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Proceeding Paper

Removal of Methylene Blue from Aqueous Solution by Application of Plant-Based Coagulants †

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Abstract: Five different plant-based coagulants were used with the objective of removing methylene blue (MB) color aqueous solution. The plant-based coagulants were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and Brunauer–Emmett–Teller (BET) which showed that these materials had high porosity and could adsorb the contaminant MB from the aqueous solution. To increase the efficiency of the plant-based coagulants, bentonite was applied as a flocculant. Results showed MB removal of 90.9%, 91.9%, 91.4%, 86.9% and 88.9%, respectively, for seeds of *Chelidonium majus* L., *Dactylis glomerata* L., *Festuca ampla Hack.*, *Tanacetum vulgare* L. and rachises of *Vitis vinifera* L. In conclusion, plant-based coagulants mixed with bentonite are a biologic, sustainable and cheap alternative for MB removal.

Keywords: plant-based coagulants; methylene blue; Brunauer–Emmett–Teller (BET); *Chelidonium majus* L.

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1. Introduction

Textile finishing industries are chemical industries in which dyes and pigments are used in very large quantities with a great volume of water. The presence of these textile dyes in wastewaters discharged in aquatic environments, such as wadis, rivers, seas and oceans, and their lack of biodegradability under normal ecological conditions can destroy the vital conditions of these different environments while preventing the penetration of light to the depths of aquatic environments [1]. In order to treat these wastewaters, a coagulation–flocculation–decantation process (CFD) can be applied to remove the textile dye. Traditionally, coagulants such as Poly Ferric Sulfate (PFS), Poly Aluminum Chloride (PAC) and Poly Aluminum Ferric Chloride (PAFC) have been used for textile dye removal. However, these types of materials release iron and aluminum to the wastewater causing problems for the environment [2]. Natural macromolecular coagulants extracted from plants have been identified as promising materials for wastewater treatment and have attracted a lot of attention due to advantages such as abundancy, low toxicity, being multi-purpose and biodegradable [3]. In this work, the application of seeds from *Chelidonium majus* L., *Dactylis glomerata* L., *Festuca ampla Hack.*, *Tanacetum vulgare* L. and rachises of *Vitis vinifera* L. was tested for removal of a textile dye contaminant from an aqueous solution. The aim of this work is to (1) produce and characterize the plant-based coagulants, (2) optimize the CFD process, and (3) evaluate the application of bentonite as a flocculant agent.

2. Materials and Methods

2.1. Reagents

The activated sodium bentonite (Na-Mt) was supplied by Angelo Coimbra & Ca., Lda, Maia, Portugal, and the methylene blue (MB) was acquired from VWR Chemicals, Amadora, Portugal. NaOH and H_2SO_4 (95%) were both obtained from Analar Normapur. Deionized water was used to prepare the respective solutions.

2.2. Analytic Techniques

The maximum absorbance wavelength (λ_{max}) of MB was found at 665 nm, and the concentration of the residual dye in solution was calculated using the Beer–Lambert law. Dye discoloration was analyzed as follows (Equation (1)):

$$\text{Dye concentration } (\%) = \left(\frac{1 - C_{dye,t}}{C_{dye,0}} \right) \times 100 \quad (1)$$

where $C_{dye,t}$ and $C_{dye,0}$ are the concentrations of dye at reaction time t and 0, respectively.

2.3. Plant-Based Coagulant Preparation

All the plants used in this work were collected from 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 1, the plants sub species, part collected for this study and the herbarium number attributed by UTAD for the plant's identification are shown. All the plant-based coagulants were prepared in accordance with Martins et al. [4].

Table 1. Plant identification with description of specie, sub specie, part collected and herbarium number.

Plant Specie	Sub Specie	Part Collected	Herbarium Number
Chelidonium majus L.		Seed	
Dactylis glomerata L.	*lusitanica Stebbins et Zohary*	Seed	HVR22101
Festuca ampla Hack.	*ampla*	Seed	HVR22102
Tanacetum vulgare L.		Seed	HVR22099
Vitis vinifera L.		Rachis	

2.4. Characterization of Plant-Based Coagulants

The chemical composition of the plant-based coagulants was evaluated by FTIR analysis (Shimadzu, Kyoto, Japan) and the microstructural characterization was carried out with a scanning electron microscope (FEI QUANTA 400 SEM/ESEM, Fei Quanta, Hillsboro, WA, USA). The textural parameters of samples were obtained from N_2 adsorption–desorption isotherms at 77 K using a Micromeritics ASAP 2020 apparatus (TriStar II Plus, Micromeritics Instrument Corporation, Norcross, GA, USA).

