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Research article

Evaluation of the treatability of a winery distillery (vinasse) wastewater by UASB, anoxic-aerobic UF-MBR and chemical precipitation/adsorption

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ABSTRACT

A multi-stage pilot-scale treatment cycle consisting of an Upflow Anaerobic Sludge Blanket reactor (UASB) followed by an anoxic-aerobic Ultra Filtration Membrane Bio Reactor (UF-MBR) and a post treatment based on chemical precipitation with lime or adsorption on Granular Activated Carbons (GAC), was applied in order to evaluate the treatment feasibility of a real winery distillery wastewater at laboratory and bench scale. The wastewater was classified as high strength with acidic pH (3.8), and concentrations of 44,600, 254, 604 and 660 mg/l for COD_{tot}, total nitrogen, total phosphorous and phenols, respectively. The UASB reactor was operated at Organic Loading Rates (OLR) in the range 3.0–11.5 $kgCOD_{tot}/m^3/d$ achieving treatment efficiency up to 97%, with an observed methane production of 340 L of CH_4/kgCOD. The MBR system was operated with an organic load in the range 0.070–0.185 kgCOD/kgVSS/d, achieving a removal up to 48%, 67% and 65% of the influent COD, total nitrogen and phenols, respectively. The combination of UASB and UF-MBR treatment units was not effective in phosphate and colour removal assigning to further chemical precipitation and adsorption processes, respectively, their complete removal in order to comply with legal standards for wastewater discharge. Subsequently, the optimization of the investigated treatment chain was assessed by applying a chemical precipitation step upstream and downstream the UASB reactor, and a related treatment unit cost assessment is presented in view of a further technological scale-up.

1. Introduction

Processes for wine production generate organic and inorganic pollution mostly associated with solid wastes and liquid effluents. The liquid effluents usually referred as "winery wastewater" are mainly originated in washing operations during grape harvesting, pressing and first fermentation phases of wine processing (Rodríguez-Chueca et al., 2017; Ioannou et al., 2015; Lucas et al., 2010; Mulidzi, 2010; Mosteo et al., 2007), as well as a result of the distillation process applied to wine processing residues (e.g. vinasses). As a consequence, volumes and pollution loads greatly vary over the year demanding that the treatment system must be versatile to face both the loading regimen and stream fluctuation (Bolzonella et al., 2010).

Winery wastewater contains large amounts of biodegradable organics in addition to relatively small concentrations of recalcitrant compounds such as polyphenols, organic acids and sugars and relatively low presence of solids and nutrients (Serrano et al., 2011; Braz et al., 2010). According to Andreottola et al. (2005) and Beck et al. (2005), the readily biodegradable COD represents the most relevant fraction of total COD with values ranging between 71.4% and 85%, respectively. The high percentage of this fraction is due to the prevalent presence of ethanol and, to a smaller extent, sugars and organic acids (Andreottola et al., 2009). The concentration of slowly biodegradable COD varies from 2.9% to 9.4% of total COD while the un-biodegradable soluble fraction resulted quite different in Andreottola et al. (2005) and Beck et al. (2005) probably due to the different approaches used for COD fractionation.

Nowadays, several winery wastewater treatment technologies are available and they involve, in most cases, the use of biological processes (Ioannou et al., 2015; Chai et al., 2014; Mulidzi, 2007; Thanikal et al., 2007; Brucculeri et al., 2005; Petruccioli et al., 2002) (see Table 1S, Supplementary material). Such processes ensure a significant removal of the organic content although the presence of recalcitrant compounds frequently makes the complete winery wastewater treatment impossible (Ioannou et al., 2015).

A common, simple and relatively low-cost solution may be represented by the co-treatment of municipal and winery wastewater in conventional activated sludge processes (Andreottola et al., 2009; Fernández et al., 2007; Pathe et al., 2002). Possible problems such as bulking phenomena or decrease of sludge settleability suggested the proposition of dedicated plant including aerobic/anoxic processes us-

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ing suspended biomass (activated sludge, membrane bioreactors, MBR, sequencing batch reactors, SBR), aerobic biofilm systems (conventional rotating biological contactors, RBC, innovative fixed bed biofilm reactors, FBBR, or moving bed biofilm reactors, MBBR, SBBR), anaerobic processes using suspended biomass (conventional anaerobic digesters or anaerobic sequencing batch reactors, ASBR), anaerobic biofilm systems using granules (Upflow Anaerobic Sludge Blanket, UASB), hybrid systems (Up flow Sludge Blanket Filter, USBF) (Moletta, 2005; Andreottola et al., 1998) and constructed wetlands (Andreottola et al., 2009).

The only anaerobic processes, many of which summarized in Table 1S (see Supplementary material), are not able to ensure compliance with final discharge standards set by the law. Consequently, they are generally used as pre-treatments thus requiring additional treatments downstream.

Membrane technologies, combined with conventional activated sludge-based processes, have been extensively studied over the years. They represent an interesting solution especially for small companies as highlighted in Bolzonella et al. (2010).

Other technological solutions are based on the combination of different processes, even in a single reactor, as already experienced in Andreottola et al. (2005), Farina et al. (2004), Petropoulos et al. (2016) and Molina et al. (2007), Akunna and Clark (2000), Basset et al. (2016) and Andreottola et al. (2002) with reference to FBBR, ASBR, hybrid USBF, GRABR, AnMBR and SBBR, respectively. However, organic matter removal is not the only task for winery wastewater treatment, since nitrogen, phosphorous compounds, and colour also need to be tackled following a multiple objectives approach (Ioannou et al., 2015).

In this regard, literature shows several examples such as Amaral-Silva et al. (2016) who integrated ferric coagulation, Fenton reaction and activated sludge for phosphorus removal. De Gisi et al. (2016) highlighted the use of granular activated carbons (GAC) as well as alternatively low-cost sorbents for colour removal from different wastewater. Regarding membrane technologies, Bolzonella et al. (2010) adopted a MBR system based on microfiltration (MF) for the biological activated sludge phase, while real cases based on the use of ultrafiltration MBR (UF-MBR), are rather limited. Sheldon and Erdogan (2016) have recently applied an UF-MBR for soft drink production wastewater, with different characteristics respect to the winery ones.

In this context, with the intent of strengthening the current knowledge, the article deals with the verification of the treatability of a real winery distillery (vinasse) wastewater through the application of a treatment cycle consisting in UASB, anoxic-aerobic UF-MBR, and post treatment steps (chemical precipitation with lime or alternatively GAC adsorption), in order to comply with the discharge standards set by the Italian and European regulations. More specifically, the following sub-goals have been investigated: (i) Identification of the optimal operational set-up and related criticalities of the UASB reactor as well as verification of the process efficiency with reference to high organic loading rates (OLR) in the range 6.2–11.5 kg $COD/m^3/d$; (ii) Identification of the optimal operational set-up and related criticalities of the anoxic-aerobic UF-MBR system, assessing the individual contributions referable to the biological process and the membrane separation process; (iii) Identification of the main process parameters of chemical precipitation with lime and GAC adsorption, intended as post-treatment solutions; (iv) Optimization of the treatment cycle by using chemical precipitation with lime upstream and downstream the UASB treatment unit.

2. Materials and methods

2.1. Experimental plan

The experimental trials were carried out on a real winery wastewater. A total amount of about 2 m^3 was collected from a distillery located in South Italy (Sicily) and, after a preliminary characterization, the inlet wastewater was properly stored into a stirred and refrigerated (2–4 °C) tank, also used as feeding unit.

