Flocculation and Nanofiltration Processes with Insight of Fouling Phenomena for the Treatment of Olive Mill Wastewater

Srikanth Vuppala*[a], Luca Di Palma[b], Claudio Cianfrini[a], Marco Stoller[b]

[a]Sapienza University of Rome, Dept. of Astronautics Electrical Energy Engineering, Via Eudossiana 18, 00184 Rome, Italy
[b]Sapienza University of Rome, Dept. of Chemical Engineering Materials Environment, Via Eudossiana 18, 00184 Rome, Italy
srikanth.vuppala@uniroma1.it

Olive oil production is one of the main agriculture activities in many Mediterranean countries and it usually produces huge quantities of wastewaters. The management, treatment and safe disposal causes serious environmental issues. The adverse characteristic properties of OMW, which are the main responsible of their hazardous disposal, generally do not permit the treatment only by biological processes. Combined innovative processes should be adopted to remove the various organic and inorganic hazardous compounds from these wastewaters. Among the typical olive mill wastewater (OMW) treatments the most widely used are: drying / evaporation, forced evaporation, thermal treatment, electrocoagulation, composting, lagooning, adsorption, powdered activated carbon, sand filtration, membrane filtration, precipitation / flocculation, distillation, electrolysis, co-composting, advanced oxidation processes (AOPs). To define an efficient pre-treatment and to overcome major obstacles of membrane treatment (fouling), economic organic coagulant has been tested. Chitosan, a natural linear bio-polyaminosaccharide, is obtained by alkaline deacetylation of chitin. The main purpose of this study was to investigate the effects of chitosan as coagulant aid to reduce phenols content, COD and TOC in OMW, in addition to control membranefouling, which is used in the sequential step of the treatment. A conventional jar test apparatus was employed for the flocculation tests followed by photo catalysis and membrane treatment includes Nano Filtration process by means of a pilot-scale plant.

1. Introduction

Water pollution has become a major problem in recent years(Vilardi and Di Palma, 2017; Muradova et al., 2016);among water pollution one of the most important environmental problems in the Mediterranean countries is the treatment of olive mill wastewater (OMW) (Stoller et al., 2016; Stoller et al., 2017). Every year each olive tree produces 15 to 40 kg of olives. 2 546 306 t year[-1] of olive oil is produced every year from all over the world, most the production is in the Mediterranean region which alone produces 97% of the total olive oil production, while European Union (EU) countries produce 80–84%(Rizzo et al., 2008). OMW is dark-red to black colour effluent produced in olive oil production and it is characterized by COD (Chemical Oxygen Demand) and TOC (Total Organic Carbon) generally in the range 80-200 g L^{-1} and 20-80 g L^{-1}. The organic fraction contains, among other components, 2-15% of phenolic compounds divided into low-molecular weight (caffeic acid, tyrosol, hydroxytirosol, p-cumaric acid, ferulic acid, syringic acid, protocatechuic acid etc.) and high molecular weight compounds (tannins, anthocianins, etc.) as well as catechol-melaninic polymers (Davies et al., 2004). Therefore, the OMW disposal represents a significant issue due to the presence of environmentally hazardous substances. Consequently, several studies have been performed to develop innovative and efficient technologies for the OMW treatment.

The first step usually deals with the solid separation from the OMW liquid phase, which could be carried out adopting coagulant materials or by means of centrifugation and mechanical separation processes. Chitosan itself is a nontoxic biopolymer and has a widevariety of applications in biotechnology, biomedical, environmental, microbiology, and pharmaceutical fields. Chitosan was used as natural organic coagulant in the coagulation step for OMW treatment (Rizzo et al., 2008). Various authors described chitosan as a

biopolymer characterized by excellent properties like biodegradability, biocompatibility, adsorption capacity, antibacterial property and non-toxicity, and can be used as a coagulant, bactericide, pollutant reducing agent for removal of organics, pathogens, suspended solids, turbidity, biological oxygen demand (BOD), chemical oxygen demand (COD) (Bergamasco et al., 2011).