The FTIR analysis (Figure 1) presents vibration bands at 3421.72 cm^{-1} (stretching vibrations of OH groups (from water, alcohols, phenols, carbohydrates [5])), at 2920.23 and 2850.79 cm^{-1} (C-H stretching vibrations specific to CH_3 and CH_2 from lipids, metoxy derivatives, and C-H (aldehydes) including cis double bonds) and at 898.83–1253.73 cm^{-1} (C-O-C, C-C, and C-O stretching vibrations from carbohydrates [6]).

In Figure 2, it was observed that plant-based coagulants exhibited a heterogeneous and relatively porous morphology. The spaces available (represented in dark) may facilitate adsorption of the MB contaminant [7].

The BET analysis (Table 2) showed that all plant-based coagulants had a low BET surface area. The shape of its N_2 adsorption–desorption isotherm was that of a type I isotherm, typical of microporous solids having relatively small external surfaces as defined by the International Union of Pure and Applied Chemistry (IUPAC) classification [8].

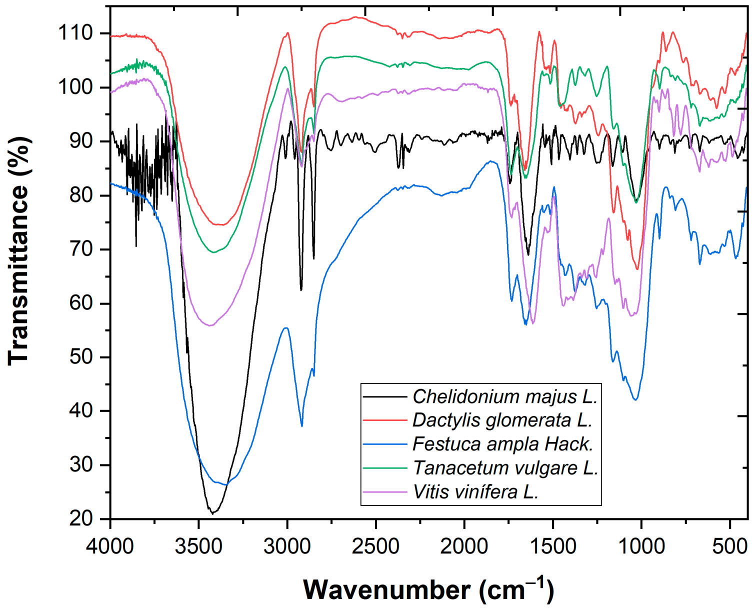

Figure 1. FTIR analysis of plant-based coagulants.

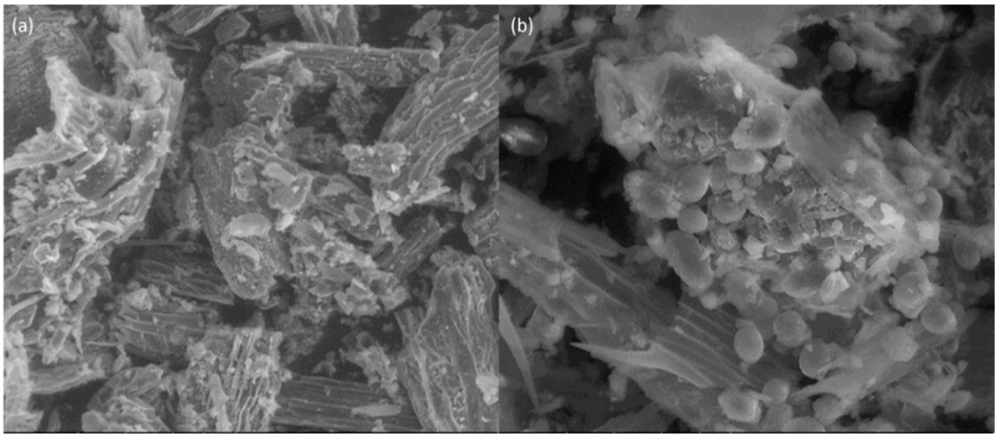

Figure 2. SEM images of (**a**) *C. majus* and (**b**) *D. glomerata*.

