Combination of coagulation-flocculation-decantation with sulfate radicals for agro-industrial wastewater treatment

Nuno Jorge[1,2 *]; Carlos Amor[2]; Ana R. Teixeira[2]; Leonilde Marchão[2]; Marco S. Lucas[2]; José A. Peres[2]

[1] Escuela Internacional de Doctorado (EIDO), Campus da Auga, Campus Universitário de Ourense, Universidade de Vigo, As Lagoas, 32004, Ourense, Spain
[2] Centro de Química de Vila Real (CQVR), Departamento de Química, Universidade de Trás-os-Montes e Alto Douro (UTAD), Quinta de Prados, 5001-801, Vila Real, Portugal

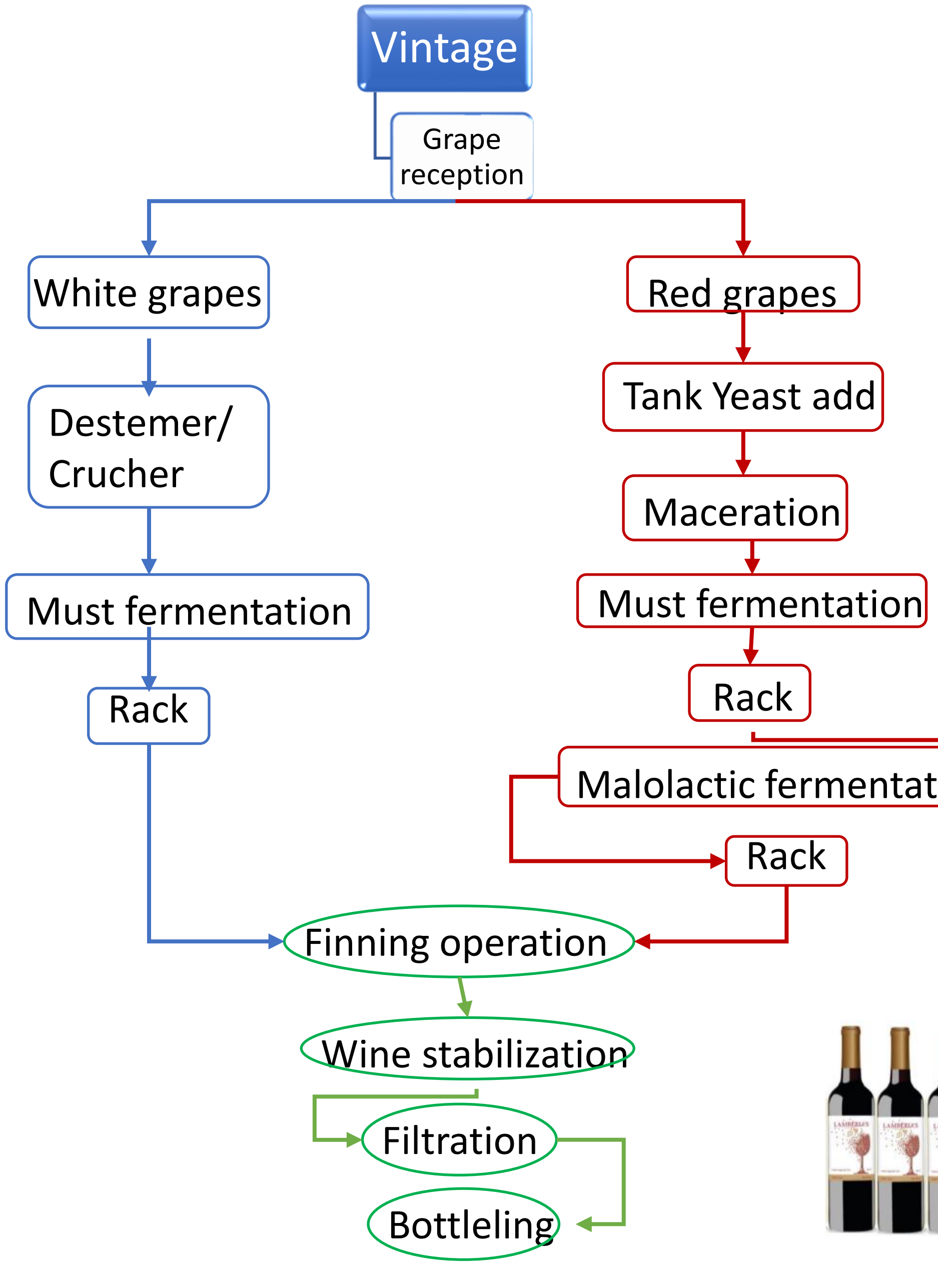
* njorge@uvigo.es

The 1st International Electronic Conference on Processes: Processes System Innovation

