SBR treatment of olive mill wastewaters: dilution or pre-treatment?

G. Farabegoli, A. Chiavola and E. Rolle

ABSTRACT

The olive-oil extraction industry is an economically important activity for many countries of the Mediterranean Sea area, with Spain, Greece and Italy being the major producers. This activity, however, may represent a serious environmental problem due to the discharge of highly polluted effluents, usually referred to as 'olive mill wastewaters' (OMWs). They are characterized by high values of chemical oxygen demand (COD) (80–300 g/L), lipids, total polyphenols (TPP), tannins and other substances difficult to degrade. An adequate treatment before discharging is therefore required to reduce the pollutant load. The aim of the present paper was to evaluate performances of a biological process in a sequencing batch reactor (SBR) fed with pre-treated OMWs. Pre-treatment consisted of a combined acid cracking (AC) and granular activated carbon (GAC) adsorption process. The efficiency of the system was compared with that of an identical SBR fed with the raw wastewater only diluted. Combined AC and GAC adsorption was chosen to be used prior to the following biological process due to its capability of providing high removal efficiencies of COD and TPP and also appreciable improvement of biodegradability. Comparing results obtained with different influents showed that best performances of the SBR were obtained by feeding it with raw diluted OMWs (dOMWs) and at the lowest dilution ratio (1:25): in this case, the removal efficiencies were 90 and 76%, as average, for COD and TPP, respectively. Feeding the SBR with either the pre-treated or the raw dOMWs at 1:50 gave very similar values of COD reduction (74%); however, an improvement of the TPP removal was observed in the former case.

Key words | granular activated carbon, olive mill wastewater, polyphenols, sequencing batch reactor

G. Farabegoli (corresponding author)
A. Chiavola
E. Rolle
Department of Civil and Environmental Engineering,
Sapienza University of Rome,
Via Eudossiana 18,
00184 Rome,
Italy
E-mail: *geneve.farabegoli@polimi.it*

INTRODUCTION

Olive mill wastewaters (OMWs), resulting from the olive oil production process, can be characterized by high organic and total suspended solids (TSS) loads as well as acidic pH (Gernjak *et al*. 2004; Sarika *et al*. 2005). The organic matter mainly consists of polysaccharides, sugars, phenols, polyalcohols, proteins, organic acids and oil (Cabrera *et al*. 1996; Belaid *et al*. 2006). The high phenols concentrations make OMW difficult to be treated by biological processes because they result in phytotoxicity and toxicity to bacteria used in conventional biological wastewater treatment plants (Gernjak *et al*. 2004).

The more common method adopted in Italy for OMWs disposal is by spreading on soil. However, this procedure can create serious problems such as contamination of surface and ground waters, alterations in soil quality, odour nuisance and colouring of natural waters. Italian law in force (L. 574/96) restricts the maximum amount of OMWs to be disposed of on soil to 50 m^3/ha and to 80 m^3/ha for wastewater deriving from a traditional or a continuous mill, respectively. An adequate treatment before discharging is therefore required to reduce the pollutant load, with particular concern to the removal of lipids and phenolic compounds.

Many different processes have been proposed to treat the OMWs such as mechanical, physical, chemical, biological or thermal processes and more often a combination of them.

A thorough review on the use of biological and advanced oxidation processes (AOPs) for OMW treatment was produced by Mantzavinos & Kalogerakis (2005). The

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authors mention that lime precipitation and water evaporation in ponds are commonly applied as they are relatively inexpensive; however, these processes alone can only partially meet the more stringent requirements posed on the discharge. A well-designed sequential treatment consisting of various chemical, physical and biological processes represents a better solution. In an aerobic batch reactor filled with OMWs, a biomass rich in fungi developed after about 30 d and was able to biodegrade phenolic compounds up to 70% (Bettazzi *et al.* 2006). Results of great significance were obtained by adding $Ca(OH)_2$ (up to pH 6.5) and 15 g/L of bentonite, and then feeding the mixture to a biological treatment without providing an intermediate phase separation (Beccari *et al.* 1999).

The reported results identified significant drawbacks and indicated that no single technology could be applied to OMW as a stand-alone treatment option. On the other hand, most of these treatment methods are also not cost effective.