The pilot scale tests involved three treatment steps arranged in series, as following reported (see Fig. 1a): (i) anaerobic treatment; (ii) anoxic-aerobic treatment; (iii) chemical and physical post-treatment. Regarding the first treatment step, an UASB reactor was used with the intent of maximizing the biogas production to be used for energy purposes. As second treatment step, an anoxic-aerobic MBR system

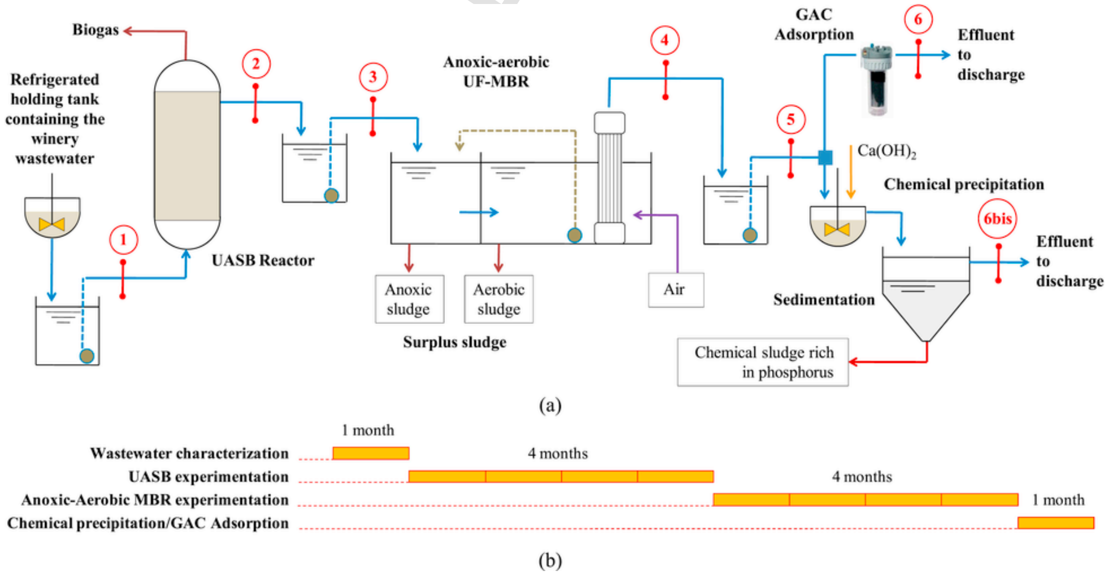


Fig. 1. Experimental treatment scheme highlighting the principal sections (in red and numbered) for material balances purposes (a); Time schedule of the individual processes investigated (b). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

equipped with an ultrafiltration membrane was realized and fed with the clarified fraction of the UASB effluent (digestate), with the main scope to provide a residual COD removal as well as a reduction of N and P content. The third step consisted in two separate treatment options: chemical precipitation based on the use of lime, and GAC adsorption. The main scope of such treatments was the residual COD, phosphorous and colour removal in order to comply with the effluent standards for wastewater discharge set by the European (Directive 91/271/EEC) and Italian Law (Legislative Decree No. 152/2006).

Each treatment step was operated separately, the effluent of each treatment unit being stored and refrigerated in order to be fed to the downstream one. At first, the UASB process was operated for 4 months, and the effluent was stored in a refrigerated tank during last 3 operation weeks before being fed to the MBR section; the MBR was operated for 4 months and the effluent was collected and stored during last 2 months of operation and then used for further chemical treatments. The whole experimental tests were carried out for 10 months and structured according to the time schedule as shown in Fig. 1b.

2.2. Inlet wastewater characterization

The real wastewater consists of vinasse resulting from the grape distillation process. Wastewater was firstly characterized by means of chemical-physical analyses, as reported in Table 1, showing an acidic pH and a high organic matter concentration, with an almost all soluble COD including a recalcitrant fraction which is, at least in part (e.g. tannic content), responsible of the dark colour as discussed hereinafter.

2.3. Reactor set up

The bench scale UASB system consists in a cylindrical reactor made of Plexiglas with an approximate volume of 24 L (H = 75 cm, D = 22 cm); a series of manual ball valves in stainless steel have been inserted on its surface in order to allow (i) the removal of the microbial sludge samples, (ii) the release of the biogas produced in the UASB reactor as well as (iii) the output of the recirculation flow. The sampling point of the recirculation flow was installed in correspondence of the three phase separator. The recirculation flow was realized by means of a peristaltic pump, with the scope of increasing the ascent rate of the liquid in the reactor and to promote of the microbial bed and influent mixing. Furthermore, both the feed points of the inlet wastewater and of the soda solution for pH regulation inside the reactor were realized on the delivery pipe. For this purpose, on the same line, a glass pH probe connected via a measuring and control system to the piston pump was positioned. When the probe detects a value of pH lower than the predetermined set point, the pump is activated and feeds soda. Considering the inlet wastewater, the feeding flow enters from the bottom of the reactor so as to allow the wastewater to pass through the whole thickness of the microbial bed, participating, thereby, to its mixing. A volumetric pump (Hydra EM24) was used to fill the reactor. Agitation was provided by recycling the mixed liquor from an intake below the inert support and injecting it upwards from the bottom of the reactor. The produced biogas was measured by an Elkro gas (BK-P) meter. Finally, the effluent is discharged from the top of the reactor by means of an overflow weir. The entire UASB reactor was placed inside a thermostatically regulated heating cable that allows operating at a constant temperature of 37 °C.

Table 1
Characteristics of the raw winery distillery wastewater.

Parameter	Unit	Average values	St. Dev
pH	–	3.8	±0.05
Conductivity	mS/cm	8.3	±0.09
Total Solids (TS)	g/l	29	±0.97
Total Volatile Solids (TVS)	g/l	18.8	±0.60
Total Suspended Solids (TSS)	g/l	0.48	±0.02
Volatile Suspended Solids (VSS)	g/l	0.39	±0.01
Total COD (COD_{tot})	mg/l	44,600	±94.5
Soluble COD (sCOD)	mg/l	44,000	±51.0
Total Nitrogen (TN)	mgN/l	254	±26.0
Ammonia Nitrogen (NH_4^+)	mgN-NH_4^+/l	135	±10.0
Total Phosphorous (TP)	mg/l	604	±29.01
Phosphates (P-PO_4)	mg/l	446	±9.5
Total phenols	mg/l	660	±11.53
Total Volatile Fatty Acids (VFA)	mg/l	3300	±66.04
Sulphates (SO_4^{2-})	mg/l	44.7	±1.76
Chlorides (Cl^-)	mg/l	128.8	±6.96
Colour	–	Dark brown	–

The working volumes of the anoxic and aerobic MBR compartments were 0.85 and 1.0 L, respectively. The system, realized in Plexiglas, is constituted by two vessels separated by a polyvinylchloride septum. The inlet wastewater is fed into the denitrification compartment, equipped with a mechanical stirring system. The internal recycle was carried out using a peristaltic pump (Watson Marlow 403U/R1) at a constant flow rate of 5.0 ml/min for the entire duration of the study. A second peristaltic pump (Watson Marlow 401U/D1), controlled by a level sensor in the reactor, was used for reactor feeding. A hollow fibre membrane module (ZW1, Zenon, Italy) with characteristics reported in Table 2S (data from the supplier, see Supplementary material), was immersed into the aerobic compartment. Membrane filtration was carried out using a programmable piston pump (Ismatec, Cole-Parmer, USA) whereas aeration was obtained using a blower with a constant flow at approx 80 L/h. The system operated inside a thermostatically regulated heating cable at a constant temperature of 20 °C.

The chemical precipitation treatment was performed by means of the Jar Test apparatus. Phosphorus removal was evaluated through lime-based precipitation. Trial tests consisted in a first step aimed at defining the most effective dosage by adding increasing amounts of chemicals (as to realize concentrations from 2.0 to 8.0 g $Ca(OH)_2$/l) with a constant reaction time of 1 min, a mixing speed rate of 300 rpm and measuring the pollutants concentration (Total phosphorous, phosphorus orthophosphate and COD), in the supernatant. Once identified the optimal dosage with the application of the system optimization methodology described in literature (De Gisi et al., 2014; De Feo et al., 2013), different reaction times of 1, 5, 10 and 20 min have been tested, maintaining all the other operating conditions as constant. After settling, the samples were centrifuged and then measured by spectrophotometric techniques after 5, 7 and 10 d contact time.

The GAC adsorption tests consisted in the arrangement of an activated carbon contact bed (84.5 g dry weight) in a Buchner filter, which was put in contact with a slow sample flow of the effluent to be treated. Samples were then measured by spectrophotometric techniques.