Table 2. B.E.T. analysis of the plant-based coagulants.

Coagulants	S_{BET} (m^2/g)
C. majus	0.05
D. glomerata	0.06
F. ampla	0.18
T. vulgare	0.03
V. vinifera	0.50

2.5. Coagulation–Flocculation–Decantation Experimental Setup

The CFD process was performed in a jar-test device (ISCO JF-4) using 500 mL of MB aqueous solution in 1000 mL beakers. The equipment was provided by a set of 4 mechanic agitators powered by a regulated speed engine. In the CFD process, 5 plant-based coagulants (*C. majus*, *D. glomerata*, *F. ampla*, *T. vulgare* and *V. vinifera*) were tested and the process was optimized as follows:

(1) The pH was varied (3.0, 5.0, 7.0, 9.0 and 11.0) under the operational conditions: [MB] = 50 mg/L, [coagulant] = 1.0 g/L, fast mix 150 rpm/3 min, slow mix 20 rpm/20 min, T = 298 K, V = 250 mL, sedimentation time = 30 min;

(2) After determining the best pH in (1), the dosage of coagulant was varied (0.1, 0.5, 1.0 and 2.0 g/L) under the operational conditions: [MB] = 50 mg/L, fast mix 150 rpm/3 min, slow mix 20 rpm/20 min, T = 298 K, V = 250 mL, sedimentation time = 30 min;
(3) With the best pH (1) and coagulant dosage (2), the mixing conditions were tested by varying the fast and slow mix under the operational conditions: [MB] = 50 mg/L, T = 298 K, V = 250 mL, sedimentation time = 30 min;
(4) Under pre-determinate values of pH, coagulant dosage and mixing conditions obtained in (1)–(3), the concentration of activated sodium bentonite (0.1, 0.5, 1.0 and 2.0 g/L) as a flocculant was varied under the operational conditions: [MB] = 50 mg/L, T = 298 K, V = 250 mL, sedimentation time = 30 min.

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

3. Results and Discussion

Coagulation–Flocculation–Decantation Experiments

In this work, five different plant-based coagulants were applied to an aqueous solution contaminated with a textile dye (MB) with the purpose of removing this contaminant.

The pH of the wastewater plays an important role in the CFD process by affecting the nature of the functional groups of dye molecules and existing forms of coagulants [3]. Initially, wastewater pH was varied from 3.0 to 11.0 and results showed MB removal of 71.0%, 47.7%, 58.8%, 73.6% and 79.3%, respectively, for *C. majus*, *D. glomerata*, *F. ampla*, *T. vulgare* and *V. vinifera* (Figure 3a) at pH 5.0. The coagulant dosage was varied (0.1–2.0 g/L) and results showed MB removal of 72.6%, 50.8%, 58.8%, 79.4% and 79.3% (Figure 3b) with 2.0, 2.0, 1.0, 2.0 and 1.0 g/L coagulant, respectively. These results were in agreement with Beltrán-Heredia et al. [9] who observed that Carmine Indigo dye concentration decreased as the *Moringa* seed extract concentration increased. The effect of mixing conditions was also considered in this work and results showed MB removal of 81.2%, 64.8%, 58.8%, 79.4% and 79.3%, respectively (Figure 3c). These results are in agreement with Sánchez-Martín et al. [10] who observed that an increase in stirring speed improved the clarification of real surface water with the application of a plant-based extract. Finally, to improve the efficiency of the CFD process, bentonite was added as a flocculant aid and results showed MB removal of 90.9%, 91.9%, 91.4%, 86.9% and 88.9% (Figure 3d) for 1.0, 0.5, 0.5, 1.0 and 0.5 g/L bentonite, respectively. These results are in agreement with Sanghi and Bhattacharya [11] and Jorge et al. [12] who demonstrated that the combination of a coagulant with bentonite increased the removal of textile dyes and organic matter, respectively, from the wastewater.

