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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 to remove the 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 plant-based coagulants efficiency, it was applied bentonite as a flocculant. Results showed a 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 rachis 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 such a great volume of water. The presence of these textile dyes in wastewater discharged in aquatic environments such as wadis, rivers, seas, oceans, and the lack of their 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 type of materials release iron and aluminium to the wastewater causing problems for the environment [2]. Natural macromolecular coagulants extracted from plants have revealed to be promising for the wastewater treatment and have attracted a lot of attention due to their advantages such as abundant source, low toxicity, multi-purposes and biodegradability [3]. In this work it was tested the application of seeds from *Chelidonium majus L.*, *Dactylis glomerata L.*, *Festuca ampla Hack.*, *Tanacetum vulgare L.* and rachis of *Vitis vinifera L.* to remove 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 aquired by 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. 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 by Beer-Lambert's law. The dye discoloration was analyzed as follows (Equation 1):

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

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

2.3. Plant-Based 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 1, it is shown the plants sub-species, part collected for this study and the herbarium number attributed by UTAD for the plant's identification. All the plant-based coagulants were prepared in accordance to 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 microscopy (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 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, 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]).

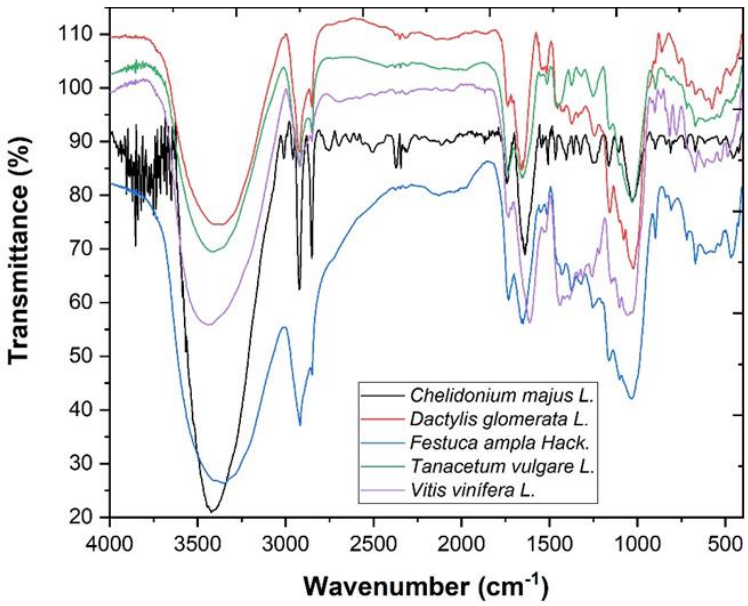

Figure 1. FTIR analysis of plant-based coagulants.

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].

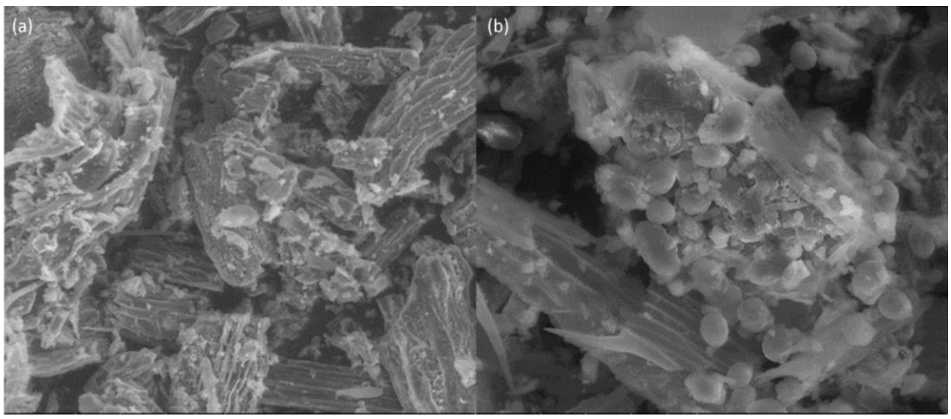

Figure 2. SEM images of (a) C. majus and (b) D. glomerata.

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 of 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].

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

Coagulants	S_{BET} (m²/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 Set-Up

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, it were tested 5 plant-based coagulants (*C. majus, D. glomerata, F. ampla, T. vulgare* and *V. vinifera*) 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), (2) and (3) it was varied the concentration of activated sodium bentonite (0.1, 0.5, 1.0 and 2.0 g/L) as a flocculant, 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 by OriginLab 2019 software (Northampton, Massachusetts, USA). 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

Coagulation-Flocculation-Decantation Experiments

In this work, 5 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, the wastewater pH was varied from 3.0 to 11.0 and results showed a 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 3(a)) at pH 5.0. The coagulant dosage was varied (0.1 – 2.0 g/l) and results showed a MB removal of 72.6, 50.8, 58.8, 79.4 and 79.3%, respectively (Figure 3(b)) with 2.0, 2.0, 1.0, 2.0 and 1.0 g/L coagulant, respectively. These results were in agreement to 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 a MB removal of 81.2, 64.8, 58.8, 79.4 and 79.3%, respectively (Figure 3(c)). These results are in agreement to Sánchez-Martín *et al*., [10], who observed that an increase of the 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 a MB removal of 90.9, 91.9, 91.4, 86.9 and 88.9%, respectively (Figure 3(d)) for 1.0, 0.5, 0.5, 1.0 and 0.5 g/L bentonite. These results are in agreement to 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.