2.4. Sampling, analyses and operating conditions for the biological processes during start-up and regime

The operation of the UASB reactor was monitored over four months as shown in Fig. 1b. Regularly, at least on weekly basis, samples were taken at feed and treated effluent, while periodically, according to specific experimental needs, track studies to monitor the trends of filtered COD, VFA (Volatile Fatty Acids), TSS (Total Suspended Solids), pH and alkalinity within a cycle treatment were performed. Total Solids (TS), Volatile Solids (VS), Total (TSS) and Volatile Suspended Solids (VSS), ammonia nitrogen ($N\text{-}NH_4^+$), were regularly performed for the untreated and treated effluents according to the Standard Methods (Standard Methods, 1995). Monovalent anions were analysed using a HPIC (Dionex 5000i). Total alkalinity (TA) was measured by titration at pH 3.8. VFA were determined, on filtered 0.45 μm samples, by gas chromatography using a DANI 8510 GC equipped with a FID detector. Total and filtered (0.45 μm) COD was analysed by Dr. Lange kit. The sludge sampled from the reactor was observed by a phase-contrast light microscopy (Jenalumar A/D contrast light microscope, 1000× magnification) in bright field phase contrast, Nomarski interferential contrast and brield field. All parameters (COD, Total Nitrogen and Ammonia, Phenols) were performed with a minimum frequency of one week in order to monitor the performances of the anaerobic digestion process and the amount of biogas produced in the reactor as well as its quality, meant in terms of percentage of methane content. The amount of biogas was daily compared to the expected production in turn evaluated with the following relationship (Metcalf and Eddy, 2003):

$$\text{Expected biogas} = [(COD_{IN} - COD_{OUT}) \cdot q_{IN} \cdot Y] / (\%CH_4) \qquad (1)$$

where:

- Expected biogas = production of expected biogas, in L;
- COD_{IN}, COD_{OUT} = inlet and outlet values of COD, in g/L;
- q_{IN} = volumetric input flow rate, in L;
- Y = specific yield (theoretical) of COD conversion into methane, in L of CH_4 per gram of COD, assumed as 350 L CH_4/kg COD for wastewater (Metcalf and Eddy, 2003);
- % CH_4 = percentage of methane in the biogas produced.

The percentage of methane was controlled by gas-chromatography with a 2–3 weeks frequency in order to assess the specific heat of the generated biogas. The reactor was started with anaerobic biomass taken from a real granular type digester operating on the processing of fruit waste, whose initial characteristics are reported in Table 3S (see Supplementary Material). On a total volume of 24 L of the experimental reactor, about one third was filled with the fresh granular sludge, while the remaining part with tap water, obtaining, in this way, an average sludge concentration (on the whole reactor volume) of about 15 g/L. Subsequently, the system was launched by providing, during the first week, a feeding for about 7 h per day, so as to realize an OLR of 1.0 kg COD/m^3/d, to be considered as very low if compared to the typical values applied for UASB-type plants (5–15 kg COD/m^3/d) (Andreottola et al., 2009). In this way, the acclimatization of the microbial biomass was facilitated. After the first week, the continuous feed was switched starting from a daily OLR of about 3 kg COD/m^3/d, corresponding to a 16-days hydraulic retention time (HRT). The feed flow rate was progressively increased to reach the load of 11.6 kg COD/m^3/d, corresponding to a 4 days HRT. The pH inside the reactor was maintained in neutral field setting the control system to a threshold of 6.7. For the pH adjustment it was first used soda 0.05 M and then, as to limit the dilution effect, a soda solution prepared with the same wastewater. However, the operating pH values have always been included in the range 7.3–8.0.

The anoxic-aerobic MBR system operation was monitored over four months (as in the time schedule reported in Fig. 1b). A full characterization (TSS, VSS, COD, TN, $N\text{-}NH_4$, $N\text{-}NO_3^-$ $N\text{-}NO_2^-$, $P\text{-}PO_4$, Cl^-, SO_4^{-2}, total phenols, colour) was provided at least on weekly basis in MBR influent and effluent samples in order to monitor the overall treatment performance, while specific parameters (TSS, sCOD, $N\text{-}NO_3^-$ $N\text{-}NO_2^-$) were performed in both anoxic and aerobic compartments in order to monitor the progress of nitrification and denitrification processes. The evaluation of ammonia nitrogen concentration in both compartments was not provided because of the intense colouration of the wastewater and the reduced reaction volumes, which did not allow the determination either by spectrophotometry or after distillation of the sample. The colour of the effluent was monitored using spectrophotometric scans and compared with the input in order to verify the effectiveness of the membrane filtration treatment. The reactor was started up with aerobic biomass taken from a municipal wastewater treatment plant, with the characteristics reported in Table 3S (see Supplementary Material). Firstly, a feeding of 0.043 L/h, corresponding to an organic loading rate (OLR) of 0.185 kg COD/kg VSS, was considered in order to provide a HRT of about 2 days. Subsequently, as better specified hereinafter, the observed trend led to the gradual reduction of the influent flow rate with a subsequent reduction of the organic loading rate (OLR) as visible in Table 4S (see Supplementary Material). Nitrates recirculation flow rate (from the aerobic to the anoxic compartment) was kept on the value of 0.024 L/h. During the experimentation, the surplus sludge from the reactor was not extracted so as to allow the optimal biomass growth up to the achievement of desired working concentrations (6–8 gTSS/l). The pH and the dissolved oxygen in both biological compartments were monitored using portable probes; the aeration in the nitrifying unit was from time to time adjusted so as to maintain a dissolved oxygen concentration (DO) in the range 5–7 mg/l, whereas in the anoxic compartment the DO was adjusted by changing the recirculation flow rate so as to maintain a value lower than 0.5 mg/l. The pH was maintained in the range of 7–9 in both units. To reduce fouling, the membrane device was operated alternating cycles of 3 and 2 min of filtration and relaxation, respectively (no back wash). The transmembrane pressure (TMP) was monitored using a digital gauge (Cole-Parmer, USA). A mechanical stirrer (RZR, Heidolph, Italy) was used for mixing the anoxic tank. Instead, a homemade wet gasmeter was used for biogas production monitoring. Sludge withdrawal was performed manually in order to control the SRT at approximately 80–100 days.

With reference to the chemical precipitation and GAC adsorption, total phosphorus (TP), phosphate, COD and colour were measured on effluent samples according to the standard methods (Standard Methods, 1995).

3. Results and discussion

3.1. UASB process

The UASB system has been started with a load of about 3.0 kg COD/m^3/d, gradually increased up to 11.6 kg COD/m^3/d. The results in terms of percentage removal are reported in Fig. 2a.

COD removal rate was roughly constant and equal to 95%, as an evidence that almost all of the organic compounds in the vinasse wastewater are relatively simple to degrade. In particular, the COD removal was 97.5, 97.2 and 96.0% in correspondence of OLR values of 3.0, 4.5 and 11.5 kg COD/m^3/d, respectively (Fig. 2a). Such results are in line with Andreottola et al. (2009) who highlights COD percentage removals in the range 80–97% for an UASB process working with OLR values in the range 5–15 kg COD/m^3/d.

