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# 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* × *acerifólia (Aiton) Willd*. (seeds) and *Tanacetum vulgare* L. (seeds), in organic coagulant powder (OCP), was utilised to treat winery wastewater (WW) through a 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 the 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 the CFD process was used to treat cork processing wastewaters [4], landfill leachates [5], winery wastewater [6–9], among others. Traditionally, it 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* × *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 none of them was ever used in winery wastewater treatment. Therefore, the aim of this work is (1) to produce and apply OCP in the CFD process, (2) to optimize the CFD process with a 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*, $Al_2(SO_4)_3 \cdot 18H_2O$) was acquired by Scharlau, Barcelona, Spain, and polyvinylpyrrolidone (10% *w*/*w*, PVPP) by A. Freitas Vilar, Lisboa, Portugal. For pH adjustment, sodium hydroxide (NaOH) from Labkem, Barcelona, Spain, and sulphuric acid ($H_2SO_4$, 95%) from Scharlau, Barcelona, Spain, were used. 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 Coagulant Preparation*

All the plants used in this work were collected in 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 use. In Table 2, the plants sub-species, parts collected for this study and the herbarium number attributed by UTAD for the plant's identification are indicated.

All the vegetable parts collected were washed and dried in an oven at 70 °C for 24 h. Them, they were ground into powder using a groundnut miller. The ground powder was sieved to a mesh size of 150 µm to obtain a 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 species, sub-species, parts 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* × *acerifolia (Aiton) Willd.* | | Seed | |
| *Tanacetum vulgare* L. | | Seed | HVR22099 |

### 2.4. Characterization of Plant Powder

The FTIR spectra were obtained by mixing 2 mg powder with 200 mg KBr. The powder mixtures were then inserted into moulds and pressed at 10 ton/cm$^2$ to obtain the transparent pellets. The samples were analysed with an IRAffinity-1S Fourier Transform Infrared spectrometer (Shimadzu, Kyoto, Japan) and the infrared spectra in transmission mode were recorded in a 4000–400 cm$^{-1}$ frequency region. The microstructural characterization was carried out with 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 to 1000 cm$^{-1}$ absorption bands, the C–O–C symmetrically stretching vibration and the aromatic C–H in-plane bending vibrations are included [15].

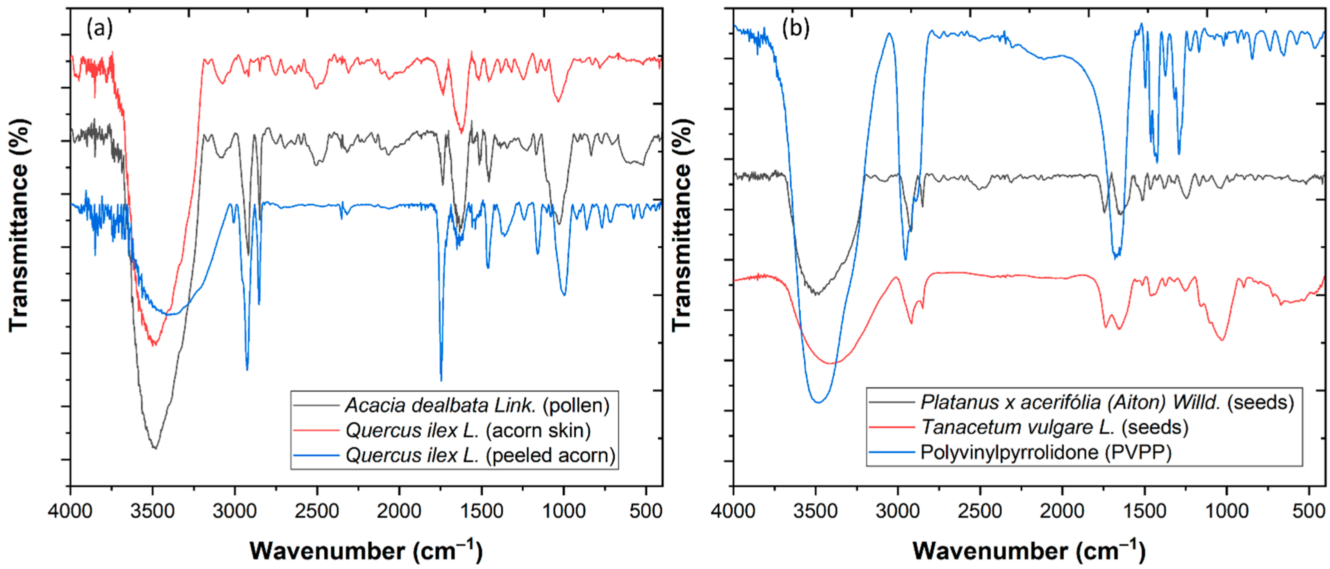


**Figure 1.** The FTIR spectrum of (**a**) coagulants powder *Acacia dealbata* Link. (pollen), *Quercus ilex* L. (acorn skin) and *Quercus ilex* L. (peeled acorn), (**b**) *Platanus* × *acerifólia (Aiton) Willd.* (seeds), *Tanacetum vulgare* L. (seeds) and Polyvinylpyrrolidone (PVPP).