Session 2. Environmental and Green Processes

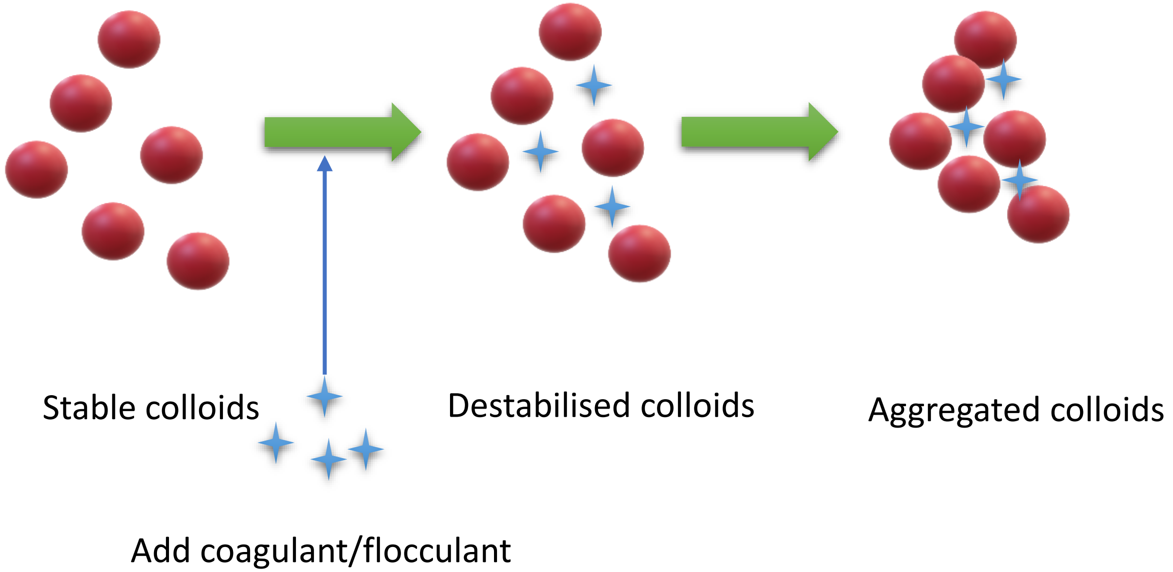
17 – 31 May 2022

Introduction



- In the vintage, the grapes are collected
- In the grape reception, the grapes are selected and separated
- In white wines the grapes are crushed and the must is fermented
- In red wines, the grapes are marecerated and the must is fermented with the grapes
- After must fermentation and wine stabilization, the wine is filtrated
- Finally, the wine is bottled

Coagulation-flocculation-decantation (CFD)



- Hydrolysable metal salts (mainly, **aluminum** and **iron**)

Most used on waster treatment

Aluminum
- Dialysis encephalopathy
- Alzheimer's disease

Iron
- Generally corrosive
- Strongly dependent on the pH
- The leach cannot be recycled

Disadvantages

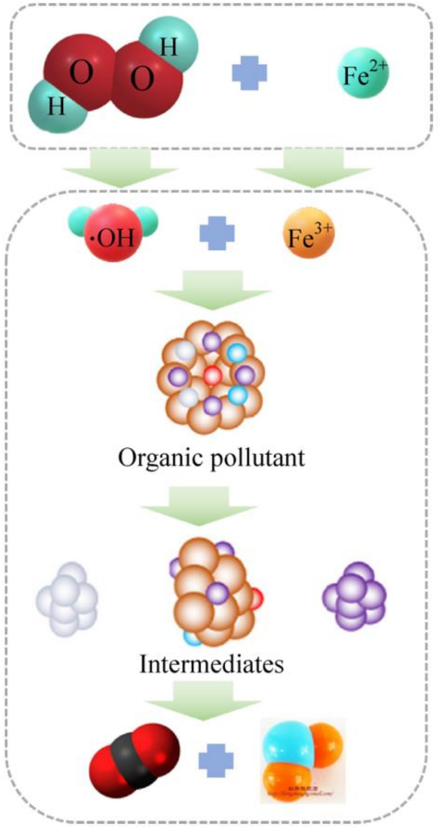
- Oenological coagulants

Used on wine treatment

Advantages

- Alimentary use
- Low cost and accessible
- Do not affect pH
- Leach can be recicled