The olive oil mill producers usually prefer, for economical reasons, to discharge the OMWs into municipal wastewater treatment plants where these are subjected to high dilution.

However, the potential of some innovative systems has not been exploited completely yet. For instance, few studies can be found on the application of discontinuous processes for the biological step, despite the fact that their capability of biodegrading several recalcitrant compounds, such as phenol and chlorophenols has been widely demonstrated (Chiavola *et al.* 2004; Tomei *et al.* 2004). In particular, a sequencing batch reactor (SBR) with its typical dynamic conditions, guarantees high flexibility, simple running, compact layout and is able to select the microbial species capable of degrading toxic compounds (Wilderer *et al.* 2001).

In previous studies by the same authors (Chiavola *et al.* 2010; Farabegoli *et al.* 2010) the following pre-treatment methods for OMWs were tested prior to a biological step: (1) lime precipitation, (2) alum and iron salt coagulation with and without acid cracking (AC), (3) activated carbon adsorption (GAC), and (4) membrane ultrafiltration (UF). The optimal operative conditions and the corresponding removal efficiencies of the different pre-treatment processes were established. The results obtained showed the highest chemical oxygen demand (COD), total phenols and total suspended solid removals by GAC adsorption, whereas lipids were mostly removed by lime precipitation. The application of the AC prior to GAC adsorption further improved the treatment efficiency.

Therefore, the aim of the present paper was to evaluate performances of the biological process in a SBR fed with combined AC and GAC adsorption pre-treated OMWs. The efficiency of the system was compared to that of an identical SBR fed with raw diluted wastewater.

METHODS

Influent characterization

The raw OMWs used for the experimental study were obtained from an olive oil continuous centrifuge processing plant located in the Province of Rome (Italy). The OMWs were first sieved at 300 μm in order to reduce the suspended solids content. Table 1 shows raw OMWs characterization after sieving.

The biological process was fed with raw and pre-treated OMWs, both diluted in tap water to reduce the influent loading and to adjust the pH to the final value of 7.5–8, so as to make the wastewater suitable for the microbial activity. The pH value of the pre-treated OMWs was adjusted through NaOH addition.

OMWs pre-treatment

The application of the AC prior to GAC adsorption further improved the treatment efficiency, as clearly demonstrated by Farabegoli *et al.* (2010). AC was applied by manually adjusting the pH value to less than 2 by dosing 98% concentrated sulphuric acid.

Different adsorption tests were then carried out using commercial GAC on the effluent from AC. GAC dosage and contact time were modified using a jar-tester. The optimal contact time was obtained by fixing the GAC dosage at 20 g/L and varying the rapid mixing time at 120 rpm, from 30 min to 40 h. Once the optimal contact time was determined (24 h), the carbon dosage was varied as follows:

Table 1 | Influent raw OMWs composition

Parameters	Sieved OMW
pH	5 ± 1
COD (g/L)	63.5 ± 5.2
TSS (g/L)	43.5 ± 5.1
VSS (g/L)	42.1 ± 2.3
TPPs (g/L)	1.9 ± 0.3
Lipids (g/L)	4.3 ± 0.9

5, 7.5, 10, 15, 20 g/L. The optimal GAC dosage (20 g/L) was determined based on the concentration of COD measured in the supernatant (COD_f). Further data on the GAC adsorption tests can be found in Farabegoli *et al.* (2010).