As a result of the UASB process, the ammonia nitrogen showed an average increase of about 18–20% (Fig. 2a), which highlights that the UASB treatment provided an almost complete removal of the organic nitrogen due to the adsorption into the sludge blanket (as evidenced by the increased total and volatile solids content in the anaer-

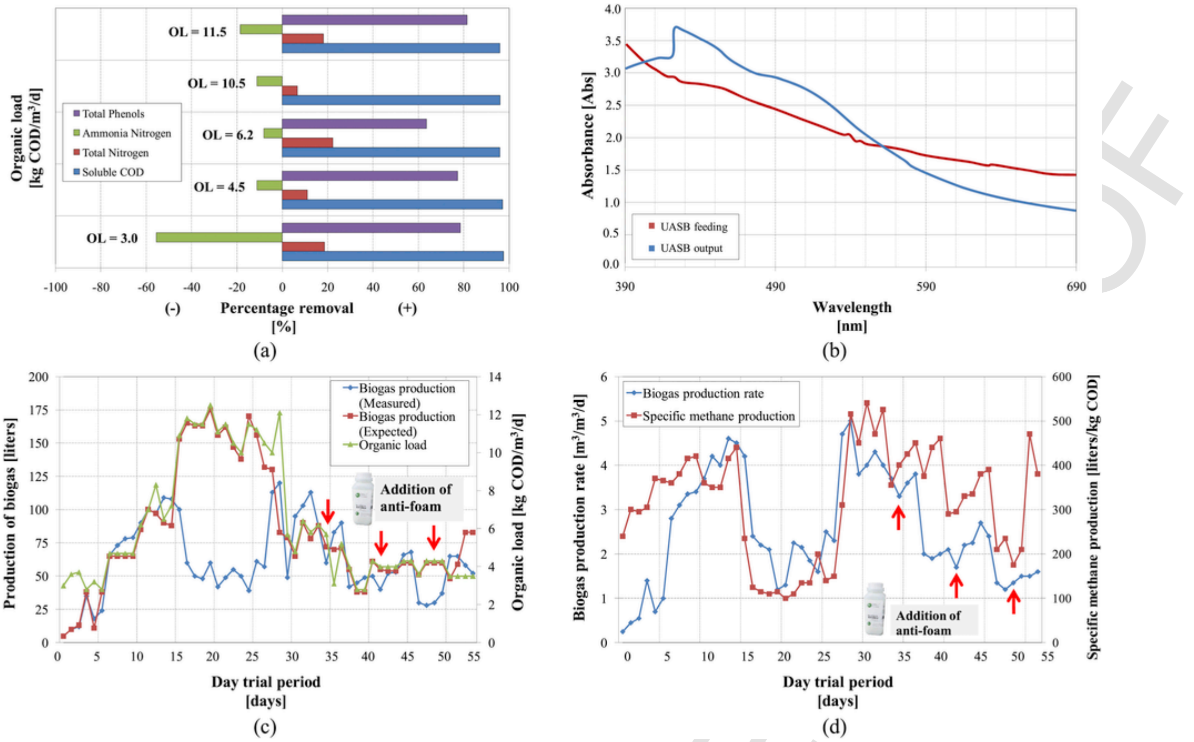


Fig. 2. UASB treatment results: (a) Performance in terms of pollutants removal; (b) Spectrophotometric scanning of the UASB feeding and effluent; (c) Comparison between the measured and expected biogas productions varying the organic load; (d) Biogas production rate and specific methane production during the experimentation.

obic sludge after the experimental trials) coupled to the ammonification process taking place in the reactor. A certain TN removal was observed with an average value of 10.6%, to be considered as quite physiological and due to a secondary ammonia stripping effect favoured by biogas production, especially during the experimental runs when operating pH values of 8–8.5 were measured in the reactor.

Concerning other parameters, total phenols removal was on average of 75.0% with lower values of about 65% in correspondence of an OLR of 6.2 kg COD/m^3/d. Similar results were obtained by Hussain et al. (2008) who, working with an OLR in the range of 4.0–4.1 kg COD/m^3/d, showed a high percentage of phenol degradation (about 90%) as well as the consequent transformation of phenols into methane.

In overall, the optimal OLR condition has to be considered that corresponding to 4.5 kg COD/m^3/d which allows relatively short retention times (HRT = 6 days), good treatment performances and low foam appearance in the reactor, as discussed herein. Despite this, the concentrations of the main parameters in the effluent did not comply with the effluent standards set by the Italian Law, with specific reference to the average effluent concentrations of COD, TN, N-NH$_4^+$ and total phenols (Table 2). The observed results were in line with Andreottola et al. (2009) who highlighted that the UASB treatment applied to winery wastewater is not able to reach the effluent standard limits given by the Italian Law.

The UASB process has consequently to be considered as a pre-treatment unit for winery wastewater treatment, according to several literature examples of biological-based pre-treatments of agro-food wastewater, such as in Sheldon and Erdogan (2016), De Gisi et al. (2013) and Buntner et al. (2013) in the cases of soft drink industry wastewater, biodiesel production wastewater and dairy wastewater, respectively. Moreover, the UASB effluent was characterized by an intense dark-orange colour as evidenced by the spectrophotometric scanning relayed to the inlet and outlet UASB wastewater (Fig. 2b).

Table 2
Characteristics of the winery distillery wastewater downstream to UASB reactor.

Organic load [kgCOD/m^3/d]	Average values and standard deviation of the main parameters											
	sCOD [mg/l]	TSS [g/l]	VSS [g/l]	TN [mg/l]		N-NH$_4^+$ [mg/l]		Total Phenols [mg/l]				
3.0	1100.0	±55.2	0.42	±0.03	0.28	±0.03	220.0	±56.0	210.0	±51.4	142.0	±8.7
4.5	1260.0	±54.3	0.90	±0.06	0.78	±0.05	240.0	±58.5	150.0	±38.6	150.0	±8.7
6.2	1780.0	±72.0	0.86	±0.05	0.72	±0.04	210.0	±55.1	146.0	±36.2	240.0	±13.7
10.5	1720.0	±67.0	1.29	±0.07	1.05	±0.05	252.0	±64.3	105.0	±27.5	n.a.[a]	–
11.5	1790.0	±69.0	1.47	±0.08	1.12	±0.04	221.0	±59.9	160.0	±41.3	122.0	±7.1
Discharge limit standards[b]	160.0	–	0.08	–	–	–	15.0	–	15.0	–	0.5	–

[a] n.a. = not available.

[b] Italian Law (D. Lgs. 152/2006).

Even this aspect was clearly reported in literature: Ioannou et al. (2015) highlighted the possibility to use a chemical post-treatment based on Fenton's oxidation in order to remove colour from a UASB reactor treating winery wastewater.

With reference to UASB process performance in terms of biogas production, the amount of produced biogas was detected during the entire experiment in order to evaluate methane specific production (in terms of litres of methane produced per kg of COD removed by the system) and the biogas production rate (in terms of m^3 of biogas/m^3/d), to be compared with the biogas expected production as to evaluate the anaerobic degradability of the inlet wastewater and, consequently, the achievable energy recovery yields. In the first case, the values were compared with the typical value of 350 L CH_4/kg COD under standard temperature and pressure conditions (according to the relation 1, Materials and methods section); in the second case, the biogas production rate was compared with the typical range of 1.5–2.9 as reported in Fernandes et al. (2010).

The observed and theoretical biogas productions were almost coincident with OLR values lower than 8 kg COD/m^3/d, with measured specific productions in the range of 300–400 L CH_4/kg COD and an average value of 320 L CH_4/kg COD. The biogas production rate amounted to an average value of 2.6 m^3 biogas/m^3/d, with the highest values observed in correspondence of an OLR of about 8.5 (although higher values have been reported with OLR equal to 11). The average methane content in the biogas was 60%. A further OLR increase, up to 11 kg COD/m^3/d, entailed a substantial decrease of the observed biogas production (Fig. 2c and d, from day 15 to day 30). This negative performance was concomitant with the detection, inside the reactor, of persistent whitish foam that caused significant pressure oscillations as well as frequent overflows (See Fig. 1S, Supplementary material), with a consequent instability of the biological processes.

The optical microscope observations of foam samples (Fig. 3) allowed determining the biological nature of the foam, due to the presence of large quantities of Yeast-like microorganisms and other anaerobic filamentous microorganisms that favoured the increase of the surface tension of the medium and, consequently, the foam production. The microscopic investigation showed the presence of significant quantities of Methanosarcina-like microorganisms and Yeast-like microorganism's colonies, inducing to correlate the foam growth to the application of the maximum OLR (11 kg COD/m^3/d) which led to the imbalance between the microbial populations and the yeast in the reactor. Similar problems were encountered by Mendes et al. (2006) and Gomes et al. (2011). However, in order to operate with high OLR as in our case (11 kg COD/m^3/d), they implemented a pre-treatment of the inlet wastewater consisting in hydrolysis (Mendes et al., 2006) coupled to enzymatic pre-treatments (Gomes et al., 2011).