Advanced Oxidation Processes (AOP)



Production of radicals to degrade the organic matter

- HR-AOP
- SR-AOP
- Ozone

Application of sulfate radicals for degradation of organic matter

Properties of PS and PMS

Properties	Potassium PS	PMS[a]
CAS number	7727-21-1	10058-23-8
Formula	$K_2S_2O_8$	$H_3K_5O_{18}S_4$
Molecular weight	270.309	614.738
Solubility[b]	520 g L^{-1}	> 250 g L^{-1}
Redox potential	2.01 V	1.82 V

Mechanisms of activation

Alkaline activation

For base activation of PS, a nucleophilic attack on the O-O bond is considered as the main mechanism

Transition metal ions and metal oxide

Transition metal and metal oxide can active the PS and PMS to degrade the organic contaminants

Thermal activation

Temperature (> 50 °C) can cause the fission of O-O bond to form the sulfate radicals

Radiation activation

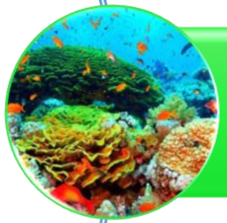
In general, 254 nm is usually used as the radiation wavelength for persulfate.

Carbonaceous-based materials

For the activation of PS and PMS by carbonaceous-based materials, the mechanism is the electron conduction

Considering the low information regarding the treatment of winery wastewater (WW) by SR-AOP, the aim of this work is:

(1) To apply oenological coagulants potassium caseinate, bentonite and polyvinylpolypyrrolidone to increase the efficiency of SR-AOPs for the treatment of winery wastewater



(2) To apply a Box-Behnken design of Response Surface Methodology to optimize the SR-AOP

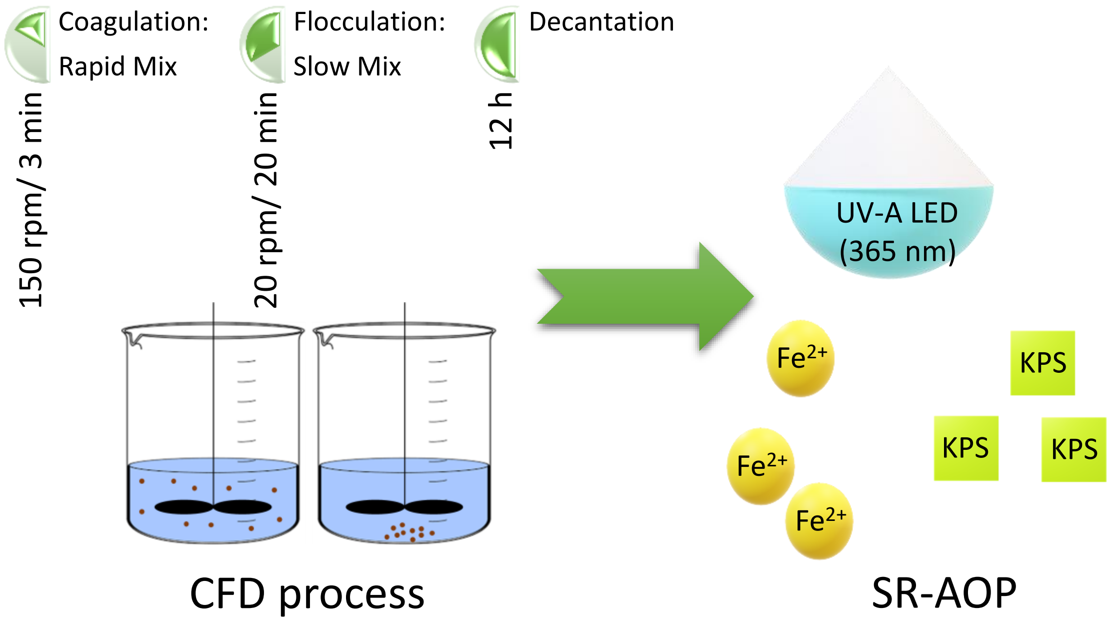
(3) To evaluate the efficiency of combined CFD-SR-AOP process in WW treatment.

Material and methods

Two different winery wastewaters (WW) were studied, and different physical–chemical parameters were monitored in order to characterize the WW, including the chemical oxygen demand (COD), the biochemical oxygen demand (BOD_5), the total organic carbon (TOC) and the total polyphenols.