SBR plant

The biological process was carried out in a lab-scale reactor of a total working volume of 10 L (V_{tot}). A detailed description of the plant is provided in Chiavola *et al.* (2010). The aeration system was composed of two porous stones located at the bottom of the reactor and provided an airflow rate of 20 L/min; the oxygen concentration in the mixed liquor was always maintained above 2 mgO_2/L. In addition, a mechanical mixer was used to provide homogenous conditions within the reactor. The biological plant was seeded with a sample of activated sludge from the oxidation tank of a municipal wastewater treatment plant of the city of Rome (Italy). During the start-up period, a batch mode of operation was adopted consisting of aerated fill and react, settle, and draw phases. The values of the time-length of the cycle and of the operative phases, the hydraulic residence time (HRT) and the feed load were properly modified based upon the observed performance of the reactor. For instance, the values of these parameters were selected in order to get complete removal of the contaminants in each cycle, so as to avoid their accumulation in the reactor which might cause microbial inhibition. Periodical analyses of COD and total polyphenols (TPP) on samples of mixed liquors from the SBR plant were carried out during each cycle. A new batch was started only when residual COD and TPP concentrations reached very low values. During start-up, the SBR received only diluted OMWs (dOMWs). No sludge wasting was applied as long as the biomass reached stable growth conditions. An increase of the removal kinetics was observed with time during start-up, as a consequence of the progressive selection and enrichment of microbial species capable of biologically degrading OMW constituents and using them as energy and carbon sources. This allowed reduction of the dilution ratio (DR) of the influent and also to gradually reduce the time-length of the operative cycle.

After about one month, regime conditions were established as constant removal efficiencies were observed; at this time, a cycle duration of 1 d was adopted, consisting of four phases: fill (1 h), aerobic react (21 h and 30 min), settle (30 min) and draw (1 h). The duration of feed, aeration, mixing and draw was controlled by a timer. A sludge retention time (SRT) of about 30 d was applied. The high SRT value was selected so as to establish a high biomass concentration within the reactor, which was required to degrade the high influent organic loadings. It was also considered that the low-biodegradable compounds, such as polyphenols contained in OMWs, are known to determine low biomass growth yields.

Excess sludge wasting was applied just a few minutes before the end of the aerobic react phase. At the beginning of each cycle a volume (V_{fill}) of 2 L was fed to the reactor; the same volume of supernatant was drawn at the end of each cycle. A Volumetric Exchange Ratio ($VER = V_{fill}/V_{tot}$) of 0.2 was always maintained throughout the experimental activity. The reactor temperature was kept equal to $20 \pm 2\,^{\circ}C$ by means of a recirculating water bath.

At regime conditions, the SBR plant was initially studied using raw dOMWs as influent. Two different DR were used: 1:50 (first phase) and 1:25 (second phase). Afterwards, the reactor received the OMWs after the combined AC and GAC adsorption pre-treatment under the optimal conditions selected in the previous tests (third phase).

Table 2 lists the main operative conditions of the SBR in the three different experimental phases.

The SBR plant performances were continuously monitored during each experimental phase until stable and representative trends were established. The results shown later on refer to the more representative cycles.

The plant's performances were monitored through periodical analyses of liquid samples from both the influent and the effluent streams. In addition, kinetic studies were also carried out by measuring the main parameters at fixed time intervals during typical operating cycles.

Analytical methods

Temperature, pH (WTW, 330/SET-1) and dissolved oxygen (DO) (YSI 5739) were monitored throughout the process. Samples of the mixed liquor in the reactor, of the influent and effluent from the reactor were periodically collected. The samples were filtered at 1.2 µm to determine TSS and volatile suspended solids (VSS), by the gravimetric method, and at 0.45 µm to determine COD in the filtered sample. TPPs content was determined spectrophotometrically

Table 2 | Average influent concentrations of COD and TPP in the three experimental phases

Average influent concentrations (mg/L)	1st phase (dOMWs DR = 1:50)	2nd phase (dOMWs DR = 1:25)	3rd phase (pre-treated OMWs)
COD	1,300	2,600	1,300
TPP	40	80	40

according to the Folin-Ciocalteau method (Mulinacci *et al.* 2001). Lipids were determined after petroleum ether extraction. The sample was acidified and extracted with a mixture containing *n*-hexan (80%) and MTBE (20%). The extracted liquid was evaporated and the residue determined gravimetrically according to IRSA (1985). COD, TSS, VSS measurements were performed according to the *Standard Methods for the Examination of Water and Wastewater* (APHA/AWWA/WEF 2005). The respirometric tests and COD fractionation were carried out according to the Activated Sludge Model n°1 (ASM1) procedure (Henze *et al.* 1987).

Measurements were performed on triplicates and the average values determined. Results obtained were found to be reproducible within ±5%.

