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Proceeding Paper

Application of NaCl-Plant Extracts to Decrease the Costs of Microfiltration for Winery Wastewater Treatment †

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Abstract: The present study aimed, for the first time, the production and application of NaCl plant extracts in a coagulation-flocculation-decantation process (CFD process) for the optimization of microfiltration process (MF process) for the treatment of winery wastewater (WW). To evaluate the efficiency of the NaCl-extracts, aluminium sulfate (10%) was applied as comparison. The CFD process was optimized, by varying the WW pH, coagulant dosage, agitation, type and dosage of flocculants, before microfiltration process. The application of *Chelidonium majus* L. (seeds) achieved 29.7, 99.7 and 95.3% total organic carbon, turbidity and total suspended solids removal, respectively, with 108 mg of filter consumption. In conclusion NaCl-plant extracts are a promising technology for WW treatment.

Keywords: *Chelidonium majus* L.; coagulation-flocculation-decantation; microfiltration

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1. Introduction

Portugal is a typical Mediterranean wine producer, with around 195,000 ha of vineyards and a wine production of about 6.7 MhL in 2019 [1]. It is the 11th largest producer worldwide and the 9th largest amongst global wine exporters [2]. This high wine production, leads to high generation of winery wastewaters (WW), during the different activities carried out for wine elaboration, mainly originating from washing and rinsing operations of fermentation tanks, barrels, and other items [3]. The coagulation-flocculation-decantation process (or CFD process) has been used by several authors for the treatment of winery wastewater, however, most of these authors employ iron and aluminium sulfates, which in excess can be responsible for several problems, due to the production of large volumes of metal hydroxide (toxic) sludge, which will create a disposal problem and an increase in metal (e.g., aluminium) concentration in the treated water, which may have human health implications [4]. To avoid these consequences, plant-based coagulants have been extensively investigated at the laboratory scale, aiming to exploit them in wastewater treatment [5], to which there is little information. Due to the characteristics of the winery wastewater, a membrane based process, such as microfiltration, can be employed as a complement treatment to CFD process. Microfiltration membranes can include polymeric or ceramic in their constitution, with a pore size ranging from 50 to 500 nm, which are capable of segregation of suspended solids and bacteria by the mechanism of convective pore flow conforming Darcy's law [6]. To our knowledge, the combined CFD-microfiltration processes were never applied to winery wastewater treatment and its effects in organic carbon, turbidity, total suspended solids and phenolic compounds reduction are unknown. Due to the lack of information regarding the production and application of NaCl plant extracts in CFD process and the application of microfiltration in winery wastewater treatment, the objectives of this work are: (1) to characterize the plants, (2) to evaluate the production and application of NaCl plant extracts in CFD process, (3) to evaluate the effect of microfiltration in WW treatment, (4) to study the effect of CFD process in microfiltration enhancement and cost reduction.

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, polyvinylpyrrolidone (10% *w/w*, PVPP) and potassium caseinate were acquired by A. Freitas Vilar, Lisboa, Portugal, activated sodium bentonite was supplied by Angelo Coimbra & Ca., Lda, Maia, Portugal, and activated charcoal by SAI Enology, Paredes, 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.

The winery wastewater was collected from a cellar located in the Douro region (Northern Portugal). The wastewater samples were placed in plastic containers to be transported to the laboratory, they were stored at −40 °C. This work was performed at the University of Trás-os-Montes and Alto Douro, located in Vila Real, Portugal, latitude 41°17′9.18″ N and longitude 7°44′21.45″ W.

2.2. Analytical Determinations

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 ± 0100
Electrical conductivity (µS/cm)		62.5 ± 0.361
Turbidity (NTU)		296 ± 2.000
Total suspended solids–TSS (mg/L)	60	750 ± 1.528
Chemical Oxygen Demand–COD (mg O_2/L)	150	2145 ± 1.000
Biochemical Oxygen Demand–BOD_5 (mg O_2/L)	40	550 ± 1.155
Total Organic Carbon–TOC (mg C/L)		400 ± 4.040
Total Nitrogen–TN (mg N/L)	15	9.07 ± 0.010
Total polyphenols (mg gallic acid/L)	0.5	22.6 ± 0.100
Biodegradability–BOD_5/COD		0.26 ± 0.015
Aluminium (mg/L)	10.0	0.00 ± 0.000

2.3. Plant Extract Preparation

All the vegetable parts (Table 2) 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. The extraction process was carried out in the following way: a 1 M NaCl solution was prepared and 5 g of plant powder was added to 100 mL of NaCl solution (the stock solution was thus considered to be 5% *w*/*w*). The NaCl solution with powder was vigorously stirred at pH 7 and room temperature for 30 min with magnetic stirring. The extract was then filtered twice: once through commercial filter paper in a Büchner funnel and once again through a fine filtering Millipore system (0.45 μm glass fiber). The result is a clear white liquid.

