Plants as natural organic coagulant powders for winery wastewater treatment

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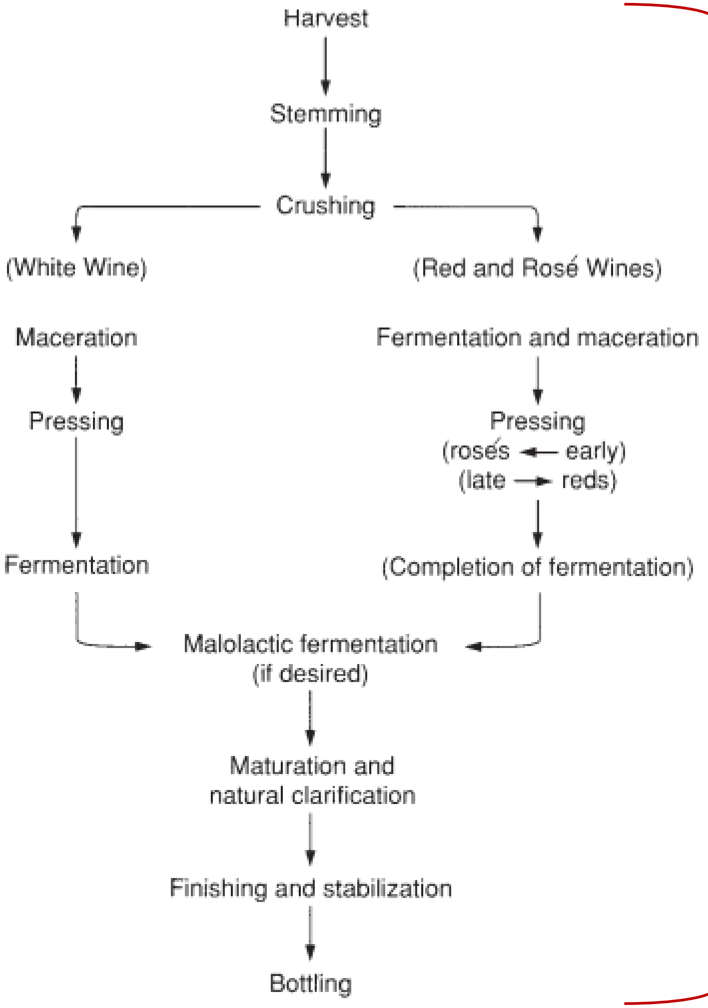
Wine production

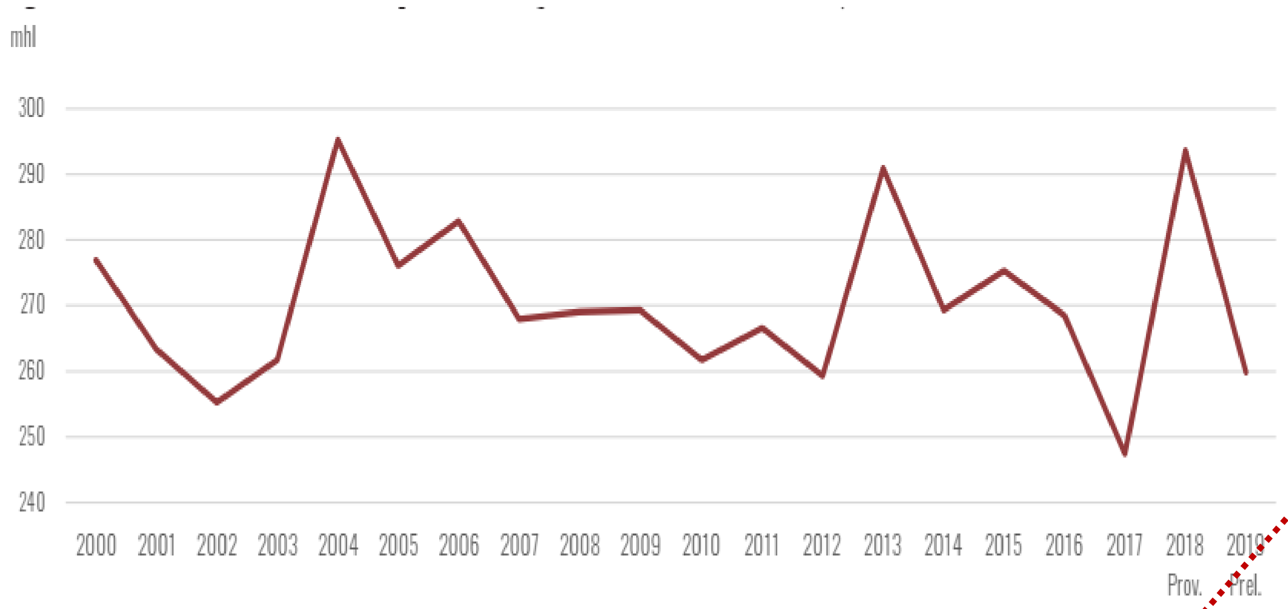


Flow diagram of winemaking process

From grape reception, must vinification to wine stabilization there is always a lot of steps

In each step, there is always a high number of materials that require washing and disinfection

World wine production, excluding juices and musts, in 2019 was estimated at **260 mhl** [1]

