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Proceeding Paper

Plants as Natural Organic Coagulant Powders for Winery Wastewater Treatment †

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Abstract: The horticulture development of several plants such as *Acacia dealbata* Link. (pollen), *Quercus ilex* L. (acorn skin), *Quercus ilex* L. (peeled acorn), *Platanus x acerifólia (Aiton) Willd*. (seeds) and *Tanacetum vulgare* L. (seeds) in natural organic coagulant powder (NOCP), was aimed to treat winery wastewater (WW) by coagulation-flocculation-decantation process (CFD). The plants were characterized by Fourier-transform infrared spectroscopy (FTIR), which showed the presence of protein, lipids and carbohydrates. The CFD results demonstrated that application of *Acacia dealbata* Link. (pollen) achieved similar turbidity, total suspended solids and chemical oxygen demand removal (97.6%, 94.7% and 46.6%) than aluminium sulfate (99.5, 95.3 and 43.5), with the advantage of low sludge production (66 mL/L) and low aluminium leaching concentration (0.10 mg Al/L). In conclusion, OCPs are a promising technology in horticulture development.

Keywords: *Acacia dealbata* Link.; Horticulture; organic coagulants powder

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1. Introduction

Winery wastewater (WW) is the waste product of many independent processing and cleaning operations in wineries, which annually generate a large volume of wastewater [1,2]. In order to treat these wastewaters, psychical-chemical treatments, such as coagulation-flocculation-decantation process (or CFD process) is one of the most commonly applied techniques to achieve efficient solid-liquid separation in water treatment [3]. There are many studies in which CFD process was used to treat cork processing wastewaters [4], landfill leachates [5], winery wastewater [6–9], among others. Traditionally, it's used metallic based coagulants such as ferric chloride and aluminium sulfate, however, the release of metal residuals in the wastewater during the CFD process, may result in adverse effects for the receiving water body, and the sludge produced in the coagulation step may not be reused because of the presence of the metals, thus the necessity of a proper disposal will increase the management costs [8]. To avoid these consequences, many authors have studied alternatives, such as the use of organic coagulants such as *Moringa oleifera* [10,11], Chitosan [8], cactus plants [12], among others. In this work the species *Acacia dealbata* Link. (pollen), *Quercus ilex* L. (acorn skin), *Quercus ilex* L. (peeled acorn), *Platanus x acerifólia (Aiton) Willd*. (seeds) and *Tanacetum vulgare* L. (seeds) were tested as possible coagulating agents, due to the fact that there is very little information about these species, and since non one of them was ever used in winery wastewater treatment. Therefore, the aim of this work is (1) to produce and apply OCP in CFD process, (2) to optimize CFD process with synthetic polymer "polyvinylpyrrolidone" and (3) to evaluate the environmental impact of NOCPs in WW treatment.

2. Material and Methods

2.1. Reagents and Winery Wastewater Sampling

Aluminium sulfate 18-hydrate (10% *w/w*, $Al_2(SO_4)_3 \bullet 18H_2O$) was acquired by Scharlau, Barcelona, Spain and polyvinylpyrrolidone (10% *w/w*, PVPP) by A. Freitas Vilar, Lisboa, Portugal. For pH adjustment, it was used sodium hydroxide (NaOH) from Labkem, Barcelona, Spain and sulphuric acid (H_2SO_4, 95%) from Scharlau, Barcelona, Spain. Deionized water was used to prepare the respective solutions.

2.2. Analytical Technics

Different physical-chemical parameters were determined in order to characterize the WW, including turbidity, total suspended solids (TSS), chemical oxygen demand (COD), biological oxygen demand (BOD_5), total organic carbon (TOC) and total polyphenols. The main wastewater characteristics are shown in Table 1.

Table 1. Winery wastewater characterization.

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
Total Nitrogen—TN (mg N/L)	15	9.07
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	0.00

2.3. Organic Coagulants Preparation

All the plants used on this work were collected on the district of Vila Real (Portugal), and transported to the Environmental Engineering Laboratory of the University of Trás-os-Montes and Alto Douro, Vila Real, where they were stored until used. In Table 2, it is indicated the plants sub-species, part collected for this study and the herbarium number attributed by UTAD for the plant's identification.

