Parametrical Study for the Effective Removal of Mordant Black 11 from Synthetic Solutions: Moringa oleifera Seeds' Extracts Versus Alum

Article *in* Water · December 2022

DOI: 10.3390/w14244109

8 authors, including:

Amina Hadadi
Université de Bouira
20 PUBLICATIONS 130 CITATIONS

Ali Imessaoudene
Université de Bouira
15 PUBLICATIONS 143 CITATIONS

Jean-Claude Bollinger
University of Limoges
193 PUBLICATIONS 5,762 CITATIONS

Cheikh Sabrina
Université de Bouira
9 PUBLICATIONS 97 CITATIONS

water

MDPI

Article

Parametrical Study for the Effective Removal of Mordant Black 11 from Synthetic Solutions: *Moringa oleifera* Seeds' Extracts Versus Alum

Amina Hadadi [1], Ali Imessaoudene [1], Jean-Claude Bollinger [2], Sabrina Cheikh [1], Aymen Amine Assadi [3], Abdeltif Amrane [3], Mohamed Kebir [4] and Lotfi Mouni [1,*]

[1] Laboratoire de Gestion et Valorisation des Ressources Naturelles et Assurance Qualité, Faculté SNVST, Université de Bouira, Bouira 10000, Algeria
[2] Laboratoire E2Lim, Université de Limoges, 123 Avenue Albert Thomas, 87060 Limoges, France
[3] Ecole Nationale Supérieure de Chimie de Rennes, Université de Rennes, CNRS, ISCR-UMR6226, 35000 Rennes, France
[4] Research Unit on Analysis and Technological Development in Environment (URADTE-CRAPC), BP 384, Bou-Ismail 42004, Tipaza, Algeria
* Correspondence: l.mouni@univ-bouira.dz

Abstract: Prior studies have examined the ability of *Moringa oleifera* (*MO*) seed extract, among other natural coagulants, to remove several types of dyes. *MO* has been proven to have a high capacity to remove some anionic dyes. The aim of the present study is to explore the possible use of aqueous and saline extracts of *MO* as biocoagulants for the removal of Mordant Black (MB11) from aqueous solution. Their performances were compared to that of aluminum sulfate (alum). To do so, various operating parameters were investigated such as coagulant dose (100–600 mg/L), pH (3–11), initial dye concentration (100–350 mg/L), sodium chloride concentration (0.2–2 M), and sedimentation time (15–90 min). The maximum percentages of MB11 removal were found to be 98.65%, 80.12%, and 95.02% for alum, aqueous extract of *MO* (MOPW), and saline extract of *MO* (MOPS), respectively, at around pH 6.5 and for coagulant doses of 400 mg/L (alum) and 500 mg/L (MOPW and MOPS). The coagulation-flocculation mechanism of biocoagulants was hypothesized to be adsorption and charge neutralization. The two biocoagulants (MOPW and MOPS) showed an interesting versatility towards pH counter to alum which was very sensitive to this parameter. pH variations were measured for the three coagulants and proven to be negligible for the biocoagulants. Faster sedimentation time was recorded when MOPW and MOPS were used, suggesting the existence of larger quickly settleable flocs. Considering their high coagulative capacity, rapid and cost-effective preparation, and eco-friendly character, *MO* extracts can be considered as powerful alternatives to aluminum sulfate in the remediation of MB11 from wastewaters.

Keywords: *Moringa oleifera*; natural coagulant; mordant black 11; effective removal; adsorption and charge neutralization; pH variation; quickly settleable flocs

check for updates

Citation: Hadadi, A.; Imessaoudene, A.; Bollinger, J.-C.; Cheikh, S.; Assadi, A.A.; Amrane, A.; Kebir, M.; Mouni, L. Parametrical Study for the Effective Removal of Mordant Black 11 from Synthetic Solutions: *Moringa oleifera* Seeds' Extracts Versus Alum. *Water* **2022**, *14*, 4109. https://doi.org/10.3390/w14244109

Academic Editors: Sílvia Santos and Xufei Yang

Received: 21 November 2022
Accepted: 14 December 2022
Published: 16 December 2022

1. Introduction

In light of a growing global population, a rise in urbanization, and the quest for industrialization, water-based natural sources are under significant stress. This prompted many water-scarce countries to seek renewable water sources or to purify used water, including industrial and domestic effluents. Due to their vast availability, they are regarded as one of the most significant renewable water sources on a worldwide scale. Concerns are exacerbated by the high concentrations of medicines, heavy metals, dyes, fertilizers, and other organic and inorganic contaminants found in industrial and household wastewater. Therefore, their treatment results in the conservation of the environment and marine life, as well as the supply of a new water source, thus achieving all sustainability standards [1].