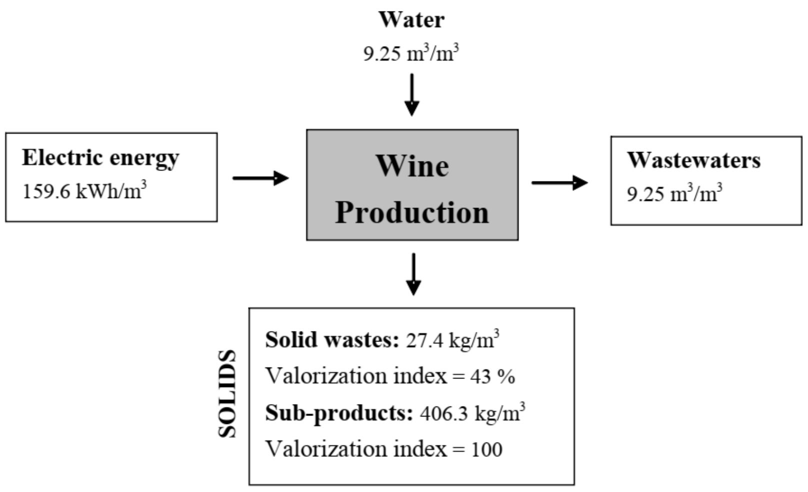


mhl	2015	2016	2017	2018 Prov.	2019 Prel.	2019/2018 % Var.	2019 % world
Italy	50.0	50.9	42.5	54.8	47.5	-13%	18.3%
France	47.0	45.4	36.4	49.2	42.1	-15%	16.2%
Spain	37.7	39.7	32.5	44.9	33.5	-25%	12.9%
USA	21.7	23.7	23.3	24.8	24.3	-2%	9.4%
Argentina	13.4	9.4	11.8	14.5	13.0	-10%	5.0%
Australia	11.9	13.1	13.7	12.7	12.0	-6%	4.6%
Chile	12.9	10.1	9.5	12.9	11.9	-7%	4.6%
South Africa	11.2	10.5	10.8	9.4	9.7	3%	3.7%
Germany	8.8	9.0	7.5	10.3	9.0	-12%	3.5%
China mainland	13.3	13.2	11.6	9.3	8.3	-10%	3.2%
Portugal	7.0	6.0	6.7	6.1	6.7	10%	2.6%
Romania	3.6	3.3	4.3	5.1	4.9	-4%	1.9%
Russia	5.6	5.2	4.5	4.3	4.6	7%	1.8%
New Zealand	2.3	3.1	2.9	3.0	3.0	-1%	1.1%
Austria	2.3	2.0	2.5	2.8	2.5	-10%	0.9%
Hungary	2.6	2.5	2.5	3.6	2.4	-34%	0.9%
Ukraine	1.1	1.1	1.9	2.0	2.1	6%	0.8%
Brazil	2.7	1.3	3.6	3.1	2.0	-34%	0.8%
Greece	2.5	2.5	2.6	2.2	2.0	-8%	0.8%
Georgia	1.2	0.9	1.0	1.7	1.8	1%	0.7%
Moldova	1.6	1.5	1.8	1.9	1.5	-23%	0.6%
Switzerland	0.9	1.1	0.8	1.1	1.0	-12%	0.4%
Other countries	13.9	13.1	12.9	14.0	14.3	2%	5.5%
World total	**275**	**269**	**248**	**294**	**260**	**-11%**	**100%**

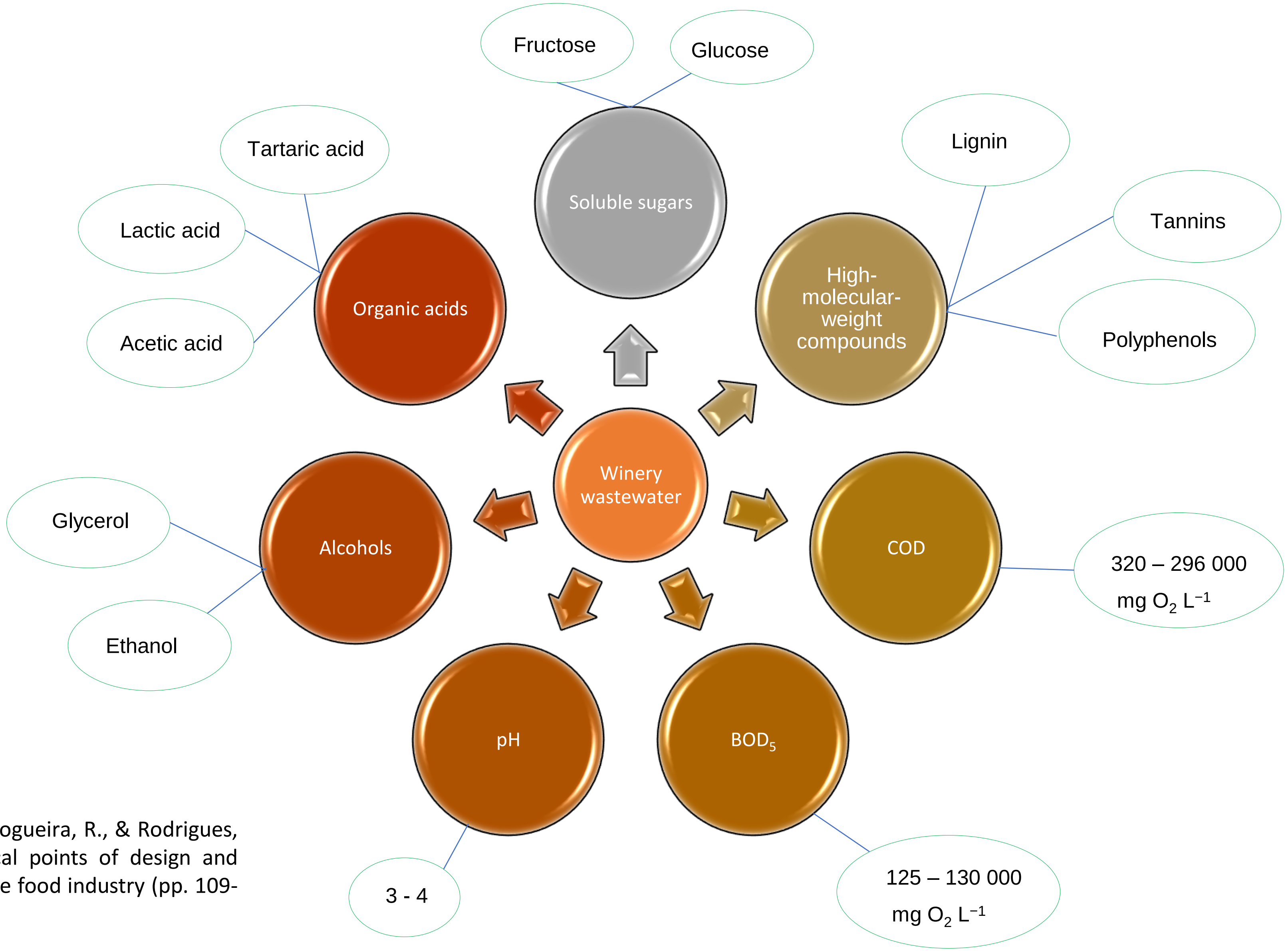
Portugal had a wine production of 6.7 MhL in 2019
Nearly 5 times this value is spent in washing and desinfection processes

[1] STATE OF THE WORLD VITIVINICULTURAL SECTOR IN 2019, OIV.