A second step may be by advanced oxidation process (AOPs), an interesting alternative to the traditional technologies. Among AOPs, the nanoparticles employment for environmental treatment (Gueye et al., 2016; Vilardi et al., 2017a) such as heterogeneous photocatalysis demonstrated high efficiency in the removal of a wide range of organic contaminants, also present in low amount in wastewater (Bavasso et al., 2016). Titanium dioxide represents the widest studied photocatalyst, because of its peculiar physico-chemical characteristics (Vaiano et al., 2016).In the case of anatase, the band gap is 3.2 eV, therefore UV light (≤ 387 nm) is required. In addition, it is possible to modify the photocatalytic activity and the physical properties of TiO_2, nitrogen doping will reduce the band gap and makes the catalyst active in visible region, producing N-doped core-shell nanoparticles. Incorporating an SiO_2 intermediate layer between a Fe_3O_4 (FM) core and the TiO_2 shell, weakens the adverse influence of Fe_3O_4 on the photocatalysis of TiO_2(Rashid et al., 2015),increases its specific surface area and grants an easier separation way by magnetic fields (Nguyen and Nguyen, 2009; Di Palma et al., 2015). The application of an intermediate layer barrier such as SiO_2 between the magnetic core and the titanium dioxide shell may lead to the avoidance of the photo dissolution of iron, magnetic core stabilization, and the prevention of the magnetic core from acting as an electron-hole recombination center which would negatively affect the photoactivity of TiO_2. The deposition of TiO_2 onto silica-coated iron oxide has been conducted by several techniques such as impregnation, precipitation, and sol–gel and Spinning Disk Reactor (SDR) technology (Stoller et al., 2009).The (SDR) has many advantages when compared with other mixing devices used for precipitation process: i) a small liquid residence time, limiting the growth rate after nucleation, that leads to the production of narrow PDSs of nanoparticles at a specific target size; ii) micro-mixing conditions attained by means of a limited energy consumption; iii) continuous operation, compatible to industrial practice, can be performed (Vilardi et al., 2017b).

The third step maybe done by membrane processes, which is considered one of the most promising treatment processes for OMW (Stoller and Ochando Pulido, 2014). The permeate stream generally reaches a quality near the legal discharge in municipal sewer system, making the disposal of the wastewater cheap. The main problem of membranes is that fouling may occur, leading to a reduction of the membrane efficiency (Stoller et al., 2015). One method to characterize membrane fouling behaviors is the boundary flux concept (Stoller and Ochando Pulido, 2015). Briefly explained, no irreversible fouling is formed at or below boundary flux conditions. Boundary fluxes may change its value as a function of the adopted pretreatment steps. The relationship between a proper pretreatment tailoring and boundary fluxes was further investigated by using coagulation and photocatalysis as a pretreatment step, by adopting magnetic core (Ruzmanova et al., 2013a) or doped titania nanoparticles (Ruzmanova et al., 2013b).

This work deals with the olive mill wastewater separation and purification by using chitin as a coagulant and novel magnetic core N-doped titania nanoparticles as photocatalyst. The effects of these pretreatment steps on the membranes in terms of fouling, productivity and selectivity are investigated in the successive separation steps (MF, UF, NF, and RO). The membrane fouling was detected in the MF and UF processes. It is found that the proper pretreatment can substantially increase the flux in NF and RO processes.

1.1 Samples characterization

Physico-chemical sample characterization has been performed by different techniques. Laser Raman spectra were obtained at room temperature with a Dispersive Micro Raman (Invia, Renishaw), equipped with 514 nm laser, in the range 100-2500 cm^{-1} Raman shift. UV-Vis reflectance spectra were recorded with a Perkin Elmer spectrometer Lambda 35. X-ray diffraction (XRD) was carried out using an X-ray micro-diffractometer Rigaku D-max-RAPID, using Cu-Kα radiation and a cylindrical imaging plate detector. The average size, morphology and EDX composition of the nanoparticles was measured by SEM (FE-SEM HR Zeiss Auriga 405).

2. Materials and Methods

2.1 Wastewater sample

OMW sample was collected from a small company located in province of Lazio (central Italy) which adopt centrifuge method for oil extraction. The sample was stored at 20°C and shakentomake solids suspended before collecting the proper volumes for coagulation experiments.

2.2 Chitosan solution

500 mg/L chitosan stock solution was prepared as follow: 500 mg of Chitosan 448877 from Sigma Aldrich (USA) were dissolved in 2.5 mL of 2 M HCl solution and 47.5 mL of deionized water; after 60 minutes, 50 mL of deionized water were added.