Following these evidences, the OLR was preliminarily brought back at 5–6 kg COD/m^3/d and, subsequently, at 4 kg COD/m^3/d. Nevertheless, the only result was the decrease of the foam growing rate, which was inversely proportional to the applied organic load. Therefore, polysiloxaneanti-foam (174 g/l) was directly injected on a weekly basis in the aqueous solution (1:75,000, 5 ml) and in correspondence of the foam, allowing the increase of biogas production according to the expected values.

The characteristics of the biological sludge after 55 days of treatment showed (see Supplementary Material, Table 5S) the strongly granular nature of the sludge which allowed an easier solid/liquid separation as well as low suspended solids in the effluent, in line with similar experimental tests (Lu et al., 2015).

Although the excellent performance in terms of organic matter removal, the UASB effluent was not able to meet the Italian standards for the discharge in superficial water bodies (Table 2), thus requiring additional treatments herein discussed.

3.2. Anoxic-aerobic UF-MBR processes

The anoxic-aerobic UF-MBR system was started with an initial load of 0.185 kg COD/kgVSS/d, which was gradually decreased according to the trends observed during system operation. The results in terms of average characteristics of the MBR effluent in correspon-

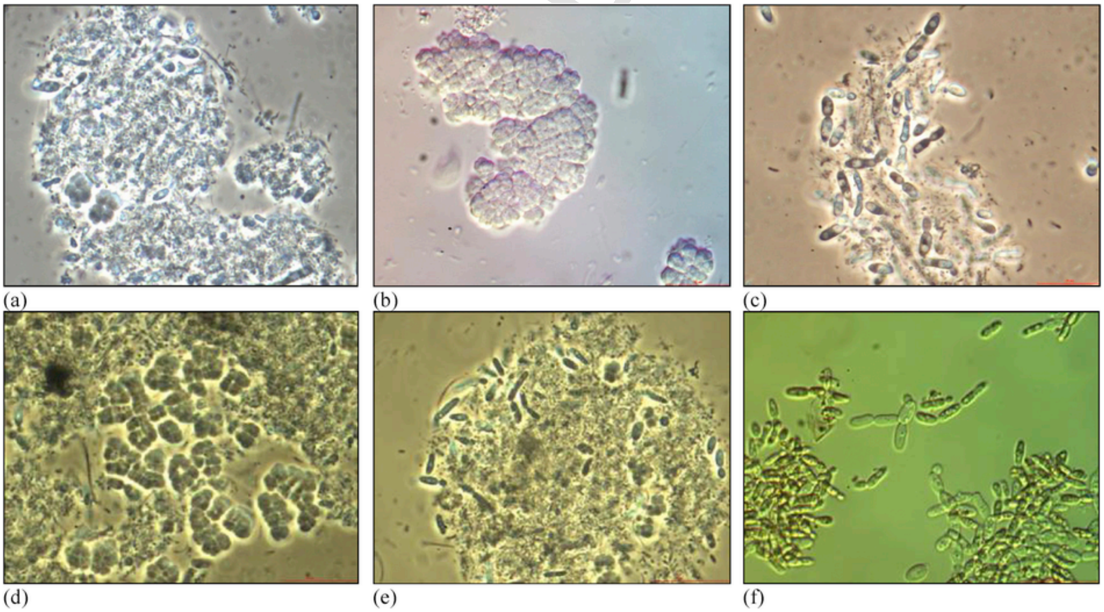


Fig. 3. Optic microscope observations of foam and sludge sampled from the UASB reactor and in fresh distillery wastewater, in interdifferential contrast (DIK, 1000× magnification): (a) Methanosarcina-like microorganisms colonies and presence of Yeast-like microorganisms in foam sample; detail of Methanosarcina-like microorganisms colonies (b) and Yeast-like microorganisms colonies (c) in foam sample; (d) Methanosarcina-like microorganisms and (e) Yeast-like microorganisms in sludge sample; (f) Yeast-like microorganisms in fresh influent wastewater.

dence of each organic loading condition applied as well as in terms of percentage removal, are reported in Table 3 and Fig. 4a, respectively.

The first run (OLR = 0.185 kg COD/kg VSS/d) was characterized by COD, TN and N-NH_4^+ removals of 48.0, 67.8 and 81.0%, respectively. This run, as discussed below, represented the best operational set up for the biological processes during the entire investigation. The second run (OLR = 0.100 kg COD/kg VSS/d) was characterized by COD, TN and N-NH_4^+ removals of 63.1, 30.0 and 86.4%, respectively. Instead, removals of 58.8, 29.1 and 90.0% for COD, TN and N-NH_4^+, respectively, were observed in the third run (OLR = 0.07 kg COD/kg VSS/d). Considering the COD removal, the findings were lower than those experienced by Bolzonella et al. (2010), Valderrama et al. (2012) and Sheldon and Erdogan (2016), with COD removals of 94, 97 and 90%, respectively. In terms of TN removal, results obtained during the first run were higher than that reported in Bolzonella et al. (2010) (54%), mostly related to a higher nitrification efficiency allowed by the modified Ludzack-Ettinger (MLE) process configuration. The performance achieved in terms of N-NH_4^+ removal during the first run was in line with Sheldon and Erdogan (2016), who obtained a removal rate of 88.1%. With reference to colour removal, Fig. 4b shows the results by comparing the absorbance detected on (i) MBR influent and effluent samples, and (ii) on the MBR influent sample previously filtered (indicated as MBR filtered influent). A decrease of absorbance in the effluent compared to the influent wastewater at all the wavelengths was observed, while the coincidence between the absorbance curves obtained by analysing the inlet filtered wastewater and the MBR effluent shows how colour removal was mostly due to the filtration effect of the membrane, with a very limited contribution of the biological treatment stage. Most probably, this colouration was due to the presence of a particular class of compounds, known as melanoidins, originating from the Maillard reaction involving residual sugar and amine compounds during the distillation step, as found by Nakajima-Kambe et al. (1999), Manisankar et al. (2004) and Shayegana et al. (2005). Melanoidins compounds are not degradable by traditional biological treatments (Ioannou et al., 2015), representing a relevant amount of non-biodegradable COD fraction. As above, it justifies the lowest performance, in terms of COD removal, compared to that obtained from Sheldon and Erdogan (2016). Considering the other parameters, a percentage increase was observed for sulphates (+200%), chlorides (+23%) and phosphates (+4.4%), while total phenols have undergone an average percentage reduction of 65% (Fig. 4a).

Table 3
Characteristics of winery distillery wastewater downstream to the anoxic-aerobic UF-MBR process (Average values and standard deviation).

Parameter	Unit	Organic loading rate (OLR) [kg COD/kg VSS/d]	Discharge standards[b]		
		0.185	0.100	0.070	
sCOD	mg/l	720.0 (±36.0)	510.0 (±35.3)	570.0 (±39.0)	160
Total Nitrogen (TN)	mg/l	73.0 (±22.2)	158.9 (±56.0)	161.0 (±52.3)	15
Ammonia Nitrogen (N-NH_4^+)	mg/l	21.0 (±7.0)	15.0 (±5.5)	10.0 (±3.8)	15
Nitric Nitrogen (N-NO_3^-)	mg/l	n.a.[a]	11.9 (±4.2)	121.0 (±47.0)	20.0
Nitrous Nitrogen (N-NO_2^-)	mg/l	3.0 (±1.1)	97.0 (±32.0)	n.a.[a]	0.6
Total Phenols	mg/l	55.0 (±6.0)	60.0 (±7.0)	55.0 (±6.0)	0.5
Sulphates (SO_4^{2-})	mg/l	–	200.0 (±21.2)	70.0 (±10.4)	1000
Phosphates (P-PO_4)	mg/l	–	150.0 (±17.2)	154.0 (±18.4)	0
Chlorides (Cl^-)	mg/l	–	160.0 (±19.0)	157.0 (±18.2)	1200
Colour	–	1:75 Run 1	1:75 Run 2	1:75 Run 3	1:20

[a] n.a. = not available.

[b] Italian Law (D. Lgs. 152/2006).