Characterization of WW1 and WW2

Parameter	Winery wastewater WW1	Winery wastewater WW2
pH	3.74	3.84
Conductivity (µS/cm)	238	245
Turbidity (NTU)	327	643
Total suspended solids (mg/L)	779	1559
Chemical oxygen demand (mg O_2/L)	1119	4640
Biochemical oxygen demand (mg O_2/L)	588	1813
Total organic carbon (mg C/L)	464	997
Total polyphenols (mg gallic acid/L)	22.5	42.9
Ferrous iron (mg Fe/L)	0.10	0.10
Biodegradability index – BOD_5/COD	0.53	0.39



Coagulation-flocculation-decantation Set-up

The coagulation-flocculation-decantation experiments were performed in a conventional model jar-Test apparatus

[potassium caseinate] = 0.4 g/L, [bentonite] = [PVPP] = 0.1 g/L, pH = 3.0, rapid mix (rpm/min) = 150/3, slow mix (rpm/min) = 20/20, sedimentation time = 12 h

Sulfate radical oxidation Set-up

The oxidation process was optimized by application of a Box-Behnken design of Re-sponse Surface Methodology. In the Box-Behnken, three variables were studied (SPS, Fe^{2+} and HA) under three levels for a total of 15 assays, under fixed conditions as follows: pH = 3.0, Temperature = 298 K, time = 300 min

Values of operating parameters at 3 levels in Box-Behnken design

Parameters	Code	Levels -1	Levels 0	Levels 1
[SPS] mM	X_1	15	45	75
[Fe^{2+}] mM	X_2	0.25	1.00	1.75
[HA] mM	X_3	0.00	4.38	8.75

Box-Behnken design

Experimental and predicted percentage of TOC and COD removal for the generated runs in Box-Behnken design

Assay	Coded level			TOC removal		COD removal	
	X1	X2	X3	Observed	Predicted	Observed	Predicted
SR – 1	45	1.75	8.75	25.5	25.8	44.0	42.6
SR – 2	75	0.25	4.38	1.0	0.0	38.0	34.0
SR – 3	15	0.25	4.38	2.8	2.5	28.0	27.3
SR – 4	45	0.25	0.00	31.6	31.4	40.0	41.4
SR – 5	45	1.75	0.00	29.1	27.3	44.0	40.6
SR – 6[a]	45	1.00	4.38	27.2	20.0	47.0	42.3
SR – 7	75	1.00	8.75	4.9	4.4	36.0	36.6
SR – 8	15	1.00	8.75	4.7	3.1	28.0	25.4
SR – 9	45	0.25	8.75	0.5	2.3	19.0	22.4
SR – 10	75	1.00	0.00	21.2	22.7	41.0	43.6
SR – 11[a]	45	1.00	4.38	18.0	20.0	40.0	42.3
SR – 12	15	1.75	4.38	3.8	5.1	30.0	34.0
SR – 13[a]	45	1.00	4.38	15.0	20.0	40.0	42.3
SR – 14	75	1.75	4.38	16.1	16.4	46.0	46.8
SR – 15	15	1.00	0.00	14.8	15.4	36.0	35.4

$$TOC = 4.65 + 1.186\,X1 - 2.99\,X2 - 4.94\,X3 - 0.01356\,X1{*}X1 - 3.40\,X2{*}X2 + 0.185\,X3{*}X3 + 0.1568\,X1{*}X2 - 0.0116\,X1{*}X3 + 2.095\,X2{*}X3 \quad (1)$$

$$COD = 26.86 + 0.488\,X_1 + 6.0\,X_2 - 1.50\,X_3 - 0.00463\,X_1{*}X_1 - 4.74\,X_2{*}X_2 - 0.152\,X_3{*}X_3 + 0.067\,X_1{*}X_2 + 0.0057\,X_1{*}X_3 + 1.600\,X_2{*}X_3 \quad (2)$$

In accordance with the statistical model, the following operational conditions were obtained

[SPS] = 51.96 mM, $[Fe^{2+}]$ = 0,90 mM, pH = 3.0, radiation UV-A (365 nm), Temperature = 298 K, t = 300 min

TOC and COD removal of 19.7 and 31.2%

$$S_2O_8^{2-} + h\nu \rightarrow 2SO_4^{\bullet -} \quad (3)$$

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{\bullet -} + SO_4^{2-} + Fe^{3+} \quad (4)$$