Winery wastewater main characteristics



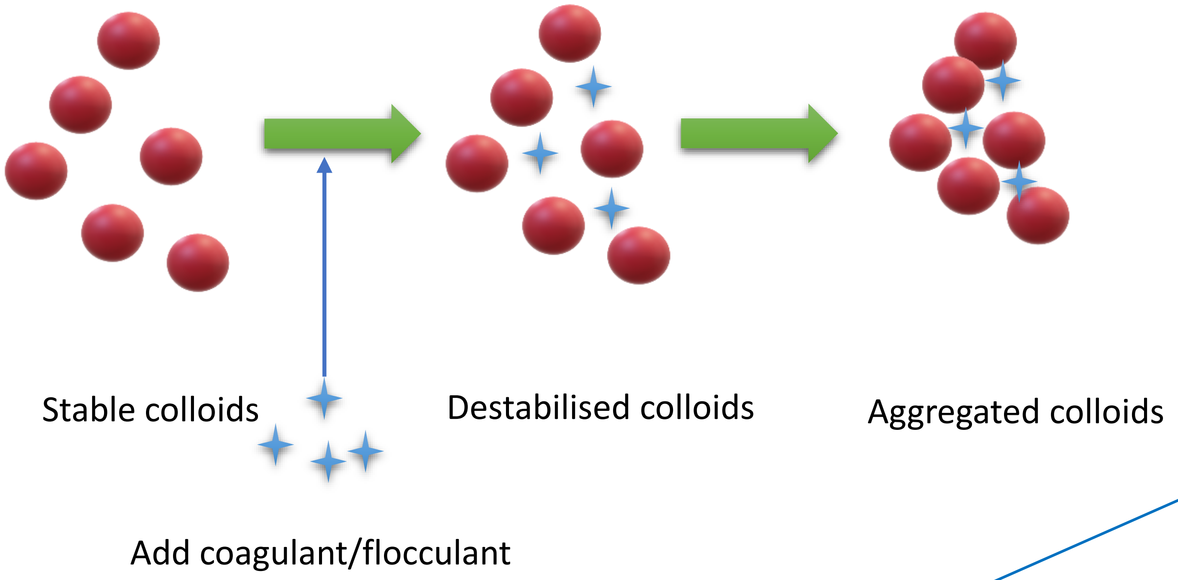
Mass balance applied to ACPB winery representing specific values, i.e., values per cubic meter of produced wine. Losses of water by evaporation were neglected [2].



[2] Brito, A. G., Peixoto, J., Oliveira, J. M., Oliveira, J. A., Costa, C., Nogueira, R., & Rodrigues, A. (2007). Brewery and winery wastewater treatment: some focal points of design and operation. In Utilization of by-products and treatment of waste in the food industry (pp. 109-131). Springer, Boston, MA.

Physical-chemical treatments of wastewater

Coagulation-flocculation-decantation (CFD)



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

  Most used on waster treatment

Disadvantages

Aluminum	Iron
Dialysis encephalopathy Alzheimer's disease	Generally corrosive Strongly dependent on the pH The leach cannot be recycled

Introduction | Objectives | Material and Methods | Results and discussion | Conclusions

Plant species colected during this work, for the development of **Natural Organic Coagulants Powder** (NOCP)

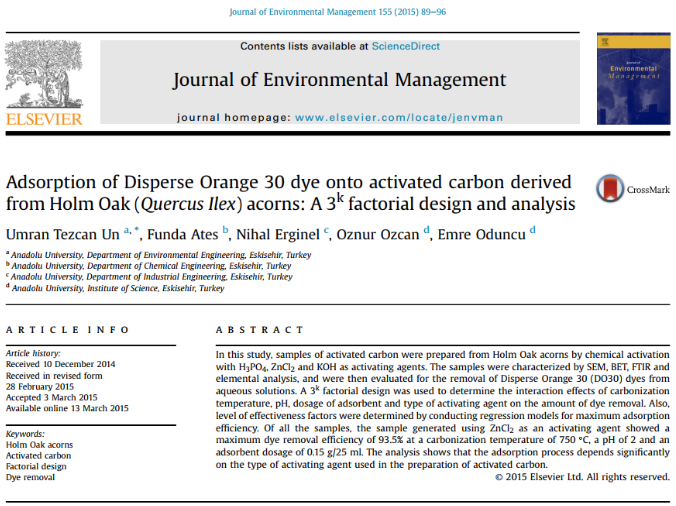
Platanus x acerifólia (Aiton) Willd

Acacia dealbata Link.

Quercus ilex L.

Tanacetum vulgare L.

Works performed with plant based coagulants



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Adsorption of Disperse Orange 30 dye onto activated carbon derived from Holm Oak (*Quercus Ilex*) acorns: A 3^k factorial design and analysis

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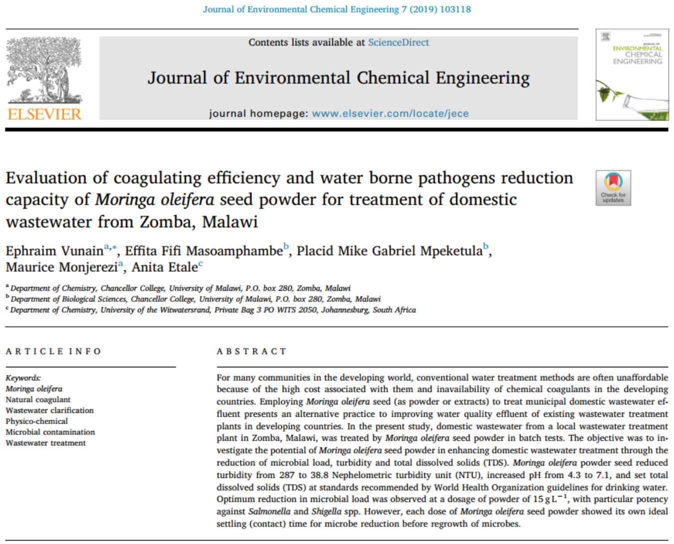
ABSTRACT