RESULTS AND DISCUSSION

Chemical–physical pre-treatments

A detailed characterization of the effluents from the combined AC and GAC adsorption process was carried out through respirometric tests and COD fractionation in order to determine variation of the biodegradability level due to pre-treatment.

Table 3 | Average results from COD fractionation

	X_s/COD_{tot} (%)	X_I/COD_{tot} (%)	S_s/COD_{tot} (%)	S_I/COD_{tot} (%)
Raw OMW	37	24	29	10
Effluent from AC + GAC	20	17	47	16

Table 3 shows the average results obtained, where S_s represents the readily biodegradable COD, X_s and X_i stand for the particulate fractions, slowly biodegradable and inert, respectively, and S_I for the inert soluble component. The AC and GAC adsorption pre-treatment showed a total COD (COD_{tot}) reduction accounting for 77%, and an appreciable increase in the percentage of the readily biodegradable fraction.

Also in terms of TPP and TSS removals, high reductions were attained by the combined AC and GAC adsorption process, whereas a low lipid reduction was observed.

Based on these results, it was decided to investigate how the SBR could perform by feeding it with the effluent from the combined treatment of AC and GAC adsorption.

Biological process

First phase (DR = 1:50)

As can be seen in Figure 1, the effluent COD concentration initially increased with time reaching a final value of 350 mg/L after eight cycles. Then, the removal efficiency became approximately constant with an average value of about 75%, with respect to the total content in the influent.

The kinetic tests (Figure 2) showed that the removal process of soluble COD (COD_f) started at the beginning of the cycle and continued throughout the entire react phase. A residual COD of about 120 mg/L was left over at the end

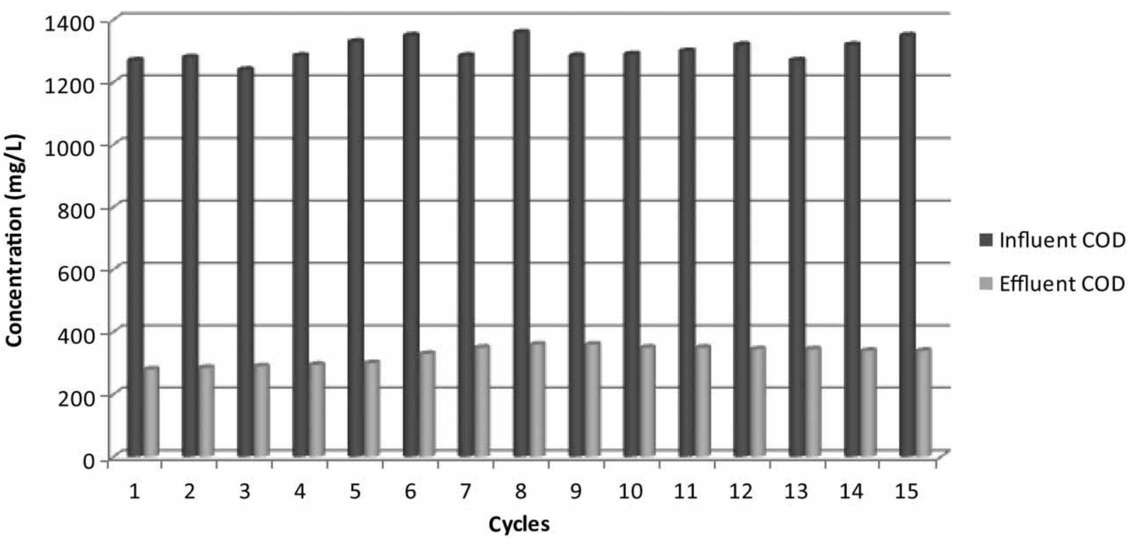

Figure 1 | Influent and effluent average COD concentrations during the first phase.