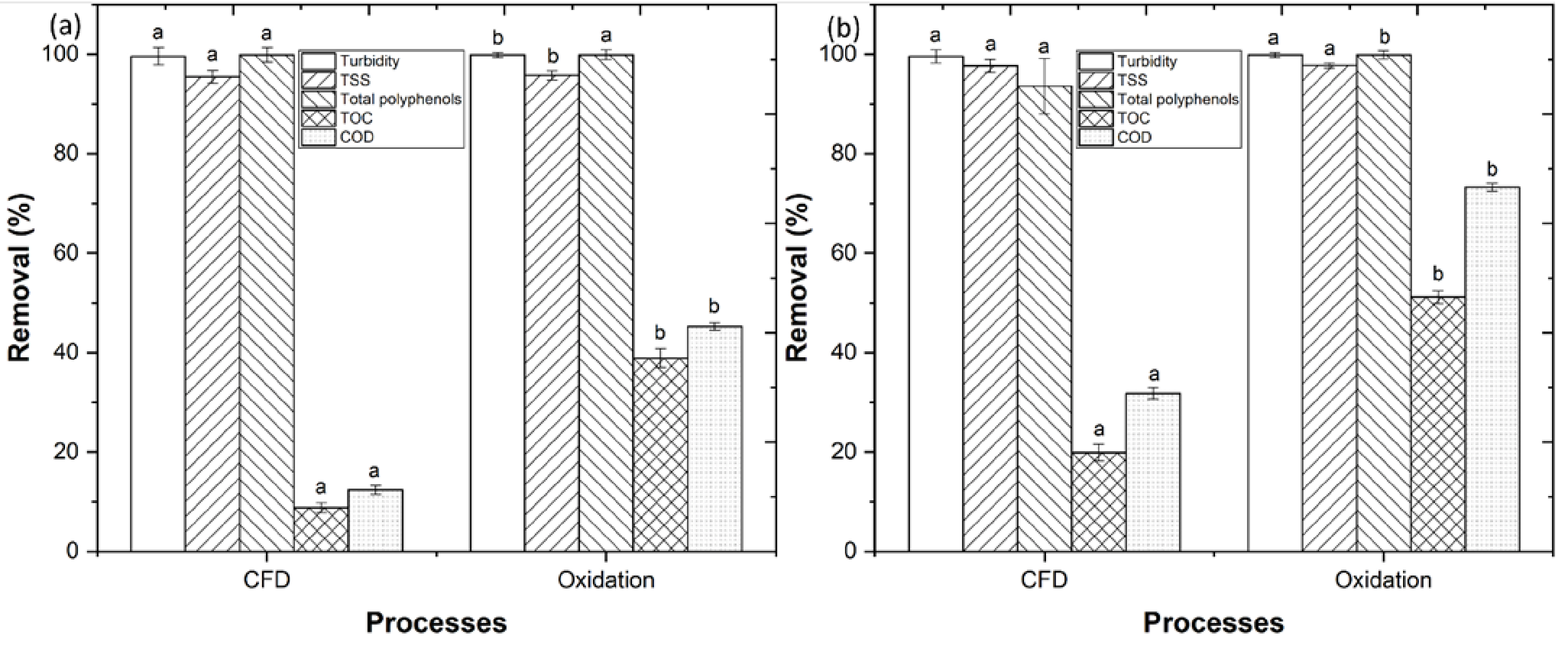
Combination of coagulation-flocculation-decantation-oxidation processes