In this study, samples of activated carbon were prepared from Holm Oak acorns by chemical activation with H_3PO_4, $ZnCl_2$ and KOH as activating agents. The samples were characterized by SEM, BET, FTIR and elemental analysis, and were then evaluated for the removal of Disperse Orange 30 (DO30) dyes from aqueous solutions. A 3^k factorial design was used to determine the interaction effects of carbonization temperature, pH, dosage of adsorbent and type of activating agent on the amount of dye removal. Also, level of effectiveness factors were determined by conducting regression models for maximum adsorption efficiency. Of all the samples, the sample generated using $ZnCl_2$ as an activating agent showed a maximum dye removal efficiency of 93.5% at a carbonization temperature of 750 °C, a pH of 2 and an adsorbent dosage of 0.15 g/25 ml. The analysis shows that the adsorption process depends significantly on the type of activating agent used in the preparation of activated carbon.



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Evaluation of coagulating efficiency and water borne pathogens reduction capacity of *Moringa oleifera* seed powder for treatment of domestic wastewater from Zomba, Malawi

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ABSTRACT

For many communities in the developing world, conventional water treatment methods are often unaffordable because of the high cost associated with them and inavailability of chemical coagulants in the developing countries. Employing *Moringa oleifera* seed (as powder or extracts) to treat municipal domestic wastewater effluent presents an alternative practice to improving water quality effluent of existing wastewater treatment plants in developing countries. In the present study, domestic wastewater from a local wastewater treatment plant in Zomba, Malawi, was treated by *Moringa oleifera* seed powder in batch tests. The objective was to investigate the potential of *Moringa oleifera* seed powder in enhancing domestic wastewater treatment through the reduction of microbial load, turbidity and total dissolved solids (TDS). *Moringa oleifera* powder seed reduced turbidity from 287 to 38.8 Nephelometric turbidity unit (NTU), increased pH from 4.3 to 7.1, and set total dissolved solids (TDS) at standards recommended by World Health Organization guidelines for drinking water. Optimum reduction in microbial load was observed at a dosage of powder of 15 g L^{-1}, with particular potency against *Salmonella* and *Shigella* spp. However, each dose of *Moringa oleifera* seed powder showed its own ideal settling (contact) time for microbe reduction before regrowth of microbes.

In order to decrease the pollution resulting from the production of wine, a more eco-friendly solution is necessary to treat the winery wastewaters.

Therefore, this work objectives are

Work objectives	
	(1) Produce, characterize and apply NOCP in CFD process
	(2) Optimize CFD process with synthetic polymer "polyvinylpyrrolidone";
	(3) Study the water recovery and environmental impact of NOCP in winery wastewater treatment

Winery wastewater characterization

Main chemical characteristics of winery wastewater (WW)

Parameters	Portuguese Law Decree nº 236/98	WW
pH	6.0-9.0	4.0
Biochemical Oxygen Demand - BOD_5 (mg O_2/L)	40	550
Chemical Oxygen Demand - COD (mg O_2/L)	150	2145
Biodegradability – BOD_5/COD		0.26
Total Organic Carbon – TOC (mg C/L)		400
Turbidity (NTU)		296
Total suspended solids – TSS (mg/L)	60	750
Electrical conductivity (µS/cm)		62.5
Total polyphenols (mg gallic acid/L)	0.5	22.6
Iron (mg/L)	2.0	0.05
Aluminium (mg/L)	10.0	
Cobalt (mg/L)		0.00
Manganese (mg/L)	2.0	
Potassium (mg/L)		20.5
Calcium (mg/L)		1.07
Magnesium (mg/L)		0.51
Sodium (mg/L)		0.19

Winery wastewater used in this work

Winery wastewater collection and storage

Storage in small containers

Conservation at -40ºC

Devices used for NOCP preparation

Groundnut miller

Sieve

Laboratory incubator

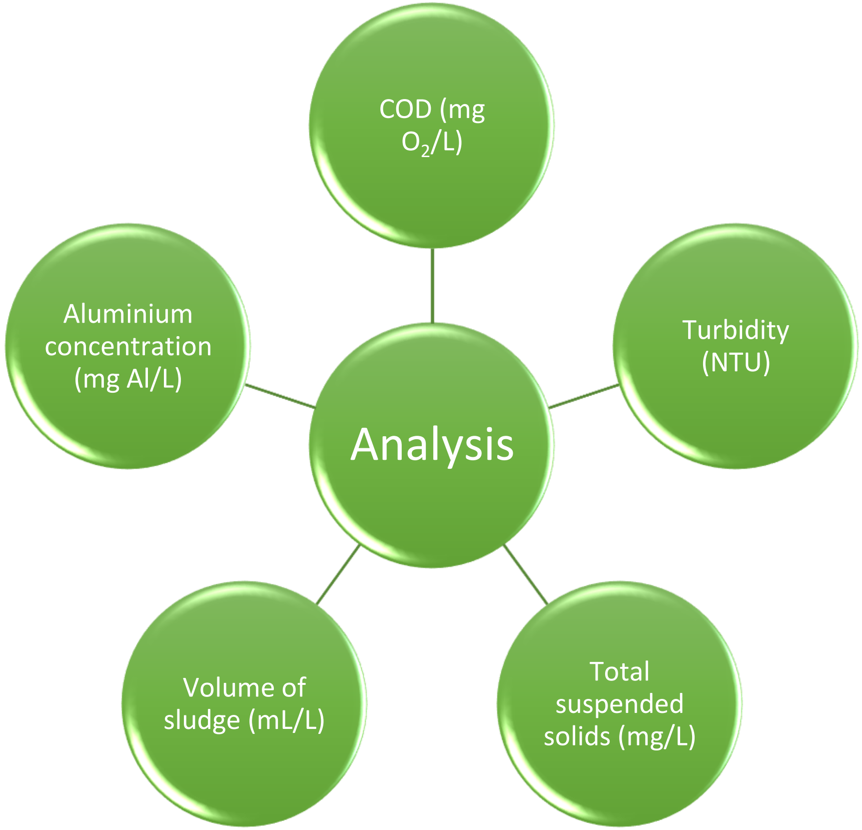
1. Separation of pollen, acorn skin, peeled acorn and seeds from the plants
2. Washing and drying for 24 h at 70 ºC
3. Crushing and sieve until reach a mesh of 150 µm
4. Dry for 24 h at 70 ºC