All the vegetable parts collected were washed and dried in an oven at 70 °C for 24 h. Them they were grounded into powder using a groundnut miller. The grounded powder was sieved to a mesh size of 150 µm to obtain the powder. Finally, the powder was once more dried in an oven at 70 °C for 30 min to remove the moisture. The powder was then left to cool and stored in a tightly closed plastic jar.

Table 2. Plant identification, with description of specie, sub-specie, part collected and herbarium number.

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

2.4. Characterization of Plant Powder

The FTIR spectra was obtained by mixing 2 mg powder with 200 mg KBr. The powder mixtures were then inserted into molds and pressed at 10 ton/cm^2 to obtain the transparent pellets. The samples were analyzed with an IRAffinity-1S Fourier Transform Infrared spectrometer (Shimadzu, Kyoto, Japan) and the infrared spectra in transmission mode were recorded in the 4000–400 cm^{-1} frequency region. The microstructural characterization was carried out with a scanning electron microscopy (FEI QUANTA 400 SEM/ESEM, Fei Quanta, Hillsboro, WA, USA).

The FTIR analysis of the plants (Figure 1) showed a band at 3481.51 cm^{-1}, which is related to the presence of the phenolic hydroxyl groups (OH stretching vibrating). The 2920.23 and 2848.86 cm^{-1} absorption bands were attributed to C–H and CH_2 vibrations of aliphatic hydrocarbon. The 1631.78, 1514.12 and 1454.33 cm^{-1} absorption bands were linked to aromatic ring stretching vibration [13,14]. The 1028.06 cm^{-1} absorption band was attributed to C–O stretching vibration from the glucose ring vibration and the holocellulose and hemicellulose [13–15]. From 1200–1000 cm^{-1} absorption bands, it is included the C–O–C symmetrically stretching vibration and the aromatic C–H in-plane bending vibrations [15].