2.3 Synthesis of Fe_3O_4-SiO_2 core-shell nanoparticles

The core-shell SiO_2/Fe_3O_4 nanoparticles (FM) were prepared by two steps. Firstly, Fe_3O_4 magnetic nanoparticles were synthesized using a spinning disk reactor. Then, FM nanoparticles were prepared by dispersing Fe_3O_4 particles in distilled water, followed by the addition of C_2H_5OH (Sigma Aldrich). Tetraethyl ortosilicate (TEOS), preliminarily diluted in C_2H_5OH, was added drop-wise to the Fe_3O_4 particle suspension. Then an aqueous solution of NH_3 (30 wt %) was added and the TEOS hydrolysis and condensation was allowed under overnight gentle stirring. The obtained FM particles were washed in a centrifuge using firstly water/ethanol mixtures then distilled water. Finally, they were dried and calcinated at 450 °C for 30 minutes (Ramp 10°C/min) (Vaiano et al., 2016).

2.3.1 Synthesis of Fe_3O_4-SiO_2/N-doped TiO_2 nanoparticles

Fe_3O_4-SiO_2/N-doped TiO_2 nanoparticles were prepared by adding urea in 50 ml water and continue the stirring for 10 minutes, then Fe/SiO_2 was added in sonicator for 5 minutes finally; TTIP was added under sonication followed by 10 minutes mechanical mixing. The mixture was centrifuged and washed two times. Subsequently, the recovered sample was calcinated at 450 °C for 30 minutes (Ramp 10°C/min) to obtain the final N-TiO_2/FM catalyst. The nominal loading of N-TiO_2 on the FM support was 37.5 wt %.

2.4 Experimental

The proposed process to treat OMW is as follows:

- **Gridding:** This technique is used to separate coarse particles higher than the cut-size (300 micron).
- **Coagulation/flocculation experiments:** The coagulation/flocculation experiments were carried on OMW samples by means of Jartests apparatusand putting 600 mL samples in 1 L bakers. Following the coagulantaddition, the samples were subjected to a rapid mix step at 100 rpm for 2 min, a slow mixing step at 30 rpm for 30 min and subsequently a sedimentation step for 60 min. The chitosan coagulation process was optimized according to both coagulant dose and pH. Chitosan dosages in the range of 600 mg/L and pH values actual condition (4.6) was investigated.
- **Sedimentation:** The created flocks in the OMW must be settled out before continuing the treatment, performed by a 24h long lasting sedimentation step. The sludge formed by this process was removedfrom the bottom of the tank.

2.5 Photocatalysis tests

The photocatalytic experiments were carried out with phenol initial concentration equal to 25 mg L^{-1}, at room temperature (25°C). The catalyst dosage was 3 g L^{-1}. The total OMW volume was 400mL. The experiments were conducted using a pyrex cylindrical photoreactor (ID=2.5 cm, height=25 cm) equipped with an air distributor device (Q_{air}=150 cm^3 min^{-1} (STP)). Continuous mixing of the aqueous solution was done by external recirculation of the same solution using a peristaltic pump. The photoreactor was irradiated with a strip composed of 25 Blue light LEDs (6W nominal power; provided by New Oralight, with wavelength emission in the range 400–800 nm with main emission peak at 475 nm. The LEDs strip was positioned around and in contact with the external surfaceof the photoreactor (incident light intensity 32mW cm^{-2}). The system was left in the dark for 30 min to reach phenol adsorption equilibrium, and then photocatalytic reaction was initiated under visible light for 180 min.

2.6 Membrane treatment process

The sequence of membrane used in this work was microfiltration (MF, model JX supplied by GE Water), ultrafiltration (UF, model GM supplied by GE Water), nanofiltration (NF, model DK supplied by GE Water) and reverse osmosis (RO, model SG supplied by GE Water), feeding the permeate stream of the previous separation step to the next one.

The jacketed feed tank in stainless steel has a volume of 500 mL. The temperature of the solution can be controlledat20°C by means of a thermostat. A gear pump feeds the solution to the flat membrane cell continuously, and the concentrate is discharged to the feed tank again. In the membrane cellnear to cross-flow conditions were reached, and the tangential velocity over the membrane surface is about 0.84 m/s. The membrane has a diameter of 75 mm, resulting in a membrane area equal to44 cm². The operating pressure is fixed beforehand and kept constant at 4bar.