Devices used for CFD process

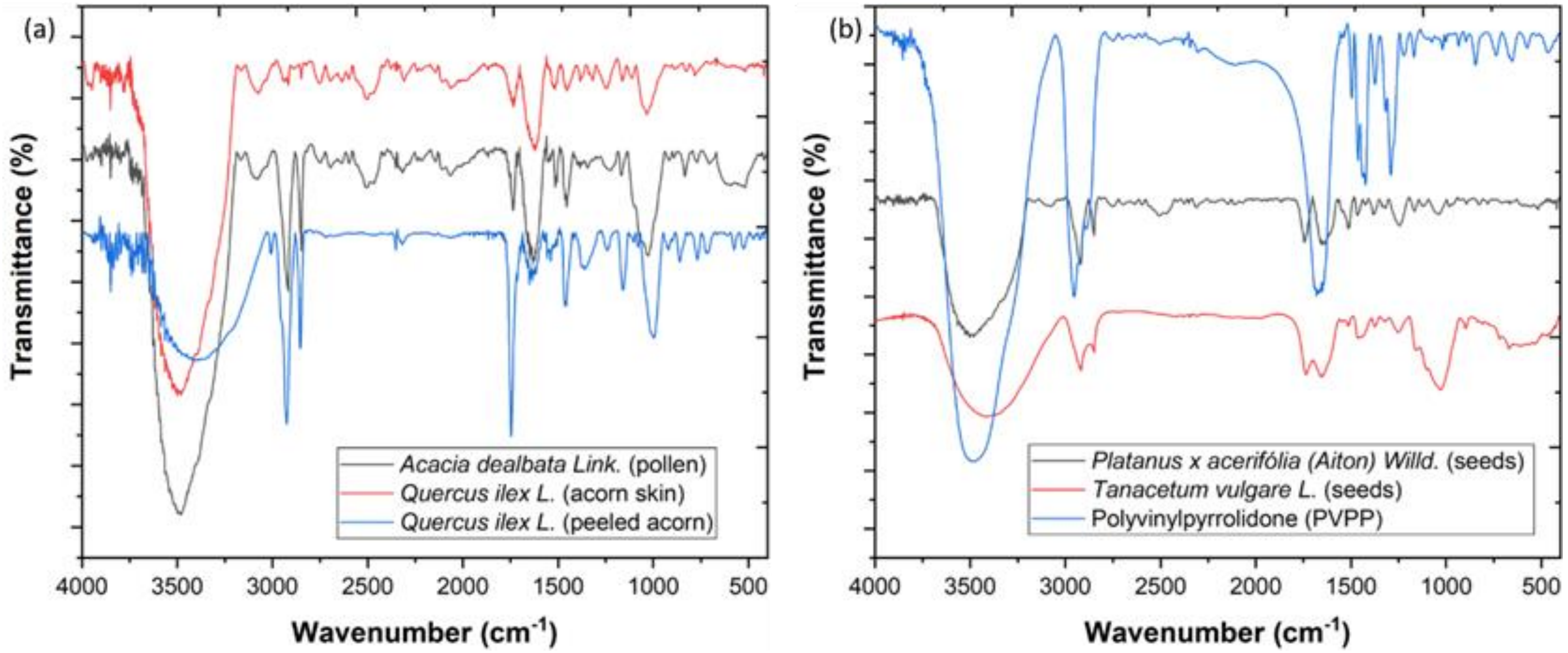
Jar-Test apparatus (ISCO JF-4)

Plant specie	Sub - specie	Part collected	Herbarium number
Acacia dealbata Link.		Pollen	
Quercus ilex L.	*ilex*	Acorn skin	
Quercus ilex L.	*ilex*	Peeled acorn	
Platanus x acerifolia (Aiton) Willd		Seed	
Tanacetum vulgare L.		Seed	HVR22099

Analysis performed after CFD process



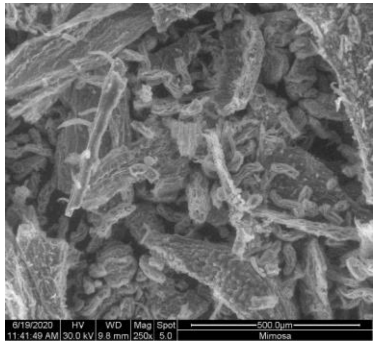
Organic Coagulants Powder characterization



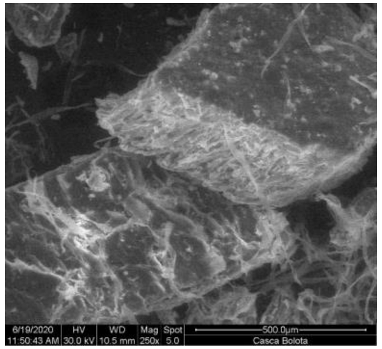
The FTIR spectrum of coagulants poder from (a) pollen (*Acacia dealbata Link*.), acorn skin and peeled acorn (*Quercus ilex L*.), (b) seeds (*Platanus x acerifólia (Aiton) Willd*.), seeds (*Tanacetum vulgare L.*) and Polyvinylpyrrolidone (PVPP).