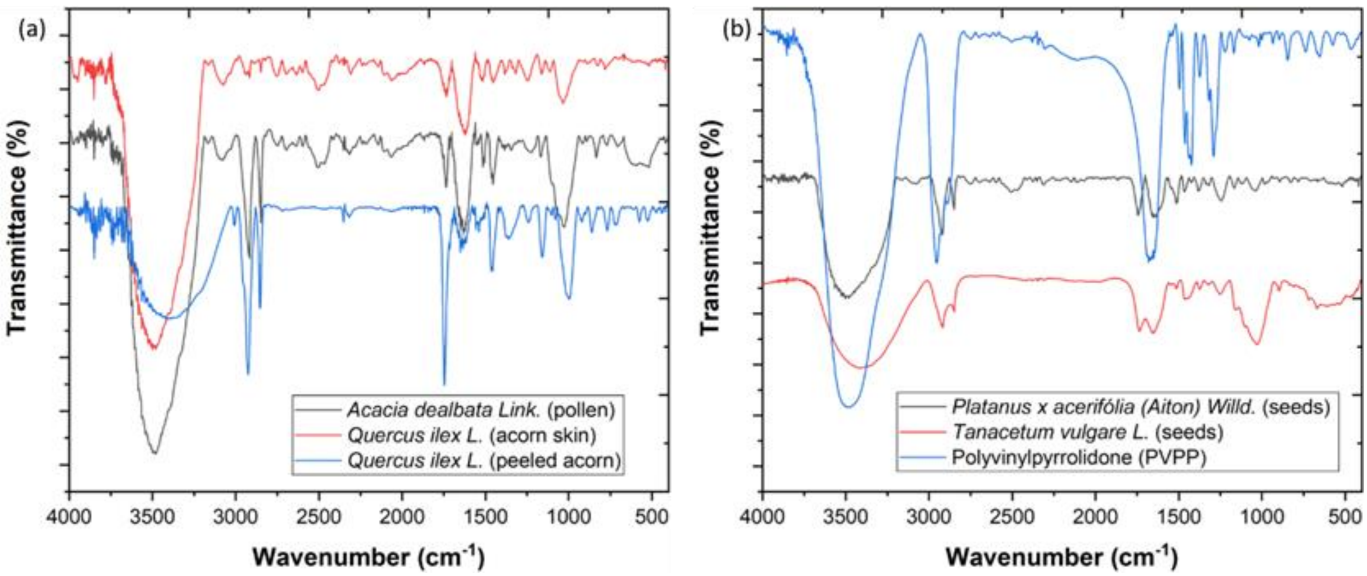

Figure 1. The FTIR spectrum of (**a**) coagulants powder *Acacia dealbata* Link. (pollen), *Quercus ilex* L. (acorn skin) and *Quercus ilex* L. (peeled acorn), (**b**) *Platanus x acerifólia (Aiton) Willd*. (seeds), *Tanacetum vulgare* L. (seeds) and Polyvinylpyrrolidone (PVPP).

In Figure 2, it is shown the SEM images of the organic coagulants powder used as coagulants in this work. It was observed that the organic materials exhibited a heterogeneous and relatively porous morphology. The spaces available could increase the adsorption process, because they provide a high internal surface area. The chainlike and spherical structures observed in the SEM images can contribute to lower the turbidity in the settled water (sludge), a fact observed by Vunain et al. [16], Boulaadjoul et al. [17] and Araujo et al. [18].

2.5. Coagulation-Flocculation-Decamtation Experimental Set-Up

The Coagulation-flocculation-decantation (CFD) experiments were performed in a conventional model jar-Test apparatus (ISCO JF-4, Louisville, KY, USA), using 500 mL of effluent in 1000 mL beakers. The equipment was provided by a set of 4 mechanic agitators, powered by a regulated speed engine. The optimization process was performed in 3 phases (1) variation of pH vs. dosage, (2) variation of mixing conditions and (3) variation of flocculant PVPP dosage, under the following fixing conditions: temperature 298 K, sedimentation time 12 h (Table 3).

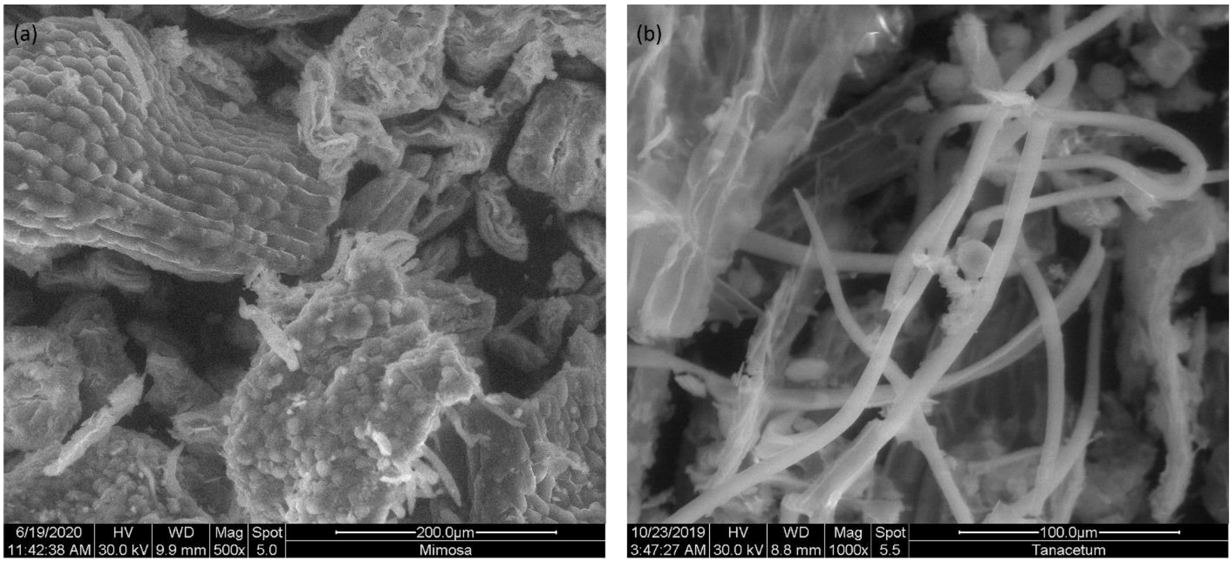

Figure 2. Scanning electron microscopy (SEM) images of organic coagulants powder (**a**) *Acacia dealbata* Link. (pollen) and (**b**) *Tanacetum vulgare* L. (seeds).

