% and 73%, respectively). From the beginning of the experiment until the 24th day, average specific removal rates of 0.049 g TCOD g$^{-1}$ X$_{VSS}$ day$^{-1}$ and 0.037 g SCOD g$^{-1}$ X$_{VSS}$ day$^{-1}$ were obtained. This indicates that solids hydrolysis was slower than the fermentation of the soluble organic matter.

A sharp change on the COD evolution was observed at about day 24. Whilst an almost constant SCOD concentration was observed, with an average specific SCOD removal rate of 0.013 g SCOD g$^{-1}$ X$_{VSS}$ day$^{-1}$, a significant increase of the average specific TCOD removal rate up to 0.084 g TCOD g$^{-1}$ X$_{VSS}$ day$^{-1}$ was detected. According to these results, at the beginning of the process hydrolysis of solids can be considered the limiting step in the anaerobic biodegradation of these cosmetic wastewaters. Nevertheless, once biodegradable SCOD is consumed, hydrolysis is clearly accelerated.
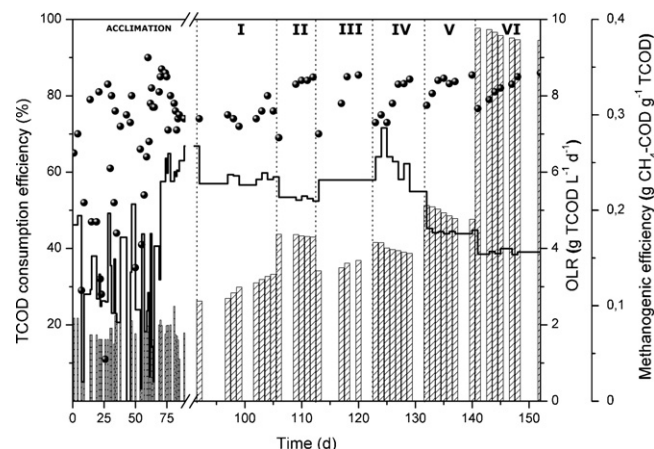
### 3.2. Continuous experiments

The performance of the UASB reactor is shown in Fig. 2 with the different stages being defined in Table 2. Although during the 92-days acclimation period the OLR was maintained almost constant around 1.8 g TCOD L$^{-1}$ day$^{-1}$, the TCOD removal efficiency varied widely between 10% and 95%. This fact can be related with the presence of non-readily biodegradable compounds, which could result in an unusual over-length of the acclimation period. This stage was considered to finish when the COD and solid removal efficiencies and methane production remained constant (Fig. 2). A decrease of the COD removal efficiency was detected at the beginning of each stage recovering shortly after every OLR change. The reactor showed a stable behaviour up to day 152 after the acclimation period, obtaining average TCOD and TSS removal efficiencies between 78–85% and 63–82%, respectively. Methanogenic efficiency between 0.15 and 0.29 g CH$_4$-COD g$^{-1}$ TCOD consumed was observed (Table 2). Finally, OLR could be increased up to 9.2 g TCOD L$^{-1}$ day$^{-1}$ (stage VI) maintaining TCOD removal efficiencies between 75% and 85%, which means that the acclimated UASB reactor is a suitable system for handling cosmetic wastewaters, with high TSS and TCOD loads showing a good response to feed variability. The increase of the OLR from 3.9 up to 9.2 g TCOD L$^{-1}$ day$^{-1}$ provoked a reduction of the methanogenic efficiency from 0.25 to 0.15 g CH$_4$-COD g$^{-1}$ TCOD, which indicates the occurrence of inhibition and/or toxicity phenomena.

The average specific COD and TSS removal rates measured at different sludge loading rates (SLRs) are reported in Table 3. Linear relationships were found between both specific COD removal rates and OLR, whereas the specific TSS removal rate evolves into an asymptotic relationship with the SLR, which implies that the specific TSS loading rate (TSSLR) treated is close to saturation. The specific TCOD removal rates were almost double than those of SCOD, suggesting the occurrence of solids degradation. The specific TSS removal rates were substantially lower than the observed for COD, supporting the hypothesis that the hydrolysis of solids is the limiting step in the anaerobic biodegradation of cosmetic wastewaters. Anyway, the stable values of methanogenic efficiency during each stage evident a great robustness of the process (Table 2).