The progressive OLR reduction from 0.185 to 0.07 kg COD/kg VSS/d was adopted as a consequence of the progressive deterioration of denitrification and nitrification processes, observed from the 30th day of the experimentation, resulting in a TN removal decrease (from 67.8 to 30.0%) and a progressive accumulation of dissolved COD in the aerobic compartment. Fig. 4c–g aim at showing the specific trends of the biological processes and the related operation of the filtration process. In detail, Fig. 4c shows the trend of COD concentrations in both compartments and in MBR effluent, highlighting the progressive soluble COD accumulation in the aerobic compartment, which values exceeded the total COD measured in the influent stream (from day 20). Such occurrence was probably related to a retaining action of the UF-membrane in respect of soluble non-biodegradable COD fractions, which, therefore, were gradually accumulated in the aerobic vessel.

Similarly, Fig. 4d shows the trend of nitric (N-NO_3^-) and nitrous (N-NO_2^-) nitrogen concentrations in the inlet wastewater as well as in the aerobic and anoxic compartments. The observed trends show that nitrification and denitrification processes initially proceeded appropriately during the first run, with a TN removal efficiency almost equal to 70% (see Fig. 4a); from day 25, a progressive accumulation of nitrites occurred in the aerobic compartment (see red lines, Fig. 4d) and, later, in the anoxic one (see blue lines, Fig. 4d), as a result of partial nitrification and denitrification processes. The lack of ammonia nitrogen observations in both compartments (as explained in Par. 2.4) did not allow further considerations on specific process kinetics.

Such decrease of performance has probably to be ascribed to a progressive recalcitrant compounds accumulation, e.g. phenols, in the aerobic compartment (and, later, in the anoxic one) caused by the selective retention provided by the UF-membrane, resulting in the gradual inhibition of nitrification and denitrification processes. Although no direct phenol detection was provided in the biological compartments, a moderate retention effect on phenols given by the UF membrane is likely to be expected, according to Acero et al. (2005), who observed an apparent rejection coefficient to the Gallic Acid of more than 20% in experiments carried out with different UF membranes modules. The consequent progressive increase of phenols concentration in the aerobic vessel may represent the main cause of the inhibition to nitrification, according to Amor et al. (2005) who in aerobic batch assays observed an inhibitory effect to the nitrification process at phenol concentrations ranging from 100 to 2500 mg/l, leading to the accumulation of nitrite and ammonium in the reactor.

Due to the low membrane fluxes applied, no severe fouling was observed during the experiments.

The trend of the transmembrane pressure (TMP) and the specific permeate flow (J_P) during the entire experiment are reported, respectively, in Fig. 4e and f. Membrane washing operations, represented with vertical lines, produced a lowering of the TMP pressure and at the same time an increase of the permeate flow. During the tests, the average TMP applied (see TMP filtration, Fig. 4e) was 214.7 mbar while the average value of the J_P flow was 0.385 L/m^2/h (see Permeate flux, Fig. 4f).

With reference to the third run, the accumulation of inhibitory substances in the two vessels slightly raised the pH up to values around 9 (Fig. 4g). The N-NH_4^+ removal observed in the MBR efflu-

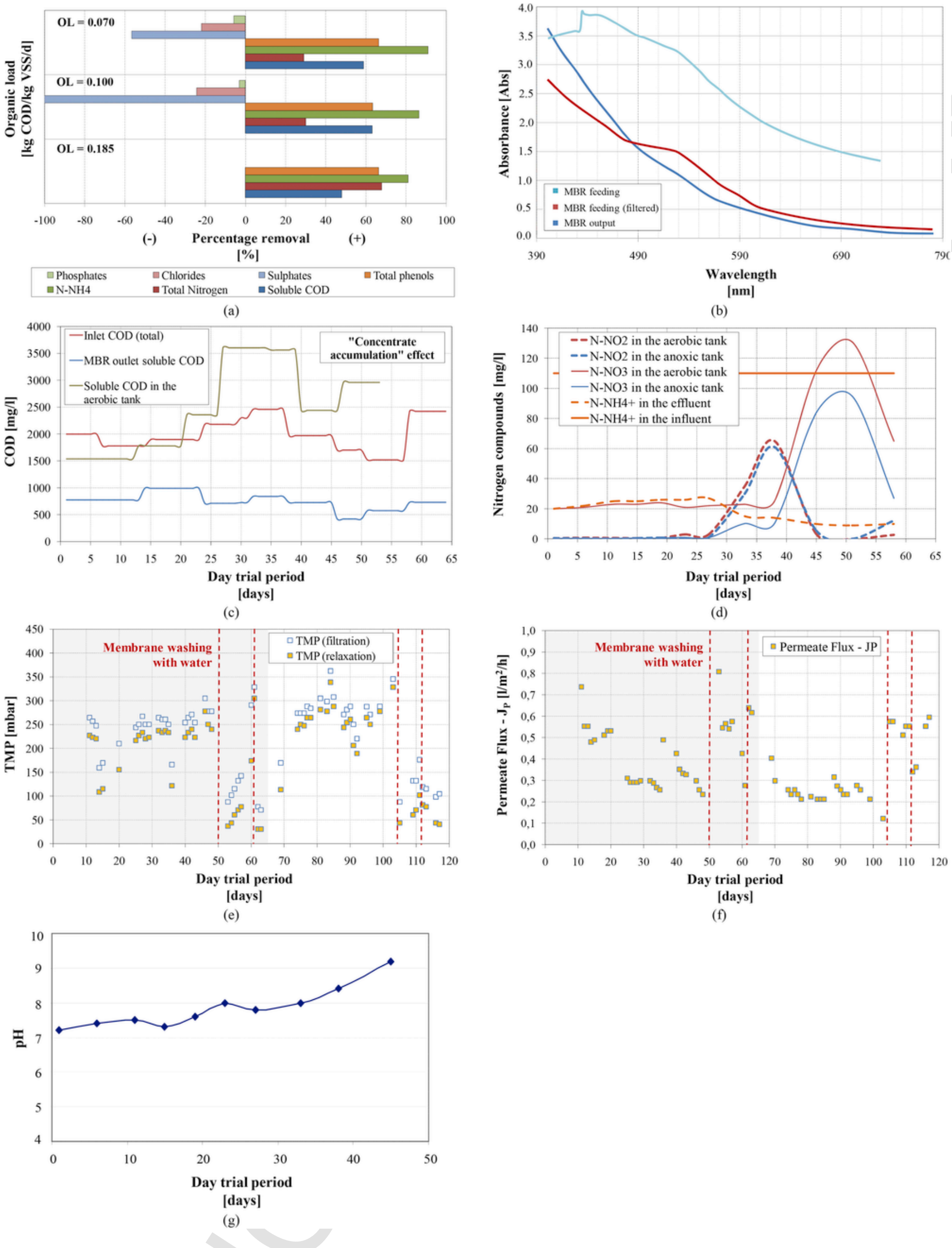


Fig. 4. Anoxic-aerobic MBR results: (a) Performance in terms of pollutants removal; (b) Spectrophotometric scanning of the MBR feeding and effluent; (c) COD values and (d) Nitrogen compounds values during the first 60 days of the experimentation; (e) TMP and (f) permeate flux values during the experimentation (120 days); (g) pH values.

ent stream was likely a consequence of the ammonia stripping favoured by high pH values and the air blown at the bottom of the tank. The process limitations observed persisted even with more prolonged periods of biomass adaptation as well as in presence of lower applied organic load conditions. Following these observations, the implementation of an additional treatment downstream to the MBR anoxic-aerobic unit was established, in order to provide the removal of recalcitrant COD residual fraction as well as colour and phosphates.

3.3. Chemical precipitation and GAC adsorption as post-treatments

Two different post treatment options, such as chemical precipitation and GAC adsorption, were tested as shown in Fig. 1a.

The first tests were carried out in order to evaluate the optimal lime ($Ca(OH)_2$) dosage. The MBR effluent was treated with increasing concentrations of lime, variable between 2 and 8 g/l, and a constant reaction time of 1 min. The maximum efficiency of phosphates removal (62%), determined immediately after precipitation, was observed with a lime dosage of 8 g/l (Fig. 5a). The supernatant was collected and analysed also after 5, 7 and 8 days from the reaction, with Fig. 5b showing the observed increase of phosphates removal with higher settling times.