Wavenumber (cm^{-1})	Compounds
3481.51	phenolic hydroxyl groups (OH stretching vibrating)
2920.23 and 2848.86	C–H and CH_2 vibrations of aliphatic hydrocarbon
1620.20 and 1519.90	amide I: C=O stretch and amide II: NH deformation and C–N stretch from proteins
1163.07, 1110.99 and 1029.98	C–O–C and C–OH stretching from Carbohydrates (Cellulose and Amylose)
1745.57, 1463.97, 1159.21, 995.26 and 713.66	C=O stretching, CH_2 deformation, C–O–C stretching and CH_2 rocking from Lipids (Triglycerides and Phospholipids)

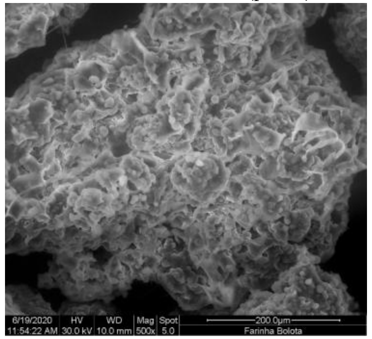
Organic Coagulants Powder characterization



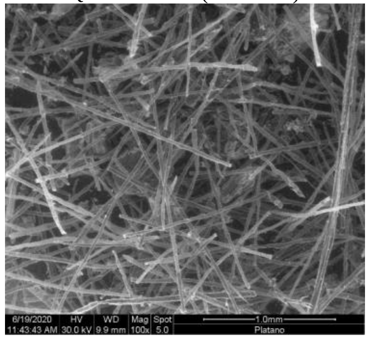
Acacia dealbata Link. (pollen)



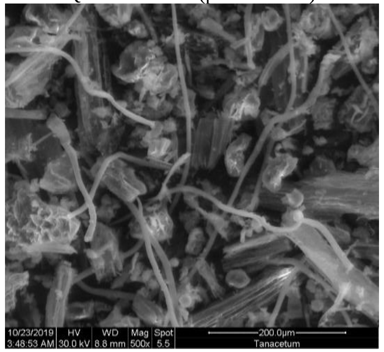
Quercus ilex L. (acorn skin)



Quercus ilex L. (peeled acorn)



Platanus x acerifolia (Aiton) Willd (seeds)



Tanacetum vulgare L. (seeds)

Scanning electron microscopy (SEM) images of pollen (*Acacia dealbata Link.*), acorn skin and peeled acorn (*Quercus ilex L.*), seeds (*Platanus x acerifólia (Aiton) Willd.*) and seeds (*Tanacetum vulgare L.*).

Results of iron, copper, sodium, potassium, calcium and magnesium present in 500 mg of coagulants powder from pollen (*Acacia dealbata Link.*), acorn skin and peeled acorn (*Quercus ilex L.*), seeds (*Platanus x acerifólia (Aiton) Willd.*) and seeds (*Tanacetum vulgare L.*) in mg/L.

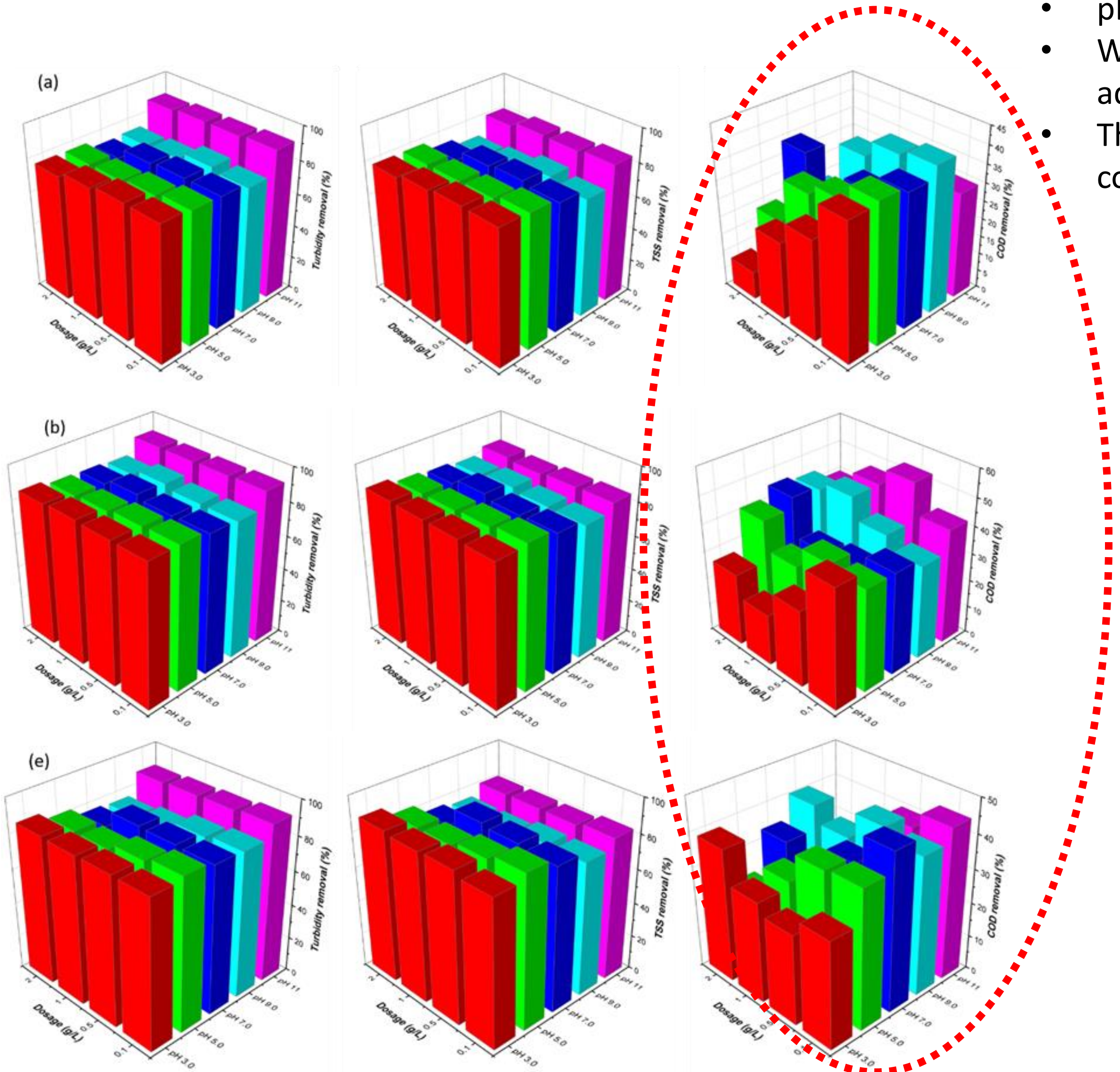
Coagulants	Iron	Copper	Sodium	Potassium	Calcium	Magnesium
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Pollen *(Acacia dealbata Link.)*	1.6	0.4	99.5	777.4	94.8	74.9
Acorn skin *(Quercus ilex L.)*	5.2	0.2	49.2	61.5	110.6	27.4
Peeled acorn *(Quercus ilex L.)*	0.5	0.2	45.0	407.8	22.7	26.9
Seeds *(Platanus x acerifolia (Aiton) Willd)*	3.1	0.3	54.1	137.1	81.5	45.0
Seeds *(Tanacetum vulgare L.)*	2.2	0.4	626.4	633.1	311.6	126.1