The residual concentration of phenol, COD and TOC in aqueous samples was monitored by observing the change in the absorbance at the maximum absorption wavelength of 270 nm, 600 nm using a UV–vis spectrophotometer (UV-2700, SHIMADZU) and TOC analyser (TOC-L, SHIMADZU), then the concentrations were calculated from a calibration curves.

3. Results and Discussion

3.1 Samples characterization

Crystal phase composition and of N-TiO$_2$/FM was determined by XRD and RAMAN. XRD result of FM sample exhibited the presence of the orthorhombic phase of Fe$_3$O$_4$ (Vaiano et al., 2016). From the XRD analysis spectra of N-TiO$_2$/FM compared with those of FM and unsupported N-TiO$_2$ powder, it was found the presence of the anatase-TiO$_2$ peaks with together the signals of FM. No diffraction peaks corresponding to SiO$_2$ were observed for FM and N-TiO$_2$/FM probably because silica has amorphous structure. The same results were obtained from Raman analysis. Anatase and Fe$_3$O$_4$crystallite size of the samples were evaluated from XRD analysis, using the Scherrer equation. For N-TiO$_2$, the anatase crystallite size was about 11 nm and slightly decreased (8 nm) after the deposition of N-TiO$_2$ on FM. Fe$_3$O$_4$ crystallite size was found to be about 20 - 30 nm which corresponds to the determined average particle size by SEM measurement (not shown). UV–vis reflectance spectra in terms of Reflectance forN-TiO$_2$. The shifting of the absorption onset from about 350 nm (for undoped TiO$_2$) to about 550 nm (for N-TiO$_2$) indicates the ability of the sample to absorb visible light, as confirmed by the band-gap energy (about 2.55 eV), which is the typical absorption property of TiO$_2$ doped with nitrogen.

3.2 Coagulation test

After gridding the OMW was processed by the coagulation process. Table 1 reports the obtained results in terms of some key parameters, such as degradation recorded for Phenols, TOC, COD is 22%, 35% and 28% respectively. The obtained results are in line with those reported elsewhere. 600 mg/l of chitosan were used for the required coagulation of the initial 600 ml of OMW.
The supernatant was then processed by photocatalysis treatment.

3.3 Photocatalytic activity

Preliminary experiments were carried out to verify that phenol, TOC and COD degradation by the heterogeneous photocatalytic process under visible light. It was found that in the absence of photocatalyst no decrease in phenol concentration was observed (Vaiano et al., 2016). Therefore, photolysis phenomena did not occur. After 180 min of visible light irradiation, no photocatalytic activity was observed for FM sample (Stoller et al., 2017). On the contrary, N-TiO$_2$/FM catalysts was effective in the degradation of phenol, TOC and COD in aqueous solutions. The degradation of Phenols, TOC and COD in OMW is 38%, 42% and 36% respectively. Degradation efficiency decreased only at photocatalysis step, due to the OMW dark colour, and solid particles presence, which inhibits the photocatalytic efficiency of the treatment. Since the separability of photocatalysts from treated wastewater in a real wastewater treatment systemis very important, magnetic N-TiO$_2$/FM sample was chosen for each treatment runs. The treated water containing N-TiO$_2$/FM catalyst was collected into a beaker after each treatment and the use of a magnet on the external surface of the beaker allows to easily separating the treated solution from the used photocatalyst. After washing with distilled water and drying at 100 °C, the photocatalyst was reused (data not shown) without further treatment.

3.4 Membrane treatment

As expected, the suggested membrane processes in sequence reaches the foreseen targets in terms of purification of the wastewater stream (Table 1).
Concerning membrane fouling, in order to check if the prefixed pressure value equal to 4 bar was suitable, the water permeability of the membrane was checked at the beginning of the experiment (m$_w$*) and at the end, after careful washing/rinsing (m$_w$). If no irreversible fouling forms, that is at sub-boundary flux conditions (SUB), these values should be almost equal; on contrary, a different value indicates the formation of irreversible fouling and thus super-boundary conditions (SUPER). Once checked this aspect, the obtained membrane performances in terms of permeate flux at 4 bar and by adopting the here reported pretreatment steps (CTN) were compared to results obtained in previous works by adopting as a pretreatment coagulation by aluminium sulphate (AL) and photocatalysis only (PC), respectively (Stoller and Bravi, 2010). The results are reported in Table 2.