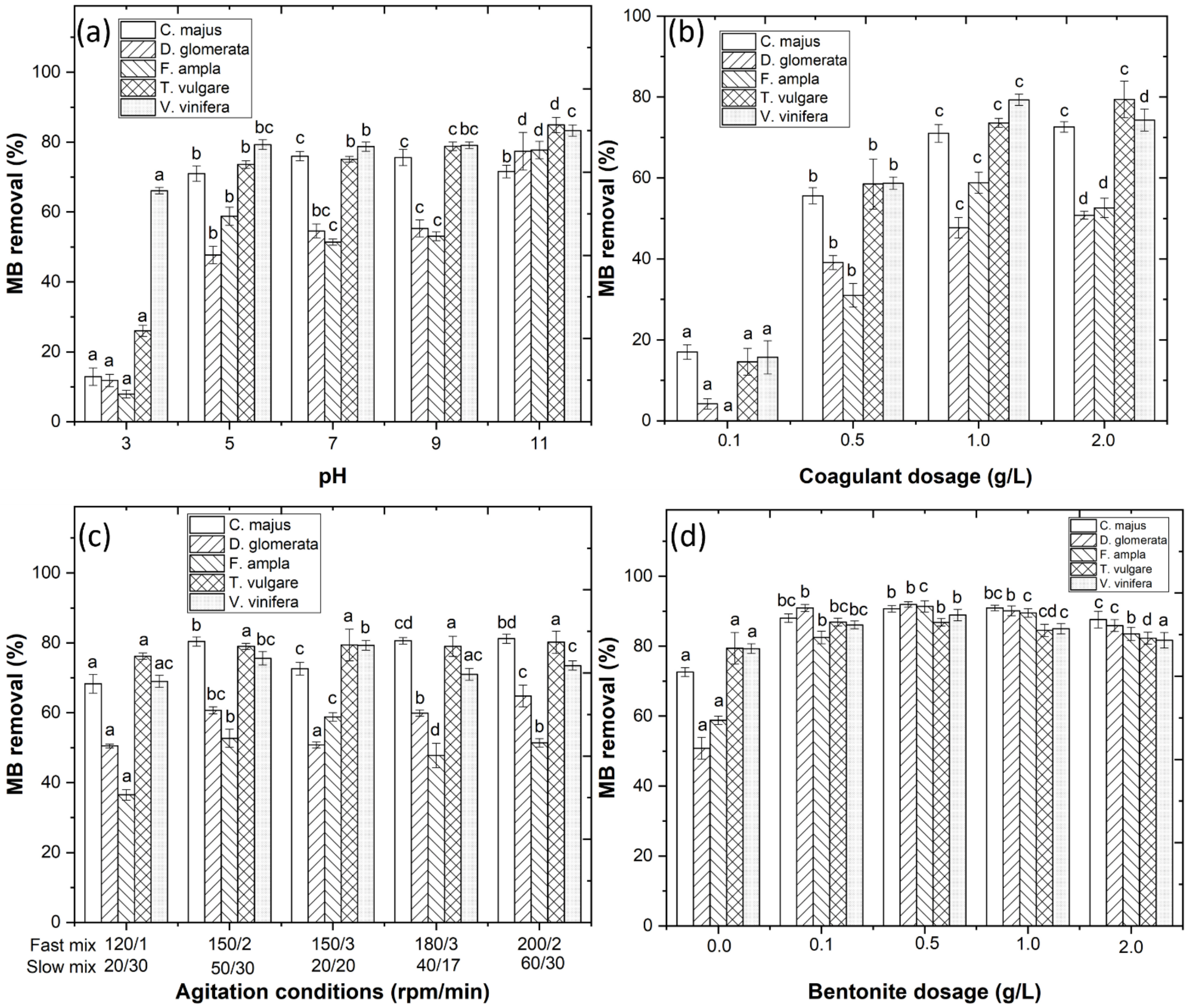

Figure 1. Optimization of CFD process with variation of (a) pH (3.0 – 11.0), (b) coagulant dosage (0.1 – 2.0 g/L), (c) agitation conditions and (d) bentonite dosage (0.0 – 2.0 g/L). Means in bars with different letters represent differences ($p < 0.05$) within each coagulant (*C. majus, D. glomerata, 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, it 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.

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