The composition of the cosmetic wastewater and the effluents from the UASB reactor were analysed by GC/MS and HPLC/RI. Fig. 3a depicts a representative GC/MS chromatogram showing a fairly complex composition (Table 4). Most of these compounds were not detected in the resulting effluents after 154 days of treatment in the continuous experiment (Fig. 3b). Some unidentified compounds appeared in the UASB effluents which may correspond to refrac-

**Table 2**
Average operating conditions and removal efficiencies in the UASB reactor.

| Time (days) | Stage | OLR (g TCOD L$^{-1}$ day$^{-1}$) | TSSLR (g TSS L$^{-1}$ day$^{-1}$) | TCOD removal efficiency (%) | TSS removal efficiency (%) | Methanogenic efficiency (g CH$_4$-COD g$^{-1}$ TCOD) |
|---|---|---|---|---|---|---|
| 0–91 | Acclimation | 1.8 ± 0.3 | 0.26 ± 0.10 | 75 ± 28 | 64 ± 23 | 0.144 ± 0.078 |
| 92–105 | I | 2.8 ± 0.3 | 0.31 ± 0.13 | 80 ± 7 | 63 ± 20 | 0.233 ± 0.004 |
| 106–112 | II | 4.5 ± 0.2 | 0.23 ± 0.11 | 78 ± 3 | 82 ± 4 | 0.213 ± 0.002 |
| 113–122 | III | 4.1 ± 0.2 | 0.18 ± 0.10 | 78 ± 5 | 77 ± 6 | 0.232 ± 0.003 |
| 123–131 | IV | 3.7 ± 0.2 | 0.21 ± 0.11 | 84 ± 10 | 76 ± 4 | 0.250 ± 0.021 |
| 132–140 | V | 5.7 ± 0.7 | 0.73 ± 0.44 | 84 ± 4 | 82 ± 3 | 0.178 ± 0.002 |
| 141–152 | VI | 9.2 ± 0.4 | 0.36 ± 0.22 | 83 ± 2 | 79 ± 1 | 0.156 ± 0.002 |

**Table 3**
Specific TCOD, SCOD and TSS removal rates at different SLRs in the UASB reactor.

| SLR (g TCOD g$^{-1}$ X$_{VSS}$ day$^{-1}$) | Specific TCOD removal rate (g TCOD g$^{-1}$ X$_{VSS}$ day$^{-1}$) | Specific SCOD removal rate (g SCOD g$^{-1}$ X$_{VSS}$ day$^{-1}$) | Specific TSS removal rate (g TSS g$^{-1}$ X$_{VSS}$ day$^{-1}$) |
|---|---|---|---|
| 0.087 | 0.011 | 0.007 | 0.0006 |
| 0.118 | 0.022 | 0.012 | 0.0016 |
| 0.142 | 0.025 | 0.014 | 0.0018 |
| 0.180 | 0.029 | 0.020 | 0.0038 |
| 0.187 | 0.035 | 0.018 | 0.0042 |
| 0.256 | 0.045 | 0.026 | 0.0043 |
| 0.397 | 0.064 | 0.036 | 0.0046 |

tory intermediates. The analysis of the wastewaters by HPLC/RI allowed to quantify the concentration of some alcohols and organic acids such glycerol ($100 \pm 3.1$ mg L$^{-1}$), ethanol ($30 \pm 2.5$ mg L$^{-1}$), 2-propanol ($4 \pm 1.3$ mg L$^{-1}$), acetic acid ($417 \pm 2.5$ mg L$^{-1}$), formic acid ($12.7 \pm 2.3$ mg L$^{-1}$) and oxalic acid ($1.1 \pm 0.2$ mg L$^{-1}$), whose concentrations in the UASB effluents were beyond the detection limit of this analytical technique.