Table 1: Degradation efficiency of each stage of treatment

S.No	Type of Sample	Phenols (%)	COD (%)	TOC (%)	pH
1	RAW OMW	0	0	0	4.6
2	Coagulation	22	35	28	5.2
3	Photocatalysis	38	42	36	5.8
4	MF	43	59	44	6.1
5	UF	61	73	58	6.3
6	NF	84	84	73	6.8
7	RO	95	99	86	7.2

Table 2: Determination of presence of irreversible fouling and comparison of performances

Membrane	m_w*	m_w	Boundary flux conditions	J_p (at 4 bar)		
Pre treatment				CTN	AL	PC
MF	1608,1	535,7	SUPER	22,3	8,4	16,8
UF	17,9	10,8	SUPER	13,4	5,5	8,5
NF	5,1	5,0	SUB	8,9	13,2	18,0
RO	6,7	6,6	SUB	5,4	4,1	10,5

From the data in Table 2, it appears that MF and UF were operated in super-boundary, NF and RO in sub-boundary flux conditions. Nevertheless, performances of both MF and UF appeared to be higher than those obtained by adopting other pretreatment steps, and therefore improved results may be obtained in sub-boundary flux conditions. This aspect appears to be very promising, and will be checked in future by boundary flux measurements. Moreover, in previous works UF was noticed to be the step with highest membrane area requirements: improvement of performances of the UF step are therefore to consider highly valuable. Concerning NF and RO, it appeared that the proposed pretreatment is in line with the performances obtained by adopting AL or PC.

4. Conclusions

Coagulation tests were successfully performed by using natural coagulant Chitosan for the degradation of pollutants in OMW.Nanocomposite $N-TiO_2/SiO_2/Fe_3O_4$ ($N-TiO_2/FM$), which are visible-active and magnetically separable, was synthesized successfully and tested in the photocatalytic removal of phenol under visible light irradiation. The photocatalytic tests were carried out in a recirculating batch cylindrical photoreactor irradiated by a strip of Blue LEDs surrounding the external surface of the reactor and emitting in the visible region. After an irradiation time of 180 min, the experimental results showed that $N-TiO_2/FM$ nanoparticles are effective in the removal of phenol, COD and TOC reaching a value range of 36 -42 % of removal efficiency. Finally, the membrane treatment plant was employed to reach maximum degradation of Phenols, COD and TOC in the range of 86 to 99 % including pH reached up to 7.1 from initial pH of OWM 4.6. The final COD was 0.5 g L^{-1}; it implies that an additional treatment is not necessary to discharge in to municipal sewer systems, the Italian regulations with regards to the maximum COD allowed for liquid discharge in municipal sewer systems (limit equal to 500 mg L^{-1}) or superficial aquifers (limit equal to 125 mg L^{-1}).

In the future work, boundary flux conditions will be checked for each membrane: it appears that promising improvement of membrane performances can be expected on UF, which would have as a consequence great benefit (reduction) on the overall process investment and operating costs.

Reference

Bavasso I., Vilardi G., Stoller M., Chianese A., Di Palma L., 2016. Perspectives in nanotechnology based innovative applications for the environment. Chemical Engineering Transactions, 47, 55-60. doi: 10.3303/CET1647010.

Bergamasco, R., Konradt-Moraes, L. C., Vieira, M. F., Fagundes-Klen, M. R. and Vieira, A. M. S. 2011.'Performance of a coagulation–ultrafiltration hybrid process for water supply treatment', *Chemical Engineering Journal*, 166(2), pp. 483–489. doi: 10.1016/j.cej.2010.10.076.

Davies, L. C., Vilhena, A. M., Novais, J. M. and Martins-Dias, S. 2004. Olive mill wastewater characteristics: modelling and statistical analysis', *Grasas y Aceites*, 55, pp. 233–241. doi: 10.3989/gya.2004.v55.i3.171.

Di Palma L., Medici F., Vilardi G., 2015. Artificial aggregate from non metallic automotive shredder residue', Chemical Engineering Transactions, 43,1723–1728. doi: 10.3303/CET1543288.