2.6. Statistical Analysis

All the experiments were performed in triplicate and differences among means were determined by analysis of variance (ANOVA) using OriginLab 2019 software (Northampton, MA, USA) and the Tukey's test was used for the comparison of means, which were considerate different when $p < 0.05$. The data are presented as mean and standard deviation (mean ± SD).

3. Results and Discussion

This study was performed in order to answer to one of this works main objectives, to produce and apply OCP in CFD process for the treatment of WW. To study the efficiency of OCP's, it was performed an additional coagulation with application of aluminium sulfate. In Table 3 it is shown the best operational conditions for each coagulant.

Table 3. Best operational conditions of coagulants powder *Acacia dealbata* Link. (pollen), *Quercus ilex* L. (acorn skin), *Quercus ilex* L. (peeled acorn), *Platanus x acerifólia (Aiton) Willd*. (seeds), *Tanacetum vulgare* L. (seeds) 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).

Coagulant	**pH**	**Coagulant Dosage**	**Fast Mix**	**Slow Mix**	**[PVPP]**
		g/L	**rpm/min**	**rpm/min**	**mg/L**
Acacia dealbata Link. (pollen)	3	0.1	120/1	20/30	45
Quercus ilex L. (acorn skin)	3	0.1	150/3	20/20	45
Quercus ilex L. (peeled acorn)	3	0.1	180/3	40/17	100
Platanus x acerifólia (Aiton) Willd. (seeds)	3	0.1	150/3	20/20	5
Tanacetum vulgare L. (seeds)	3	0.1	120/1	20/30	5
Aluminium sulfate	5	1.0	120/1	20/30	5

With the application of the best operational conditions in Table 3, it was observed ad a turbidity removal of 97.6%, 98.8%, 98.2%, 97.3%, 98.3% and 99.5% respectively, a TSS removal of 94.7%, 94.8%, 94.5%, 93.7%, 94.7% and 95.3% respectively and a COD removal of 46.6%, 42.0%, 46.6%, 48.2%, 52.8% and 43.5% respectively, for *Acacia dealbata* Link. (pollen), *Quercus ilex* L. (acorn skin), *Quercus ilex* L. (peeled acorn), *Platanus x acerifólia (Aiton) Willd*. (seeds), *Tanacetum vulgare* L. (seeds) and aluminium sulfate. After selection of the best operational conditions the coagulants in combination with PVPP produced a low sludge volume (66, 46, 63, 38, 63 and 33 mL/L) allowing a higher recuperation of water. The high removal levels of turbidity, TSS and COD observed with the application of OCP are related to the existence of proteins, which was reveled after the FTIR analysis. According to Ndabigengesere et al. [19], the active agents of coagulation are dimeric cationic proteins with a molecular weight of approximately 13 kDa having an isoelectric point between 10 and 11. Therefore, from pH 3.0 to 7.0, the behavior of the coagulants was consistent with a charge interaction/neutralization mechanism between the positively charged proteins and the negatively charged colloidal suspensions. Finally, the environmental impact of the coagulants was evaluated, by determination of the residual aluminium present in the wastewater. Results showed an Al^{3+} concentration of 0.10, 0.07, 0.09, 0.19 and 739.43 mg Al/L, respectively. Clearly the application of aluminium sulfate can be toxic to the environmental due the high aluminium leaching, above the Portuguese legislated value (10 mg Al/L <).

4. Conclusions

Based in the results it is concluded that: (1) OCPs can be produced from *Acacia dealbata* Link. (pollen), *Quercus ilex* L. (acorn skin), *Quercus ilex* L. (peeled acorn), *Platanus x acerifólia (Aiton) Willd*. (seeds) and *Tanacetum vulgare* L. (seeds) and applied as coagulants; (2) NOCPs in combination with PVPP achieve high removal of turbidity, TSS and COD with low sludge volume; (3) NOCPs are environmentally safer than aluminium sulfate.

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