### 3.3. Inhibition assay

To learn more on the biodegradation process, methanogenesis was studied since it is the most critical stage of anaerobic digestion in connection with the existence of inhibition phenomena. The dilution of the cosmetic wastewater at different ratios led to a wide range of average TCOD consumption rates, which were found to be linearly related with the SMA (Fig. 4). The resulting slope of 0.160 g CH$_4$-COD g$^{-1}$ TCOD ($R^2 = 0.93$) suggests that beside methane other gases were produced upon COD consumption. From the analysis of the carbon dioxide trap solution a production of 5.26 mol of CO$_2$ per mol of CH$_4$ was calculated, which means a CH$_4$:CO$_2$ ratio of 20:80 in the cosmetic wastewater digestion.
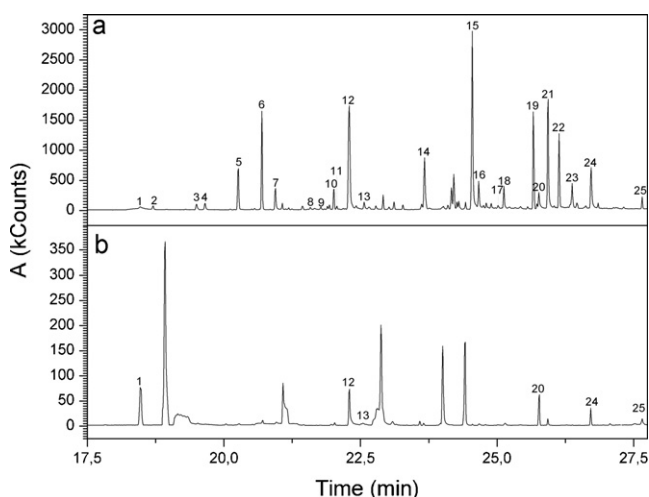
In order to study the inhibition phenomenon, the resulting sludge from the inhibition assay was drawn and washed to be used in additional batch assays adding 4 g glucose L$^{-1}$ as substrate. Likewise, short chain organic compounds were quantified, being acetate the major intermediate reaching a concentration of around 0.8 g/L after 8 days, which was not further removed. The accumulation of acetate indicates that acetoclastic methanogenesis was inhibited, which could explain the reduction of the CH$_4$:CO$_2$ ratio detected during the inhibition assay. This fact suggests that the methane produced can be majorly due to the activity of hydrogenotrophic methanogens.

Most of the kinetic models applied to anaerobic wastewater treatment are based on the Monod equation. Nevertheless, first order models are commonly used to simplify methanogenesis under inhibitory conditions [19,25,30]. Taking into account the



**Fig. 3.** GC/MS chromatograms for cosmetic wastewater (a) and the resulting effluent from UASB (b).

**Table 4**
Removal efficiencies for the compounds identified by GC/MS.

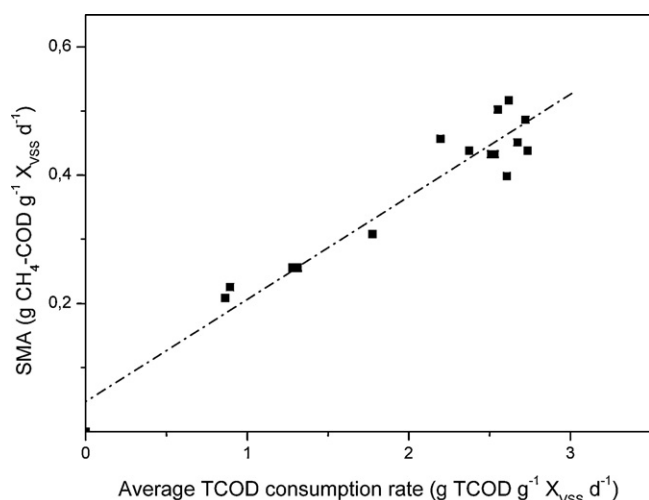| Number | Compound | Removal efficiency[a] (%) |
|---|---|---|
| 1 | 4-Hydroxi-bencenosulfonic acid | 29.4 |
| 2 | 3-Decanol | >99 |
| 3 | 2-Ethyl-1-hexanol | >99 |
| 4 | Benzyl alcohol | >99 |
| 5 | 2-Methyl-6-metylene-2-octanol | >99 |
| 6 | 3,7-Dimethyl-1,6-octadien-3-ol | >99 |
| 7 | Phenylethyl alcohol | >99 |
| 8 | Benzyl acetate | >99 |
| 9 | 3,7-Dimethyl-1,6-nonadien-3-ol | >99 |
| 10 | 1-Methanol-3-cyclohexen | >99 |
| 11 | 1,5,5-Trimethyl-6-methylene-cyclohexene | >99 |
| 12 | 2-Phenoxyethanol | 96.4 |
| 13 | 3,7-Dimethyl-2,6-octadiene-1-ol | >99 |
| 14 | 2,4-Diisocianate-1-methylbenzene | 74.0 |
| 15 | Methylparaben | >99 |
| 16 | Cyclododecane | >99 |
| 17 | 3-Methyl-ciclopentyl-benzene | >99 |
| 18 | Ethylparaben | >99 |
| 19 | Diethyl-phthalate | >99 |
| 20 | Methyl p-tert-butylphenylacetate | 77.7 |
| 21 | Propylparaben | >99 |
| 22 | Methyl 3-oxo-2-pentylcyclopentane acetate | >99 |
| 23 | Isobutylparaben | >99 |
| 24 | Butylparabene | 95.9 |
| 25 | Dibutyl phthalate | 87.8 |