Gueye M.T., Di Palma L., Allahverdiyeva G., Bavasso I., Petrucci E., Stoller M., Vilardi G., 2016. The influence of heavy metals and organic matter on hexavalent chromium reduction by nano zero valent iron in soil. Chemical Engineering Transactions, 47, 289-294. doi: 10.3303/CET1647049.

Nguyen, V.-C. and Nguyen, T.-V. 2009. Photocatalytic decomposition of phenol over $N–TiO_2 –SiO_2$ catalyst under natural sunlight', *Journal of Experimental Nanoscience*, 4(3), pp. 233–242. doi: 10.1080/17458080902773707.

Muradova G. G., Gadjieva S. R., Di Palma L., Vilardi, G., 2016. Nitrates Removal by Bimetallic Nanoparticles in Water. Chemical Engineering Transactions, 47, 205-2010. doi: 10.3303/CET1647035.

Rashid, J., Barakat, M. A., Ruzmanova, Y. and Chianese, A. 2015. $Fe_3O_4/SiO_2/TiO_2$ nanoparticles for photocatalytic degradation of 2-chlorophenol in simulated wastewater', *Environmental Science and Pollution Research*, 22(4), pp. 3149–3157. doi: 10.1007/s11356-014-3598-9.

Rizzo, L., Lofrano, G., Grassi, M. and Belgiorno, V. 2008. Pre-treatment of olive mill wastewater by chitosan coagulation and advanced oxidation processes', *Separation and Purification Technology*, 63(3), pp. 648–653. doi: 10.1016/j.seppur.2008.07.003.

Ruzmanova Y., Ustundas M., Stoller M., Chianese A., 2013a, Photocatalytic treatment of olive mill wastewater by n-doped titanium dioxide nanoparticles under visible light, CET 32, 2233-2239.

Ruzmanova Y., Stoller M., Chianese A., 2013b, Photocatalytic treatment of olive mill wastewater by magnetic core titanium dioxide nanoparticles, CET 32, 2269-2275.

Stoller M., Miranda L., Chianese, A., 2009. Optimal feed location in a spinning disc reactor for the production of TiO 2 nanoparticles. Chemical Engineering Transactions17, 993-998.

Stoller M., Azizova G., Mammadova A., Vilardi G., Di Palma L., Chianese A. 2016. Treatment of Olive Oil Processing Wastewater by Ultrafiltration , Nanofiltration , Reverse Osmosis and Biofiltration, 47, pp. 409–414. doi: 10.3303/CET1647069.

Stoller, M., Ochando Pulido, J.M., Di Palma, L., Ferez, A.M., 2015, Membrane process enhancement of 2-phase and 3-phase olive mill wastewater treatment plants by photocatalysis with magnetic-core titanium dioxide nanoparticles, Journal of Industrial and Engineering Chemistry 30, 147 – 152.

Stoller M., Bravi M., 2010, Critical flux analyses on differently pretreated olive vegetation waste water streams: some case studies, Desalination 250 (2), 578.

Stoller M., Ochando-Pulido J.M., 2014, About Merging Threshold and Critical Flux Concepts into a Single One: The Boundary Flux, Sci. World J., ID:656101.

Stoller M., Ochando Pulido J.M., 2015, The boundary flux handbook, ISBN 9780128015896.

Stoller M., Ochando-Pulido J.M., Vilardi G., Vuppala S., Bravi M., Verdone N., Di Palma L., 2017, Technical and economic impact of photocatalysis as a pretreatment process step in olive mill wastewater treatment by membranes, Chemical Engineering Transactions, 57, 1171-1176. DOI: 10.3303/CET1757196.

Vilardi G., Di Palma L., 2017. Kinetic Study of Nitrate Removal from Aqueous Solutions Using Copper-Coated Iron Nanoparticles.Bulletin of Environmental Contamination and Toxicology, 98(3), pp.359–365.doi:10.1007/s00128-016-1865-9.

Vilardi G., Verdone N., Di Palma L., 2017.a The influence of nitrate on the reduction of hexavalent chromium by Zero Valent Iron nanoparticles in polluted wastewater. Desalination and Water Treatment. doi:10.5004/dwt.2017.20710.

Vilardi G., Stoller M., Verdone N., Di Palma L., 2017.b Production of nano Zero Valent Iron particles by means of a spinning disk reactor. Chemical Engineering Transactions, 57, 751-756.DOI: 10.3303/CET1757126.