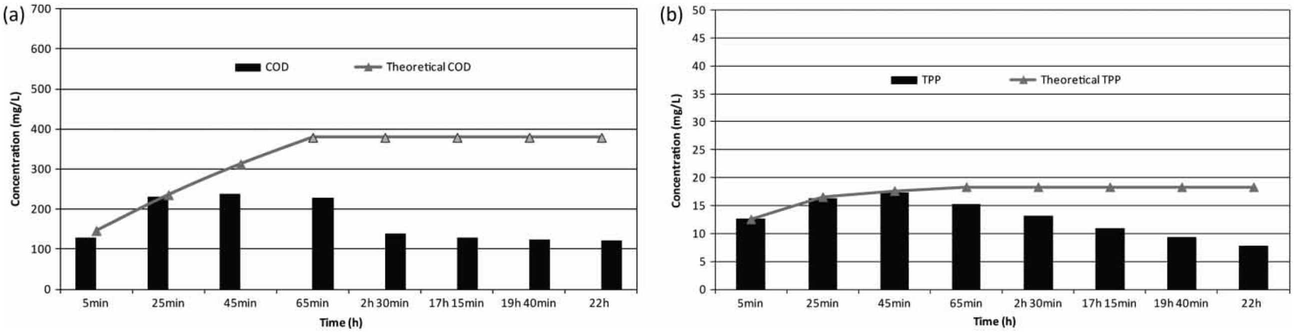

Figure 2 | COD (a) and TPP (b) concentration with time during a typical kinetic test of the first phase.

of the cycle, which likely corresponded to the inert soluble fraction. Theoretical values refer to the concentration which would have been measured in the absence of any reaction, i.e. due to dilution only. The TPP removal started only after the end of the fill phase and TPP concentration progressively decreased throughout the react phase. The initial lag phase in the biodegradation process was probably due to the inhibiting effect exerted by the high TPP concentration at the beginning of the phase, which caused the biological process removal to initially slow down. The average TPP removal efficiency measured throughout the entire cycle was 73%.

Second phase (DR = 1:25)

The results of the second experimental phase, shown by Figure 3, highlighted a higher COD removal efficiency with respect to the previous phase, which rapidly reached a stable value of about 90%. The increased influent load applied to the SBR significantly improved the performances in terms of COD removal. In the first phase, with the DR of 1:50, the very low organic load determined a slow removal kinetic with its rate being strictly dependent on the residual substrate concentration (pseudo-first order); furthermore, the reduced availability of substrate brought the biomass into an endogenous respiration state which led to its partial mineralization. In the second phase, instead, the higher substrate concentration in the reactor increased the removal rate; furthermore, the progressive acclimation of the biomass likely contributed to further accelerate the biodegradation process.

Figures 4(a) and (b) show the results of a typical kinetic test performed during the second phase of the study, in terms of COD and TPP, respectively. The TPP removal in this case was about 76%.

Third phase

During the third phase, the SBR was fed with the effluent from the AC and GAC adsorption treatment under the

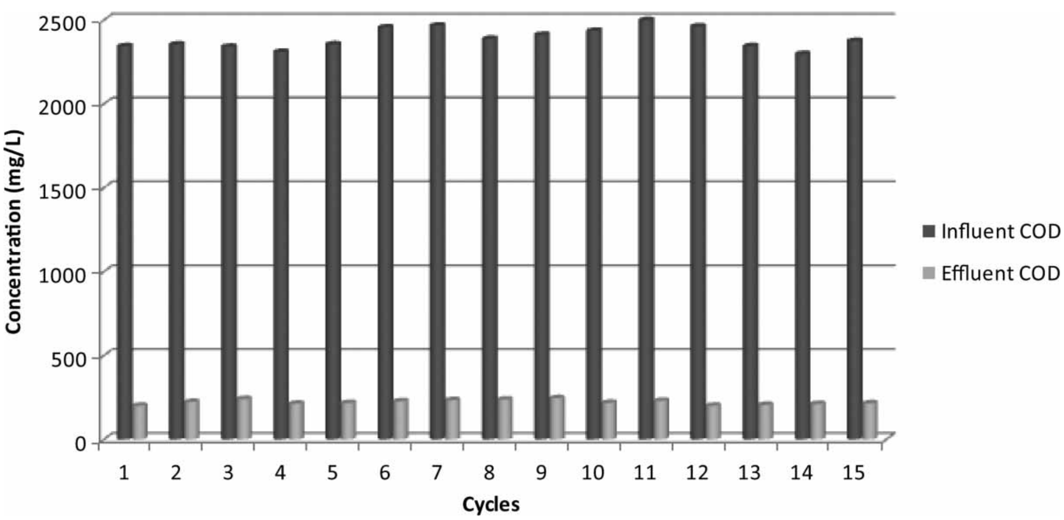

Figure 3 | Influent and effluent average COD concentrations during the second phase.