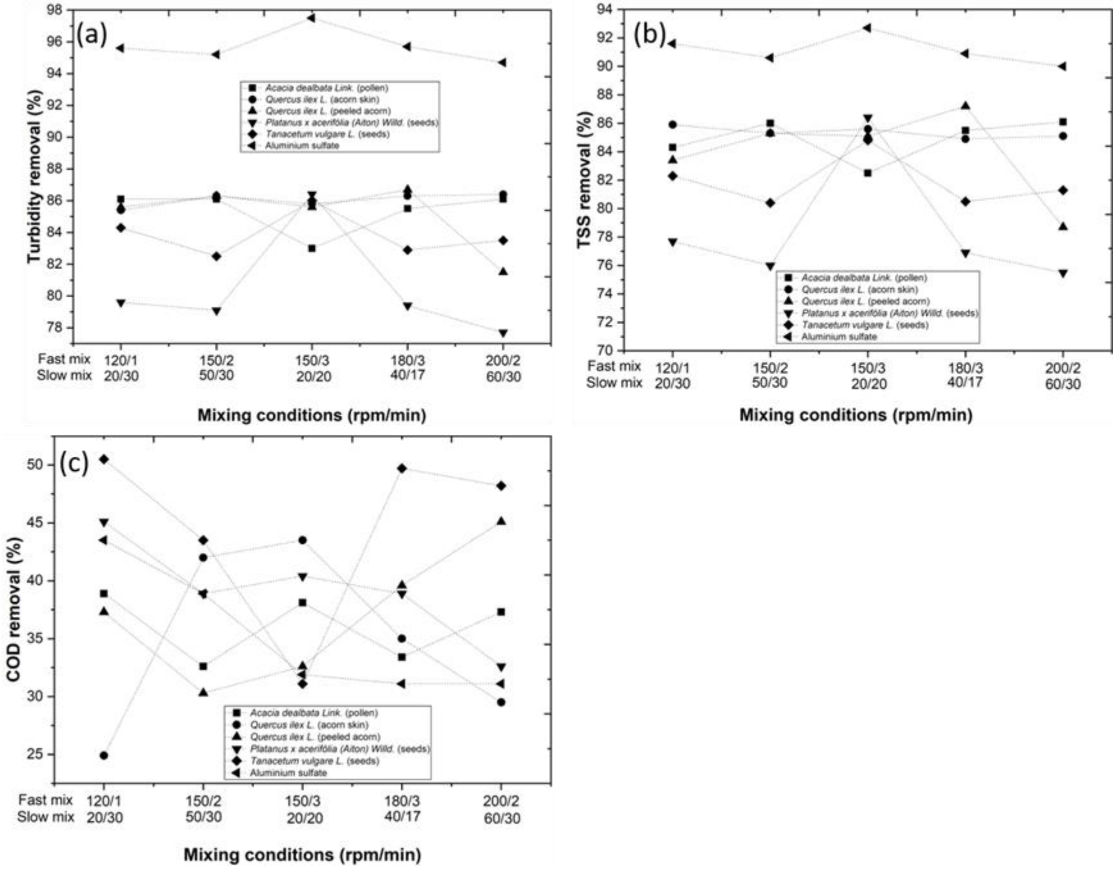
Low toxicity due to low iron and copper concentration

pH vs Dosage optimization (Phase one)