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	
Chelidonium majus L.		Seed	
Daucus carota L.	*carota*	Seed	HVR22100
Tanacetum vulgare L.		Seed	HVR22099
Vitis vinífera L.		Rachis	

2.4. Coagulation-Flocculation-Decantation/Microfiltration Experimental Setup

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 microfiltration experiments were performed by a VACUUBRAND GMBH + CO pump (Germany) with a flow rate of 1.9 m^3/h, coupled with a magnetic filter funnel (Gelman Sciences). The wastewater samples were filtered by glass microfiber filters (Prat Dumas) with a thickness of 270 μm, a micrometric retention of 1.2 μm and a weight of 108.39 mg. Several trials were performed in order to optimize coagulation-flocculation-decantation before microfiltration processes:

(1) 0.1, 0.2, 0.5 and 1.0 g/L of NaCl extracts and aluminium sulfate were added to 500 mL of wastewater sample, and the pH was varied to 3.0, 5.0, 7.0, 9.0 and 11.0;

(2) Pre-determined optimum values (pH and dosage) of NaCl extracts and aluminium sulfate obtained in (1) were added to the WW sample. Then the stirring process (rpm/min) was varied under different fast mix (rpm/min)–slow mix (rpm/min) conditions (120/1–20/30; 150/3–20/20; 150/2–50/30; 180/3–40/17; 200/2–60/30);

(3) To the best conditions obtained in (1) and (2), four different types of flocculants (potassium caseinate, polyvinylpyrrolidone, activated sodium bentonite and activated charcoal) with a concentration of 0.5 g/L were added;

(4) Pre-determined optimum values (coagulant dosage, pH, mixing conditions, type of flocculant) obtained in (1), (2) and (3) were added to the WW sample. Different flocculant concentrations (5, 50, 100, or 500 mg/L), were added and the liquid was mixed in accordance to optimal conditions obtained in (2). After the withdrawal of supernatant, the volume of wet sludge produced was determined by an Imhoff cone, from the sludge level on the bottom of the jar-test beakers. The WW was then filtered through a glass microfiber filters, and both filter consumption and filtered sludge were quantified.

2.5. Statistical Analysis

Differences among means were determined by analysis of variance (ANOVA) using OriginLab 2019 software (Northampton, MA, USA) and Minitab Statistical Software 2018 (State College, PA, 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 error (mean ± SE).

3. Results and Discussion

3.1. Characterization of Plant Powders

The Fourier-transform infrared spectroscopy (FTIR) analysis showed a band at 3421.72 cm^{-1}, which corresponds to stretching vibrations of OH groups (from water, alcohols, phenols, carbohydrates, peroxides) as well from amides [7]. The adsorption bands at 2920.23 and 2850.79 cm^{-1} corresponds to C-H stretching vibrations specific to CH_3 and CH_2 from lipids, metoxy derivatives, C-H (aldehydes), including cis double bonds. The 1741.72 cm^{-1} adsorption band indicates the presence of glycerides. The 1639.49 cm^{-1} adsorption band corresponds to bending vibrations N-H (amino acids), C=O stretchings (aldehydes and cetones, esters) as well to free fatty acids [8,9]. The 1028.06 cm^{-1} absorption band was attributed to C–O stretching vibration from the glucose ring vibration and the holocellulose and hemicellulose [10–12]. 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 [12].

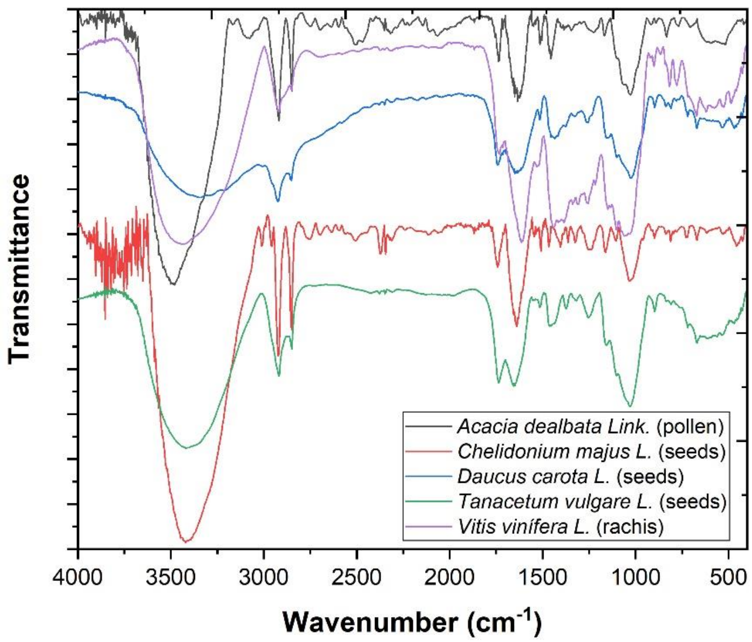

Figure 1. The FTIR spectrum of *Acacia dealbata Link*. (pollen), *Chelidonium majus* L. (seeds), *Daucus carota* L. (seeds), *Tanacetum vulgare* L. (seeds) and *Vitis vinifera* L. (rachis).