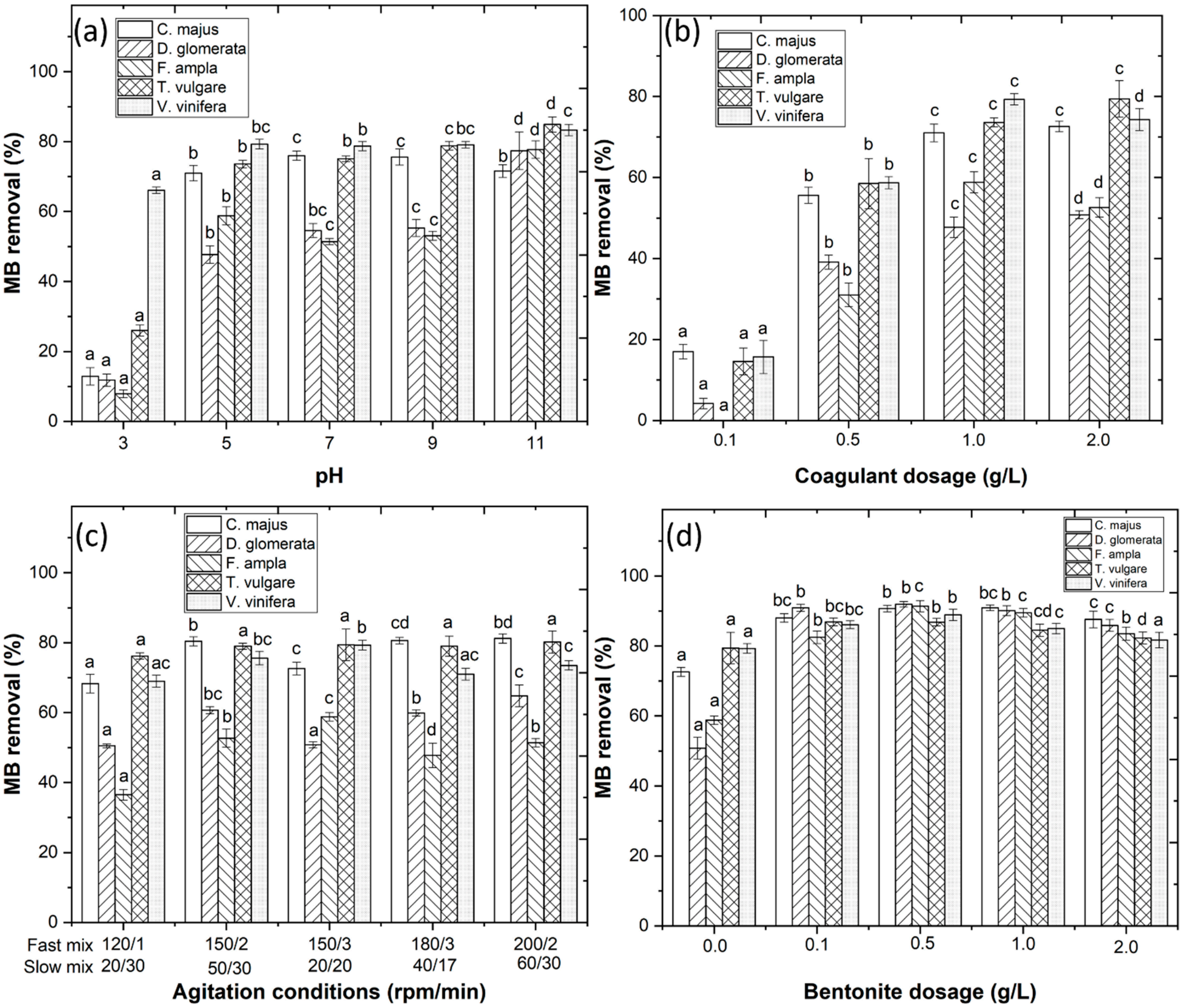

Figure 3. Optimization of the CFD process with variations of (**a**) pH (3.0–11.0); (**b**) coagulant dosage (0.1–2.0 g/L); (**c**) agitation conditions; and (**d**) bentonite dosage (0.0–2.0 g/L). Means in bars with different letters represent differences ($p < 0.05$) within each coagulant (*C. majus*, *D. glomerata*, *F. ampla*, *T. vulgare* and *V. vinifera*) by comparing wastewaters.

4. Conclusions

The application of plant-based coagulants in combination with bentonite presents excellent results for MB removal from aqueous solution. Considering the results, the following is concluded:

(1) The plant-based coagulants are carbon-based materials with porous structures that can adsorb the contaminants;
(2) Under the best operational conditions, the plant-based coagulants achieve a high removal of MB from aqueous solution;
(3) The addition of bentonite significantly increases the efficiency of the CFD process.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/ECP2022-12659/s1.

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