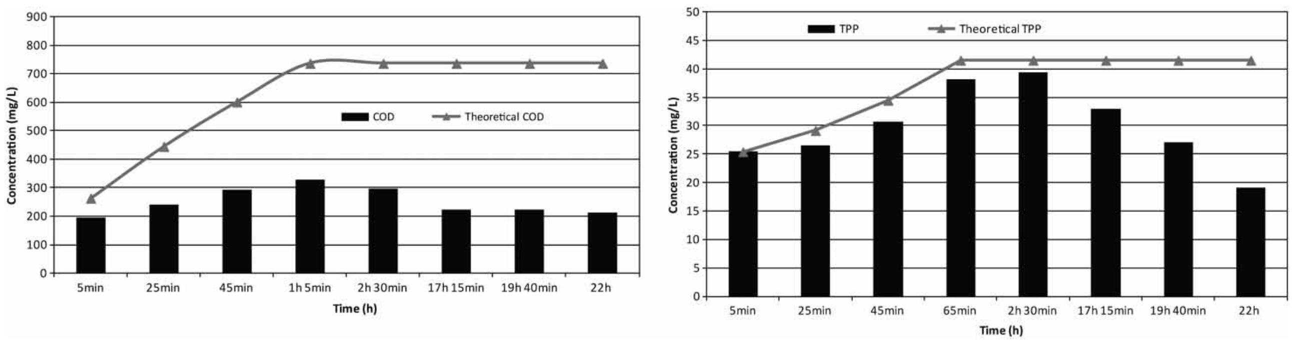

Figure 4 | COD (a) and TPP (b) concentration with time during a typical kinetic test of the second phase.

optimal conditions described in the methods section. The effluent was also diluted prior to being used to feed the SBR so as to achieve a similar total influent COD as used in the first phase. This value was also similar to that used in Chiavola *et al.* (2010) where the SBR was fed with the effluent from lime precipitation, so as to compare the effects of different chemical pre-treatments.

As shown in Figure 5, the effluent COD concentration from the SBR progressively increased during the first 8 cycles of operation and then it levelled off giving an average total COD removal efficiency of about 74%.

Figures 6(a) and (b) show the results of a typical kinetic test performed during the third phase of the study, in terms of COD and TPP, respectively. The COD biodegradation started immediately after the beginning of the cycle and proceeded continuously throughout the react phase. By contrast, TPP removal started only at the end of the fill phase.

These results are in a quite good agreement with those obtained in the first phase, when the SBR was fed with the raw diluted wastewater (DR 1:50) and the same influent organic loading.

However, with respect to the previous phase, the overall TPP removal efficiency showed a significant increase, reaching about 85%. This might be due to the removal of the higher molecular weight TPP compounds, known to be difficult to be biodegraded, achieved by the GAC adsorption. Furthermore, the long experimental run of the biological process in the SBR might have determined complete acclimation and selection of the microbial species which have developed the capability to biodegrade TPP compounds more efficiently.

Different results were achieved by the same authors (Chiavola *et al.* 2010) investigating SBR performances when fed with the effluent from lime precipitation. In that case, both the removal processes of COD and TPP did not show any significant improvement as compared to the efficiency observed when the SBR was fed with raw dOMWs.