In Figure 2, the SEM images of the organic coagulant powder used as coagulants in this work are shown. 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 in lowering the turbidity in the settled water (sludge), a fact observed by Vunain et al. [16], Boulaadjoul et al. [17] and Araujo et al. [18].

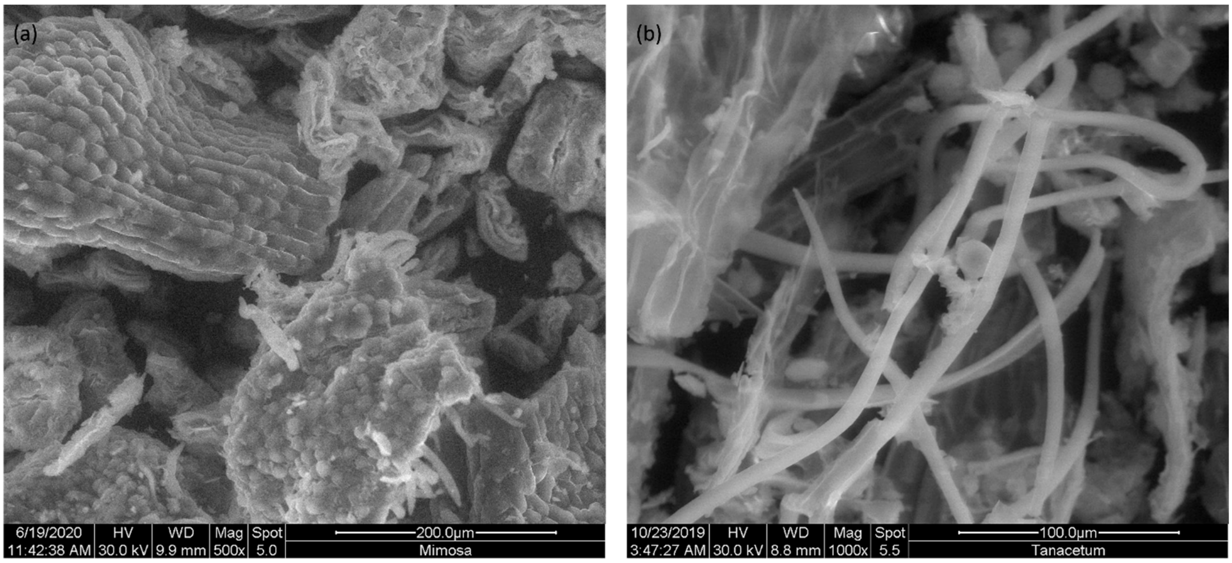


**Figure 2.** Scanning electron microscopy (SEM) images of organic coagulants powder (**a**) *Acacia dealbata* Link. (pollen) and (**b**) *Tanacetum vulgare* L. (seeds).

### 2.5. Coagulation–Flocculation–Decantation 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 in pH vs. dosage, (2) variation in mixing conditions and (3) variation in flocculant PVPP dosage. Fixing conditions are as follows: temperature 298 K, sedimentation time 12 h (Table 3).

**Table 3.** Best operational conditions of coagulants powder *Acacia dealbata* Link. (pollen), *Quercus ilex* L. (acorn skin), *Quercus ilex* L. (peeled acorn), *Platanus × 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 × 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 |

### 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 Tukey's test was used for the comparison of means, which were considered different when $p < 0.05$. The data are presented as mean and standard deviation (mean $\pm$ SD).

## 3. Results and Discussion

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

With the application of the best operational conditions in Table 3, it was observed at 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* × *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 for 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 revealed 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 behaviour 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 environment due the high aluminium leaching, above the Portuguese legislated value (10 mg Al/L).

## 4. Conclusions

Based on 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* × *acerifólia (Aiton) Willd*. (seeds) and *Tanacetum vulgare* L. (seeds) and applied as coagulants; (2) OCPs, in combination with PVPP, achieve a high removal of turbidity, TSS and COD, with a low sludge volume; (3) OCPs are environmentally safer than aluminium sulfate.

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