WW1

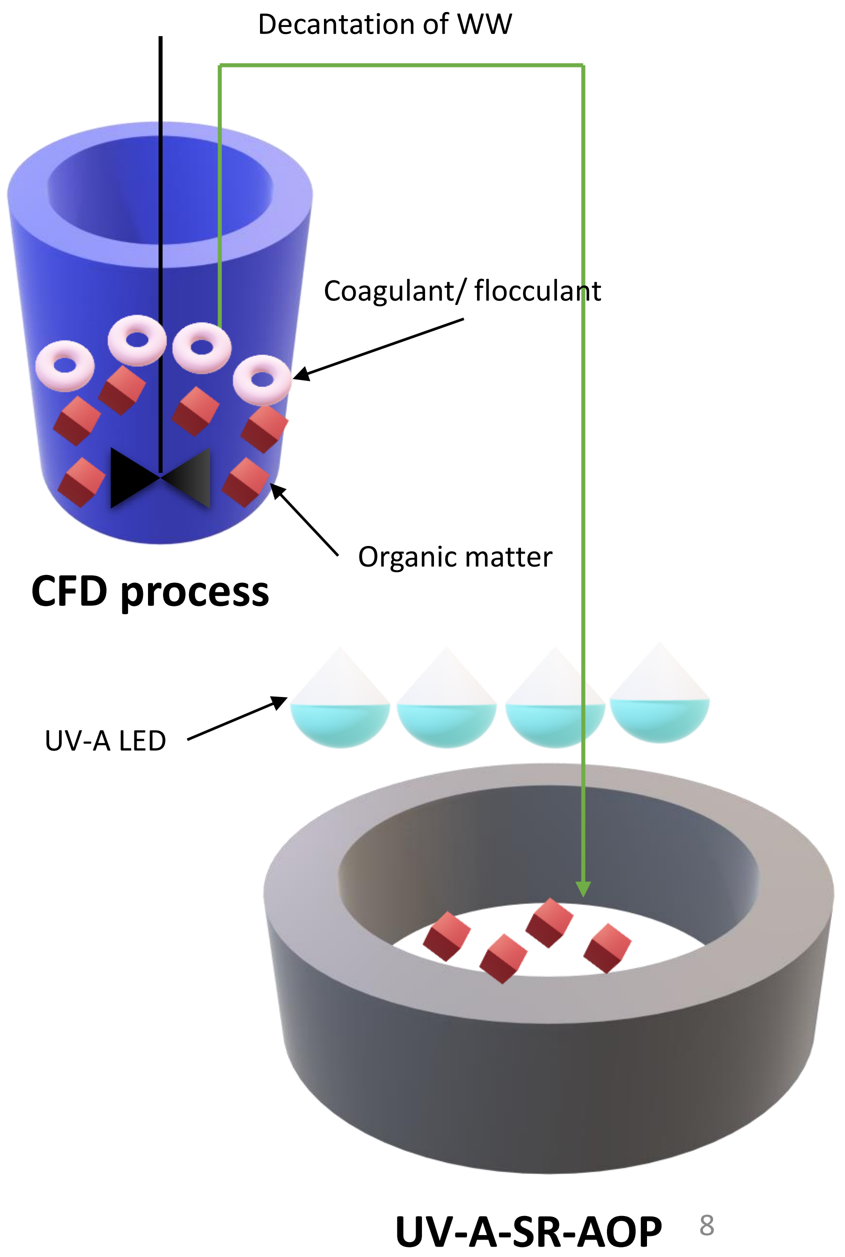
- The CFD process achieved a turbidity, TSS, total polyphenols, TOC and COD removal of 99.6, 95.5, 99.9, 8.8 and 12.4%, respectively
- With performance of oxidation process, it was observed a significant increase to 99.9, 95.8, 99.9, 38.9 and 45.3% removal, respectively

WW2

- With performance of CFD process it was observed a removal of 99.6, 97.7, 93.6, 19.9 and 31.8%, respectively
- With the application of oxidation process, it was observed a significant increase to 99.9, 97.8, 99.9, 51.2 and 73.3% removal, respectively



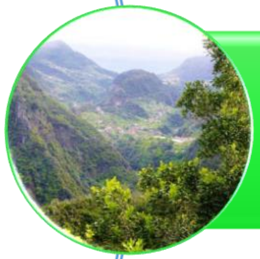
Assessment of the CFD and oxidation processes efficiency in the treatment of (a) WW1 and (b) WW2.



Conclusions

Based in this work's results, it is concluded

1. With the optimization performed by the Box-Behnken design, it is achieved a TOC and COD removal of 19.7 and 31.2%, respectively



2. The application of CFD process to WW1 and WW2 achieves a high removal of turbidity, TSS and total polyphenols

3. The combination of CFD-oxidation processes achieves a high TOC and COD removal for the treatment of WW2 (51.2 and 73.3%, respectively)

Acknowledgements

- The authors thank the North Regional Operational Program (NORTE 2020) and the European Regional Development Fund (ERDF), and express their appreciation for the financial support of the Project AgriFood XXI, operation nº NORTE-01-0145-FEDER-000041, and to the Fundação para a Ciência e a Tecnologia (FCT) for the financial support provided to CQVR through UIDB/00616/2020. Ana R. Teixeira also thanks the FCT for the financial support provided through the Bolsa de Doutoramento UI/BD/150847/2020.

FCT Fundação para a Ciência e a Tecnologia NORTE2020 PORTUGAL 2020 UNIÃO EUROPEIA Fundo Europeu de Desenvolvimento Regional

Thank you for your attention