Once the best optimal dosage of 8 g $Ca(OH)_2$/L was identified, the effect of the reaction (contact) time (1, 5, 10 and 20 min) on TP, phosphates and COD removal was investigated, as shown in Fig. 5c–e. TP and phosphates removal improved as the contact time increased, with values in the range of 64–82% for TP and 64–85% for phosphates. The shortest contact time applied (1 min) allowed TP removal efficiencies higher than 60%, and a phosphate removal of about 70% (Fig. 5c and d). Conversely, lime was much less effective in COD removal with observed efficiencies always lower than 30% (Fig. 5e). The pH of the treated effluent is on average in the range 8–9, thus requiring a further correction upstream to the final discharge.

The use of the multi-criteria analysis methodology (De Feo et al., 2013) made it possible to identify the optimal operating condition after measuring the process yield in terms of TP, phosphates and COD percentage removal. The results of this methodology, starting from the alternatives matrices of Tables 6S and 7S (see Supplementary Material) show how 8 g/l of $Ca(OH)_2$ and 15 min of reaction time were identified as the optimal condition.

Further chemical precipitation trials were carried out in order to evaluate the colour removal efficiency, seeking to achieve the compliance with discharge standards set by the Italian Law. Tests with lime dosage consisted in evaluating the residual colour after 5, 7 and 10 d contact time with the optimal conditions previously identified. The observed results show that longer contact time improved colour removal although the absorbance spectra (Fig. 1S, Supplementary Material) showed that the Italian legislation standards were only met with 7 d contact time.

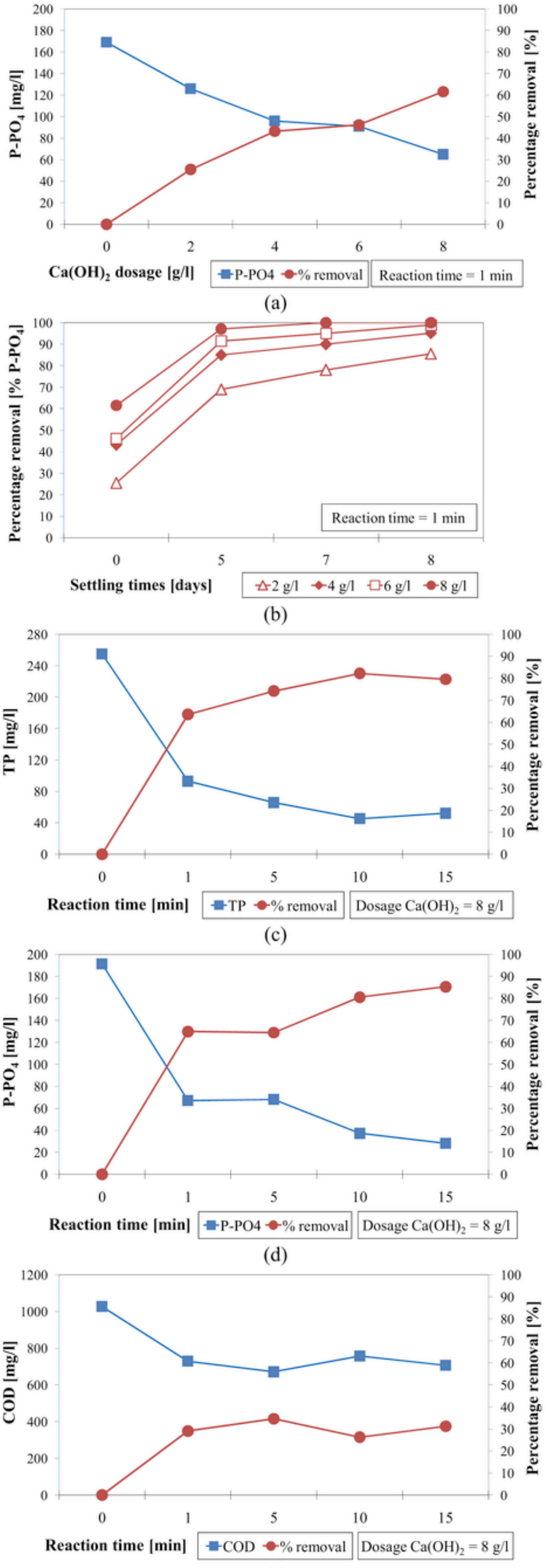
All the experiments using activated carbon resulted in a non-detectable colour with 1:20 dilution at the effluent, confirming a high effectiveness in colour removal. The activated carbon treatment unit also resulted in a 95% COD removal, whereas no significant TP and phosphate removal was observed with values of 3% and 4%, respectively. The performances of the two treatment options are reported in Table 4.

The comparison highlighted the suitability of chemical precipitation to remove phosphorous compounds while the colour was removed only after high sedimentation days (7 days). Instead, the adsorption on GAC was suitable for recalcitrant COD and colour removal.

3.4. On the optimization of the investigated treatment chain

Table 5 shows the material balances referred to the main parameters such as COD, TN and TP/phosphates. Additionally, the table summarizes the optimal operating conditions of biological processes (in terms of OLR) as well as the main dysfunctions identified during the trial.

The inlet wastewater, characterized by acidic pH, required a preliminary correction in order to obtain a value of 6.2. The feeding of UASB process was optimal for an OLR value of 4.5 kg COD/m^3/d. The adoption of higher values resulted in a higher risk of biological



(a)

(b)

(c)

(d)

(e)

foams formation with consequent negative effects on biogas production and process stability.

The anoxic-aerobic UF-MBR system allowed the removal most of the organic load and almost all of the nitrogen compounds. The feeding was optimal with an OLR of about 0.185 kgCOD/kg VSS/d. Although the UF-membrane determined a better solid/liquid separation with an almost complete suspended solids removal, it contributed to a progressive accumulation in the basins of recalcitrant compounds that negatively affected the yields of biological processes (as resulted during the long-term MBR treatment tests).

The presence of residual COD as well as other compounds such as phosphates, chlorides, sulphates and the colour in the MBR effluent made it necessary an additional finishing treatment. Chemical precipitation was found effective for phosphorus removal while GAC adsorption resulted as the best option for residual COD and colour removal. Thus, a combined use of such technologies may represent a suitable solution in order to achieve both the goals of surface water discharge and agricultural reuse. The use of chemical precipitation as a post-treatment on the entire flow to be treated entails an overall unit cost of about 5.0 €/m^3 for the whole treatment train (see Table 5), excluding the cost of excess sludge treatment and disposal. Moreover, the anoxic-aerobic UF-MBR treatment unit requires a further reduction of the recalcitrant influent load in order to avoid drawbacks to biological processes. Such considerations suggested the need of further improvements to the treatment chain.

Considering the technologies already tested in the present study, tests aimed at evaluating the benefits given by the adoption of chemical precipitation with lime upstream and downstream to the UASB reactor were performed. In such tests, a lime dosage of 8 g/l was hired as detailed in Par. 3.3.

As shown in Table 6, lime dosage allowed high phosphorous compounds (97–100%) and COD removals (67–68%) in raw wastewater, thus improving the performance observed by Braz et al. (2010) (COD removal = 18.9–29.7%). Furthermore, lime dosage allowed the removal of part of the recalcitrant COD in the UASB effluent, with an expected improvement of the downstream biological processes. Consequently, the combined adoption of anoxic-aerobic UF-MBR and activated carbons (resulted as the most effective method for colour removal) can be considered as an appropriate solution for the compliance with the effluent legal standards. Based on these considerations, the most appropriate distillery wastewater treatment cycle should include the following unit processes: (i) Chemical precipitation with lime; (ii) UASB treatment; (iii) Chemical precipitation of UASB effluent; (iv) Anoxic-aerobic UF-MBR; (v) GAC adsorption. The corresponding unit costs of the entire treatment train is estimated to be about 6.3 €/m^3, which could be decreased up to 5.0 €/m^3 if the lime dosage is provided only to a partial amount of the total flow-rate upstream and downstream to UASB process unit. However, such option requires further experimental investigations aimed at verifying the specific removal performances in order to guarantee the compliance with the final effluent standards.