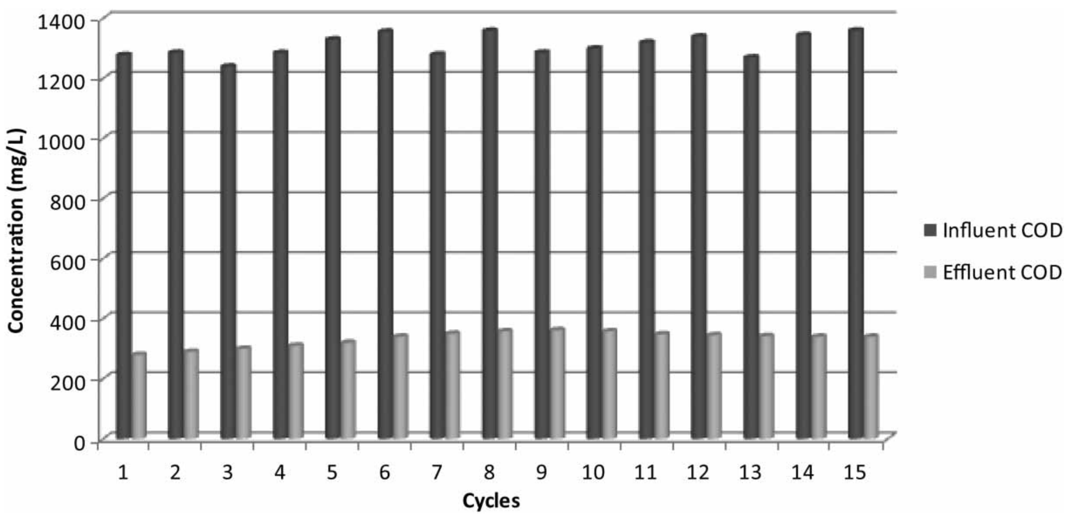

Figure 5 | Influent and effluent average COD concentrations during the third phase.

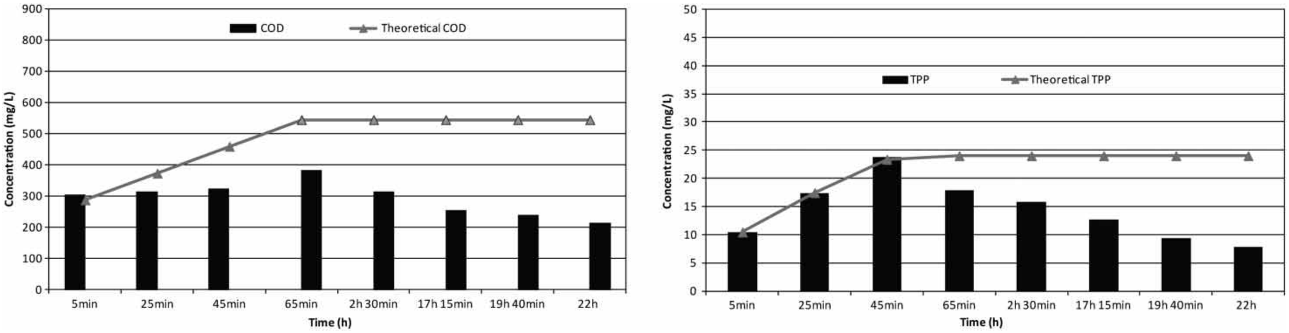

Figure 6 | COD (a) and TPP (b) concentration with time during a typical kinetic test of the third phase.

Table 4 | Results obtained during the experimental activity

Average removal efficiencies (%)	1st phase	2nd phase	3rd phase
COD	75	90	74
TPP	73	76	85

Table 4 lists the average results obtained in the different experimental phases of the present study.

CONCLUSIONS

The present study evaluated performances of a biological SBR process for the treatment of OMWs for different influent compositions. Better performances in terms of COD and TPP removals were achieved with raw dOMWs and at the higher influent organic loading (i.e., for the lowest DR of 1:25). The chemical–physical pre-treatment consisting of AC followed by GAC adsorption did not determine a significant improvement of the COD removal process; nonetheless, a higher TPP degradation was observed.

Based on the results obtained in both the present and the previous studies, it can be concluded that the more suitable treatment plant lay-out is represented by a SBR fed with raw dOMWs. This system avoids the technical and economic issues related to operating chemical–physical treatments, which are not fully justified based on the slight improvement of the biological process achievable. With the aim of implementing at the full-scale the SBR process herewith proposed, a combined treatment of different waste streams from the same mill (such as domestic sewages) along with the OMWs might be planned. This would allow adjustment of the influent load and characteristics so as to bring about an efficient biological process in the SBR plant.

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