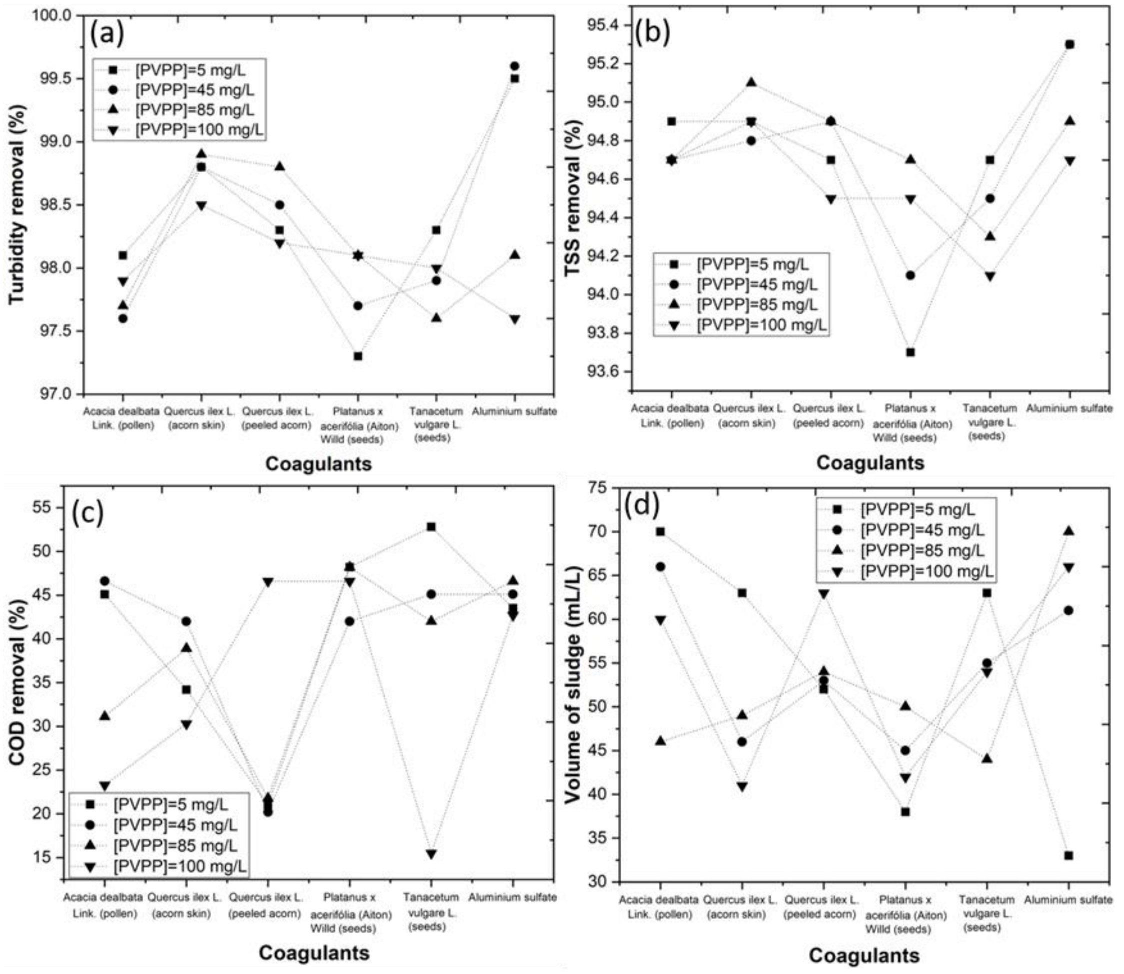
Mixing optimization (Phase two)

- pH 3.0 is the most efficient;
- With the increase of the coagulant dosage, more carbon is been added to the WW;
- The efficiency of the coagulants is dependent of the mixing conditions.





Effect of polyelectrolyte (PVPP) on coagulation-flocculation-decantation process (Phase three)



Effect of polyelectrolyte (PVPP) addition in the removal of (a) turbidity, (b) TSS, (c) COD, (d) volume of sludge. CFD operational condition ($[COD]_0$ = 2145 mg O_2/L, turbidity = 296 NTU, TSS = 750 mg/L, temperature 298 K, sedimentation time 12 h).

Best operational conditions of coagulants powder from pollen (*Acacia dealbata Link.*), acorn skin and peeled acorn (*Quercus ilex L.*), seeds (*Platanus x acerifólia (Aiton) Willd.*), seeds (*Tanacetum vulgare L.*) and aluminium sulfate for CFD process ($[COD]_0$ = 2145 mg O_2/L, turbidity = 296 NTU, TSS = 750 mg/L, temperature 298 K, sedimentation time 12 h).

Optimization phases	Phase One				
	Phase Two				
	Phase Three				
Coagulant	pH	Coagulant dosage	Fast mix	Slow mix	[PVPP]
		g/L	rpm/min	rpm/min	mg/L
Pollen *(Acacia dealbata Link.)*	3	0.1	120/1	20/30	45
Acorn skin *(Quercus ilex L.)*	3	0.1	150/3	20/20	45
Peeled acorn *(Quercus ilex L.)*	3	0.1	180/3	40/17	100
Seeds *(Platanus x acerifolia (Aiton) Willd)*	3	0.1	150/3	20/20	5
Seeds *(Tanacetum vulgare L.)*	3	0.1	120/1	20/30	5
Aluminium sulfate	5	1.0	120/1	20/30	5

- COD removal of 46.6, 42.0, 46.6, 48.2, 52.8 and 43.5% respectively
- TSS removal of 94.7, 94.8, 94.5, 93.7, 94.7 and 95.3% respectively
- Turbidity removal of 97.6, 98.8, 98.2, 97.3, 98.3 and 99.5% respectively
- A sludge volume of 66, 46, 63, 38, 63 and 33 mL/L was produced after CFD process

Effect of polyelectrolyte (PVPP) on coagulation-flocculation-decantation process (Phase three)

Residual aluminium test

	[Polyelectrolyte] (mg/L)			
Coagulants	**5**	**45**	**85**	**100**
Pollen (*Acacia dealbata Link.*)	0.24	0.10	0.13	0.14
Acorn skin (*Quercus ilex L.*)	0.08	0.07	0.06	0.12
Peeled acorn (*Quercus ilex L.*)	0.04	0.06	0.07	0.09
Seeds (*Platanus x acerifólia (Aiton) Willd.*)	0.24	0.13	0.25	0.10
Seeds (*Tanacetum vulgare L.*)	0.19	0.08	0.09	0.07
Aluminium sulfate	739.43	762.53	824.12	777.93

Residual aluminium concentration above legal limit (> 10 mg Al/L)

Based in the results it is concluded that

1. The pollen of *Acacia dealbata Link.*, the acorn skin and peeled acorn of *Quercus ilex L. and the seeds of Platanus x acerifólia (Aiton) Willd.* and *Tanacetum vulgare L.* can be used to produce NOCPs for WW treatment

2. The NOCPs achieve higher turbidity, TSS and COD removal at WW pH 3.0 and lower dosage (0.1 g/L) in comparison to aluminium sulfate (pH 5.0, dosage 1.0 g/L)

3. With addition of PVPP it is possible to increase the turbidity, TSS and COD removal from the wastewater, and achieve low sludge volume production

4. The performance of CFD process with NOCPs is concluded to be safer to the environment, due to the reduced concentration of aluminium present in the wastewater (10 mg Al/L<) regarding aluminium sulfate (> 10 mg Al/L)

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Thank you for your attention