Thirty-seven fatty acids were separated via capillary gas chromatography (GC) using a Shimadzu GC- 2010 Plus (Shimadzu, Kyoto, Japan) equipped with an autosampler and an automatic split/splitless injector. Results showed the presence of major concentrations of fatty acids, such as Erucic (25.69%), Arachidic (20.65%), cis-10-Pentadecenoic (13.61%), cis-5,8,11,14,17-Eicosapentaenoic (20.48%) and Arachidic (38.82%), respectively, for *Acacia dealbata Link*. (pollen), *Chelidonium majus* L. (seeds), *Daucus carota* L. (seeds), *Tanacetum vulgare* L. (seeds) and *Vitis vinifera* L. (rachis).

The quantitative analysis of individual phenolic compounds was carried out on a Gilson (Villers-le-bel, France) high-performance liquid chromatography (HPLC) instrument consisting of an autosampler, binary pump, column compartment, and a Finnigan photodiode array detector (DAD 81401; Thermo Electron, San Jose, CA, USA). Results showed the presence of a major percentage of ellagic acid (55.84%), kaempferol (33.28%), caffeic acid (10.37%), ellagic acid (31.12%) and gallic acid (9.59%), respectively, for *Acacia dealbata Link*. (pollen), *Chelidonium majus* L. (seeds), *Daucus carota* L. (seeds), *Tanacetum vulgare* L. (seeds) and *Vitis vinifera* L. (rachis).

3.2. Coagulation-Flocculation-Decantation/Microfiltration Batch Treatment Experiments

With the optimization of the coagulation-flocculation-decantation-microfiltration process, it was achieved the best operational conditions, which are presented in Table 3.

Table 3. Best operational conditions of NaCl plant extract *Acacia dealbata Link*. (pollen), *Chelidonium majus* L. (seeds), *Daucus carota* L. (seeds), *Tanacetum vulgare* L. (seeds) and *Vitis vinifera* L. (rachis) and aluminium sulfate for CFD process, as follows: $[TOC]_0$ = 400 mg C/L, turbidity = 296 NTU, TSS = 750 mg/L, temperature 298 K, sedimentation time 12 h, pump flow rate of 1.9 m^3/h, glass microfiber filters, with micrometric retention of 1.2 µm.

Coagulant	pH	Dosage	Fast Mix	Slow Mix	Flocculant Type	Flocculant Dosage	Cfd → Microfiltration
		g/L	rpm/min	rpm/min		mg/L	
Acacia dealbata Link. (5%)	3.0	0.5	150/3	20/20	Activated sodium bentonite	50	Glass microfiber filters
Chelidonium majus L. (5%)	3.0	0.5	150/2	50/30	Activated sodium bentonite	5	
Daucus carota L. (5%)	3.0	0.5	150/3	20/20	Activated charcoal	5	
Tanacetum vulgare L. (5%)	3.0	0.1	150/3	20/20	Potassium caseinate	100	
Vitis vinifera L. (5%)	3.0	0.1	150/3	20/20	Potassium caseinate	5	
Aluminium sulfate (10%)	5.0	0.5	150/2	50/30	Activated charcoal	50	

By application of the best operational conditions (Table 3), it was observed a TOC removal of 8.4, 8.5, 29.7, 17.7, 40.8, 38.6 and 26.1%, a turbidity removal of 97.2, 97.1, 99.7, 98.2, 99.2, 98.4 and 99.7% and a TSS removal of 94.8, 94.7, 95.3, 94.8, 95.5, 95.0 and 95.6%, respectively, for raw WW (no coagulant), *Acacia dealbata Link*., *Chelidonium majus* L., *Daucus carota* L., *Tanacetum vulgare* L., *Vitis vinifera* L. and aluminium sulfate. These results indicated that performance of pre-treatment with coagulation-flocculation-decantation, enhanced TOC, turbidity and TSS removal after microfiltration process, regarding raw WW. One of this works objectives, is the reduction of microfiltration costs, which derives mainly from the consumption of filters, and therefore, the cost in filter consumption was evaluated (in mg of filter consumed) after the microfiltration process. after the application of the best operational condition, it was observed a filter consumption of 1301, 217, 108, 217, 325, 217 and 108 mg, respectively, for raw WW (no coagulant), *Acacia dealbata Link*., *Chelidonium majus* L., *Daucus carota* L., *Tanacetum vulgare* L., *Vitis vinifera* L. and aluminium sulfate. Despite the immediate removal of turbidity and TSS from raw WW, the costs are very high. These results showed a positive correlation between sludge compaction by coagulation-flocculation-decantation process, and filter consumption by microfiltration process ($y = 2.55x + 12.68$, $r^2 = 0.949$), which indicated that CFD process had a direct effect in microfiltration cost reduction.

4. Conclusions

In this work, a WW was treated by a combined CFD/MF treatment. It is concluded that: (1) it is possible to produce NaCl-plant extracts and apply them as coagulants, (2) the Na-Cl plant extracts enhance the microfiltration process and decrease the costs, (3) the application of CFD/MF process is an economic and sustainable technology for WW treatment.

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