[a] With respect to peak area.

**Fig. 4.** SMA values for different specific TCOD consumption rates.

aforementioned linear relationship between the SMA and the TCOD consumption rate, as well as the detected inhibition of methanogenesis, the SMA can be described following the equation:

$$SMA = \frac{k \cdot TCOD}{1 + (TCOD/K_i)^n} \qquad (1)$$

where $k$ is the first order apparent constant for COD consumption (g $CH_4$-COD L g$^{-1}$ $X_{VSS}$ g$^{-1}$ TCOD day$^{-1}$), $K_i$ is the inhibition constant (g TCOD L$^{-1}$) and $n$ is the inhibition order (dimensionless). The kinetic parameters of Eq. (1) were obtained using the Microcal® Origin 7.0 with the Levenberg–Marquardt algorithm. Fig. 5a shows the experimental and predicted values of SMA obtained for different TCOD initial concentrations. TCOD concentrations above 4.5 g TCOD L$^{-1}$ led to decreasing values of SMA, which indicates that methanogenesis was inhibited. The $k$, $K_i$ and $n$ values obtained were $0.055 \pm 0.003$ g $CH_4$-COD L g$^{-1}$ $X_{VSS}$ g$^{-1}$ TCOD day$^{-1}$, $6.86 \pm 0.28$ g TCOD L$^{-1}$ and $3.97 \pm 0.69$, respectively ($R^2 = 0.94$).

### 3.4. Kinetic analysis

The time evolution of SCOD and VSS is shown in Fig. 5b. High removal efficiencies were obtained in both cases (91.4% of SCOD and 83.8% of VSS in 50 days). A simultaneous degradation of both SCOD and VSS was detected at the beginning of the process. A residual fraction of SCOD and VSS remains at the end of the experiment, indicating the presence of refractory compounds. As standard ADM1 cannot predict residual fractions of organic matter after anaerobic biodegradation, we propose a modification of ADM1 for the anaerobic biodegradation of cosmetic wastewater.
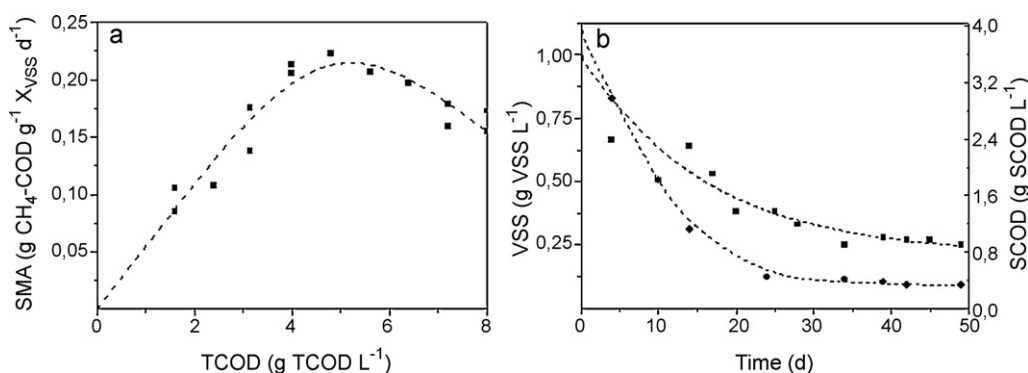
Taking into account the characteristics of the wastewater and the experimental results obtained, the following statements were assumed:

1. Biomass production was negligible respect to COD consumption.
2. The VSS were hydrolyzed following a first order kinetics because hydrolytic activity is not coupled directly with the bacterial metabolism [31].
3. The BVSS (biodegradable volatile suspended solids) are defined as the difference between the VSS and the NBVSS (non-biodegradable volatile suspended solids):

$$BVSS = VSS - NBVSS \qquad (2)$$

Thus, the hydrolysis model can be described following the equation:

$$\frac{d(VSS - NBVSS)}{dt} = -K_h(VSS - NBVSS) \qquad (3)$$

where BVSS and NBVSS are expressed in g L$^{-1}$, and $K_h$ is the hydrolysis constant (day$^{-1}$).

4. The COD is considered as organic matter. The VSS:TSS ratio obtained ($\approx 0.94\%$) suggests that almost all the insoluble organic matter (ICOD) can be related with VSS as described in Eq. (4). Insoluble (VSS) and soluble (SCOD) organic matters were expressed as g VSS L$^{-1}$ and g SCOD L$^{-1}$, respectively.

$$VSS = a \cdot ICOD = a \cdot (TCOD - SCOD) \qquad (4)$$

where $a$ is the empirical proportionality factor between VSS and ICOD (g VSS g$^{-1}$ ICOD), and it was calculated from the initial values of VSS, TCOD and SCOD.

5. Insoluble or "non-accessible" substrate is transformed into "accessible substrate" during the anaerobic treatment of solids-bearing wastewaters [19]. The dissolved organic matter, whether resulting from the hydrolysis or initially presented in the settled wastewater, is consumed following a Monod kinetic model without biomass growth [32]. This can be expressed by the equation:

$$\frac{dSCOD}{dt} = -V_{max} \cdot \frac{SCOD}{K_s + SCOD} \qquad (5)$$

where d$SCOD$/d$t$ is the soluble substrate removal rate (g SCOD L$^{-1}$ day$^{-1}$), $K_s$ is the half-saturation constant (g SCOD L$^{-1}$) and $V_{max}$ is the maximum SCOD consumption rate (g SCOD L$^{-1}$ day$^{-1}$).

The scheme of the theoretical approach can be represented as follows:



**Fig. 5.** Relationship between SMA and TCOD (a) and time evolution of VSS (squares) and SCOD (circles) (b). Experimental values (symbols) and model predictions (dash lines).

$$
\text{TCOD}
\begin{cases}
\begin{array}{l}
\text{ICOD} \\
\text{(VSS)}
\end{array}
\begin{cases}
\text{NBICOD (NBVSS)} \\
\text{BICOD (BVSS)} \\
\qquad\searrow \text{ HYDROLYSIS (Pseudo first order)}
\end{cases} \\
\\
\text{SCOD}
\begin{cases}
\text{BSCOD} \longrightarrow \text{CH}_4 + \text{CO}_2 + \varepsilon + \text{VSS} \\
\qquad\text{Soluble substrate consumption (Monod)} \\
\text{NBSCOD}
\end{cases}
\end{cases}
$$
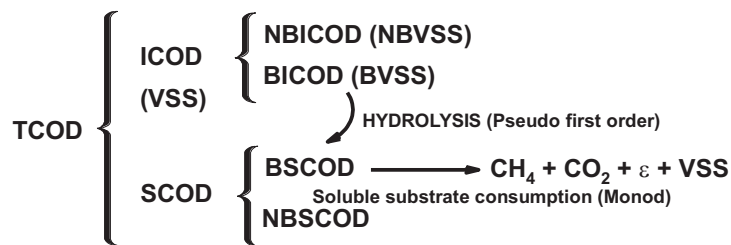
Taking into account that biodegradable SCOD can be expressed by:

$$BSCOD = SCOD - NBSCOD \tag{6}$$

The balance of the BSCOD includes the biodegradation of the starting BSCOD, the generation of soluble organic matter through the solids hydrolysis and its further biodegradation, according to:

$$
\frac{d\text{BSCOD}}{dt} = \underbrace{\frac{d(\text{VSS} - \text{NBVSS})}{dt} \cdot \frac{1}{a}}_{\text{BSCOD production by hydrolysis}} - \underbrace{\frac{d(\text{SCOD} - \text{NBSCOD})}{dt}}_{\text{Starting BSCOD}}
$$
$$
- \underbrace{\frac{d\text{SCOD}_{\text{VSS}}}{dt}}_{\text{Consumption of BSCOD from hydrolysis}} \tag{7}
$$

where $SCOD_{VSS}$ represents the amount of VSS transformed into SCOD. Both the starting BSCOD and that generated from hydrolysis were expressed by Monod equation, assuming the same kinetic parameters for their prediction. Thus, the SCOD balance can be rearranged to:

$$
\frac{d\text{BSCOD}}{dt} = K_h \cdot \frac{1}{a} \cdot (\text{VSS} - \text{NBVSS})
$$
$$
- V_{\max}\left(\frac{1/a \cdot (\text{VSS} - \text{NBVSS})}{K_s + 1/a \cdot (\text{VSS} - \text{NBVSS})} + \frac{\text{SCOD} - \text{NBSCOD}}{K_s + (\text{TSCOD} - \text{NBSCOD})}\right) \tag{8}
$$

The kinetic parameters were calculated by fitting Eqs. (3) and (8) to the experimental data by means of a non-linear least squares minimization of the error using a simplex algorithm followed by a Powell minimization algorithm (Micromath® Scientist 3.0). Integration was done with the following boundary conditions: $a = 0.337$ g VSS $g^{-1}$ ICOD, starting SCOD $= 3.901$ g SCOD $L^{-1}$ and initial VSS $= 0.947$ g VSS $L^{-1}$.

Both the hydrolysis and SCOD consumption kinetics were satisfactorily described by the kinetic model proposed (Fig. 5b). The values of the fitting parameters were $K_h = 0.062 \pm 0.006$ day$^{-1}$, $NBVSS = 0.209 \pm 0.0041$ g L$^{-1}$ for the hydrolysis kinetics and $V_{\max} = 0.55 \pm 0.02$ g L$^{-1}$ day$^{-1}$, $K_s = 1.54 \pm 0.35$ g L$^{-1}$ and $NBSCOD = 0.29 \pm 0.03$ g L$^{-1}$ for the COD kinetics ($R^2 = 0.998$). The small deviations obtained (lower than 23%) between the experimental and predicted values suggest that the parameters obtained represent accurately the activity of the anaerobic consortium involved in the cosmetic wastewater biodegradation. Moreover, the residual fractions of both SCOD and VSS detected at the end of the experiment were well predicted by the model. These results indicate that around 21% of the VSS and 7% of the SCOD are hardly biodegradable by anaerobic granular biomass.

In addition, the experimental data were fitted to a simplified ADM1 model, considering that the hydrolysis follows a first order kinetics and the COD consumption a Monod model, under the same boundary conditions. Whilst the experimental data were accurately predicted by our model, the ADM1 gave rise to parameter values without statistical significance or biological sense.

## 4. Conclusions

The results indicate that pre-settled cosmetic wastewater can be satisfactorily biodegraded by anaerobic granular sludge in an upflow anaerobic sludge blanket reactor. These wastewaters show a low methanogenic potential. The observed inhibition of acetotrophic methanogenesis can be caused by the presence of an inhibitory fraction of the COD. Hydrogenotrophic methanogenesis inhibition is accurately predicted by a pseudo-first order with inhibition model. Biodegradation of cosmetic effluents can be described by pseudo-first order and Monod-based kinetic equations for hydrolysis and substrate consumption, respectively.

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