Among the "external technologies", not tested in the present experimentation, struvite precipitation in UASB effluent can indeed be considered a suitable option to achieve nitrogen recovery, also in order to unload the biological units expected downstream. In particular, anaerobically pre-treated wastewater is the most suitable for struvite crystallization, due to the previous ammonification of the organic nitrogen with ammonium formation (Altinbaş, 2009). Temperature, pH, TSS and wastewater chemical composition are among the main parameters to be assessed for an optimal struvite precipitation process. Generally, optimum pH values are in the range 8–11. However, further site-specific experimentations need to be carried out at laboratory scale.

Fig. 5. Chemical phosphorous removal: (a) Identification of the optimal $Ca(OH)_2$ dosage for P-PO_4 removal; (b) trend of P-PO_4 removal with increasing settling time; Trend of (c) total phosphorous removal, (d) P-PO_4 removal and (e) COD removal vs. reaction (contact) time, with a dosage of 8 g $Ca(OH)_2$/l.

Table 4
Performance comparison between chemical precipitation with lime and GAC adsorption as post-treatments for colour removal.

Processes	Performance [Percentage removal]			
	%COD	%TP	%P-PO_4	Colour removal[b]
Chemical precipitation with lime[a]	31.2	79.6	85.3	Complete after 7-days
GAC adsorption	95.0	3.0	4.0	Complete

[a] Optimal conditions: dosage of 8 g/L of $Ca(OH)_2$ and 15-min of reaction time.

[b] Complete = Not perceptible with 1:20 dilution.

Table 5 shows further aspects to be optimized for a successful technological scale-up: a) the specific flow of permeate to be applied, since the adopted value (0.385 L/m^2/h) during the experimental tests would require a high membrane area or a large storage tank; b) the HRT in the contact tank for chemical precipitation with lime, since the optimal value achieved (7 days) would require excessive contact volumes. Therefore, future investigations are expected as to take into account the need of full-scale treatment as argued above.

4. Conclusions

The investigated treatment scheme considered the UASB treatment unit as a pre-treatment aimed at reducing the easily biodegradable COD fraction and leading to methane production. The optimal operational set up was reached at OLR of 4.5 kgCOD/m^3/d with a correspondent COD and total phenols removal efficiency of 97.2 and 75.0%, respectively. Higher OLR values (in the range of 6.2–11.5 kg COD/m^3/d) resulted in biological yeasts foams formation with a consequent decrease of biogas production and limited process stability.

The anoxic-aerobic UF-MBR unit was aimed at providing residual COD, nitrogen and colour removal. The optimal operational set up was reached at OLR of 0.185 kg COD/kg VSS/d, with a correspondent COD, TN, ammonia nitrogen and total phenols removals of 48.0, 67.8, 81.0 and 65.0%, respectively. The adoption of UF-membranes as well as the presence, in the UASB effluent, of recalcitrant compounds (i.e., phenols), led to their accumulation in the aerobic and anoxic compartments, resulting in the inhibition of biological processes and relying the treatment efficiency on the membrane filtration effect only.

Chemical precipitation with lime as post-treatment allowed TP, phosphates and COD removals of 79.6, 85.3 and 31.2%, respectively (8 g/l lime dosage and 15 min reaction time) while the GAC adsorption confirmed a high effectiveness in colour removal.

The criticalities observed during the experimentation highlighted the important role of chemical processes for the optimization of the whole treatment chain: the use of a chemical precipitation step on the UASB effluent appears a suitable solution to reduce the recalcitrant COD content, thus facilitating the long-term sustainability of the anoxic-aerobic UF-MBR treatment, with a corresponding overall unit costs between 5.0 and 6.3 €/m^3 depending on the amount of the flowrate upstream and downstream to UASB process unit to be treated with lime dosage.

Table 5
Material balances referred to the main contaminants and to the entire treatment chain, costs and main remarks.

N. Section [a]	Description	Main process parameters	Volumetric flow rate [l/d]	Mass flow rate of pollutants [g/d]	Percentage removal [%]	Biogas production [LCH_4/kgCOD]	Sludge production [cm^3/d]	Remarks	Unit costs [€/m^3][b]				
COD	TN	N-NH_4^+	COD	TN	N-NH_4^+								
1	UASB feeding 1	–	1.61	72.0	0.410	0.218	–	–	–	–	–	Acid pH requiring a correction with soda.	–
UASB feeding 2	–	2.42	108.0	0.615	0.327	–	–	–	–	–			
UASB feeding 3	–	6.19	276.0	1.572	0.835	–	–	–	–	–			
2	UASB effluent 1	OLR_1 = 3 kgCOD/m^3/d	1.61	1.766	0.355	0.034	97.5	13.4	84.0	350	–	Biological foams with OLR >6.2 kgCOD/m^3/d; Presence of colour.	0.10
UASB effluent 2	OLR_2 = 4.5 kgCOD/m^3/d	2.42	3.051	0.581	0.363	97.2	5.5	−11.1	400	–			
UASB effluent 3	OLR_3 = 11.5 kgCOD/m^3/d	6.19	11.077	1.368	0.990	96.0	13.0	−18.5	100	–			
3	MBR feeding 1	–	1.03	1.428	0.234	0.114	–	–	–	–	–	–	–
MBR feeding 2	–	0.55	0.764	0.125	0.061	–	–	–	–	–			
MBR feeding 3	–	0.38	0.531	0.087	0.042	–	–	–	–	–			
4	MBR effluent 1	OLR_1 = 0.185 kgCOD/kgVSS/d	1.03	0.743	0.075	0.022	48.0	67.8	81.0	–	70[c]	Accumulation of recalcitrant compounds. Presence of colour. Need to reduce the organic load and the ammonia toxicity. Low J_P flow.	0.28
MBR effluent 2	OLR_2 = 0.100 kgCOD/kgVSS/d	0.55	0.282	0.088	0.008	63.1	30.0	86.4	–	33[c]			
MBR effluent 3	OLR_3 = 0.070 kgCOD/kgVSS/d	0.38	0.219	0.062	0.004	58.8	29.1	90.9	–	15[c]			
Post-treatments	COD	TP	P-PO_4	COD	TP	P-PO_4							
5	Feeding	–	5.00	5.130	1.275	0.956	–	–	–		–		–
6	Adsorption effluent	–	1.00	3.530	0.261	0.141	95.0	3.0	4.0	–	–	High colour and COD removals.	3.5
6 bis	Precipitation effluent	Best condition: (i) $Ca(OH)_2$ dosage = 8 g/l; Contact time = 15 min.	5.00	3.530	0.261	0.141	31.2	79.6	85.3	–	900–1400	High sludge production; Limited colour removal. High contact time. Need to reduce the pH.	1.2

[a] See also Fig. 1.

[b] Operating costs without sludge treatment and disposal. Assumptions for the adsorption treatment: Consumption of GAC = 3.5 kg/m^3; Cost of GAC = 1.0 €/kg dry-product; Assumptions for the chemical precipitation: Cost of lime = 0.15 €/kg; Lime dosage = 8 kg/m^3. In terms of energy consumption, the main item is due to the MBR system with a values in the range 2.0–3.6 kWh/m^3. Considering the MBR, the main items are aeration (58%) and membranes (32%).

[c] Average values.

Table 6
Results related to the chemical precipitation with lime upstream and downstream the UASB reactor ("internal optimization" of the treatment chain).

Sample	Dosage of $Ca(OH)_2$ [g/L]	Reaction time [min]	Performance [Percentage removal]	
$\%P\text{-}PO_4$	%COD			
Test 1: Chemical precipitation upstream the UASB				
1	8	5	97%	67%
2	8	10	98%	68%
3	8	20	100%	67%
Test 2: Chemical precipitation downstream the UASB				
4	8	5	80%	46%
5	8	10	90%	49%
6	8	20	65%	50%

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jenvman.2017.06.042.

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