Due to their carcinogenic potential, non-biodegradability, and complex chemical structure, dyes are regarded as posing a major threat to wastewater quality [2]. Currently, there are more than 10^5 commercial dyes on the worldwide market, and their annual production rate surpasses 7×10^8 kg. Therefore, the presence of colors in water complexes significantly impacts human health and may cause skin irritation and kidney and liver injury; moreover, the presence of dyes affects the photochemical processes of the marine environment [3]. Mordant Black (MB11) is an anionic azo dye that is used to color nylon fibers as well as other textiles. It is also utilized in several industries, including the cosmetics, fabric, pulp, food, plastics, and leather sectors [4]. Furthermore, MB11 is carcinogenic and may cause serious health issues [5]; MB11 also has a harmful influence on the marine ecosystem. Consequently, this contaminant must be removed from wastewater prior to release or recycling.

Numerous techniques, including ion exchange [6], ozonation [7], adsorption [8], membrane separation [9], photocatalysis [10], and precipitation [11], have been employed to remove MB11 from aqueous solutions; however, no earlier research has shown the elimination of this dye utilizing the coagulation-flocculation approach.

Because of its efficacy in eliminating organic matter, suspended particles, turbidity, and color, the coagulation-flocculation method is widely used in water and wastewater treatment [12]. The conventional coagulation technique involves the use of divalent positively charged chemical compounds such as aluminum sulfate and ferric chloride, both of which have been linked to a number of detrimental health and environmental effects. Extensive study has been conducted on the impacts of using chemical compounds as coagulants, including high levels of chemical residuals, toxic sludge, and health issues with prolonged usage [13,14].

Transitioning from chemical to natural coagulants might be a realistic strategy for minimizing environmental pollution and health risks related to chemical coagulants. Due to their biodegradability and environmental friendliness, the use of natural coagulants in water treatment has become essential. In recent years, there have been numerous reports of natural coagulants derived from diverse plant species, including *Jatropha curcas* [15], banana peels [16], bagasse [17], Aleppo pine seeds, prickly pear and *Aloe vera* mucilage [18]. In accordance with these results, natural coagulants have a high prospect of replacing the traditional chemical coagulant, since they demonstrate promising treatment performance.

Moringa oleifera (*MO*), a cosmopolitan, tropical, drought-resistant tree that grows year-round, is considered as a promising biocoagulant with a number of acknowledged therapeutic benefits. *MO* seed has a natural organic polymer comprising 1% polyelectrolytes that neutralize colloidal particles. This cationic protein is a nonharmful natural polypeptide that may be used in the treatment of water for the sedimentation of mineral particles and organics. However, this molecule is not readily employable, requiring one or more processing steps prior to use. Typical processes are the first (powder preparation), second (extraction of edible oil), third (extraction of cationic protein), and fourth (purifying these proteins). *MO* seeds may be used as a coagulant during any of the following stages. The more advanced the treatment phase, the higher the costs, the greater the complexity, and the more diverse the water treatment outputs. The primary and secondary phases have been the subject of most works. A third purification stage, such as lyophilization, ion exchange, or dialysis, is rarely used for plant-based coagulants due to their complexity and expense. The most popular method is the aqueous extraction of the seed powder, since the relevant cationic protein is soluble in water and this solvent is easily available and inexpensive. [19]. Using in-line filtration of a synthetic water with low turbidity (25 NTU) and aqueous extraction of the whole-seed powder, a turbidity reduction of up to 98% was achieved. Nevertheless, research has shown that saline extraction (often NaCl, but also $NaNO_3$ and KCl) is preferable over aqueous extraction for turbidity reduction [20]. Okuda et al. [21] studied the turbidity removal after sedimentation of synthetic water (50 NTU) using aqueous extract and compared it to the saline extract (1 M NaCl), obtaining a turbidity reduction of 78% and 95%, respectively. Additionally, the dosage of saline extract was 7.4 times less than that of the aqueous extract. According to several studies [22,23], the biocoagulant (*MO* seed extract) is nonhazardous, inexpensive, and ecologically friendly. However, *MO* use as a biocoagulant for the removal of anionic dyes is more limited, the vast majority of studies focused on the reduction of turbidity from wastewater (real or synthetic) [24–26], and MB11 removal has not been attempted using this bio-based material in prior studies.

In this perspective, the goal of our study is to assess the use of *MO* seed-based coagulant in aqueous and saline extraction for the removal of synthetic solutions of MB11, the performance of *MO*-based coagulant was compared with that of aluminum sulfate (alum), an extensively used chemical coagulant, various operating parameters were studied including sodium chloride concentration, initial pH of the dye solution, coagulant dosages, initial dye concentrations, and sedimentation time, and a Fourier-transform infrared spectroscopy (FTIR) characterization was also undertaken to highlight the composition of MO seeds and its relationship with the coagulation efficiency.

2. Materials and Methods

2.1. Chemicals and Materials

MO was purchased in a local herbal market. Seeds that were not deteriorated, old, or contaminated with seed pests were selected. They were further dried for 24 h at 40 °C in an oven (Memmert GmbH + Co.KG, Bavaria, Germany), then ground into powder using a domestic blender. The obtained powder is referred to as MOP. A saline extraction was performed according the method described earlier [18]; the resulting mixture is referred to as MOPS. An aqueous extraction was also undertaken for comparison purposes (MOPW). Preweight MOP was blended with 100 mL of distilled water (DW) [27], and both solutions were freshly prepared for each set of experiments to prevent degradation or alteration of the biocoagulant properties (Figure 1).

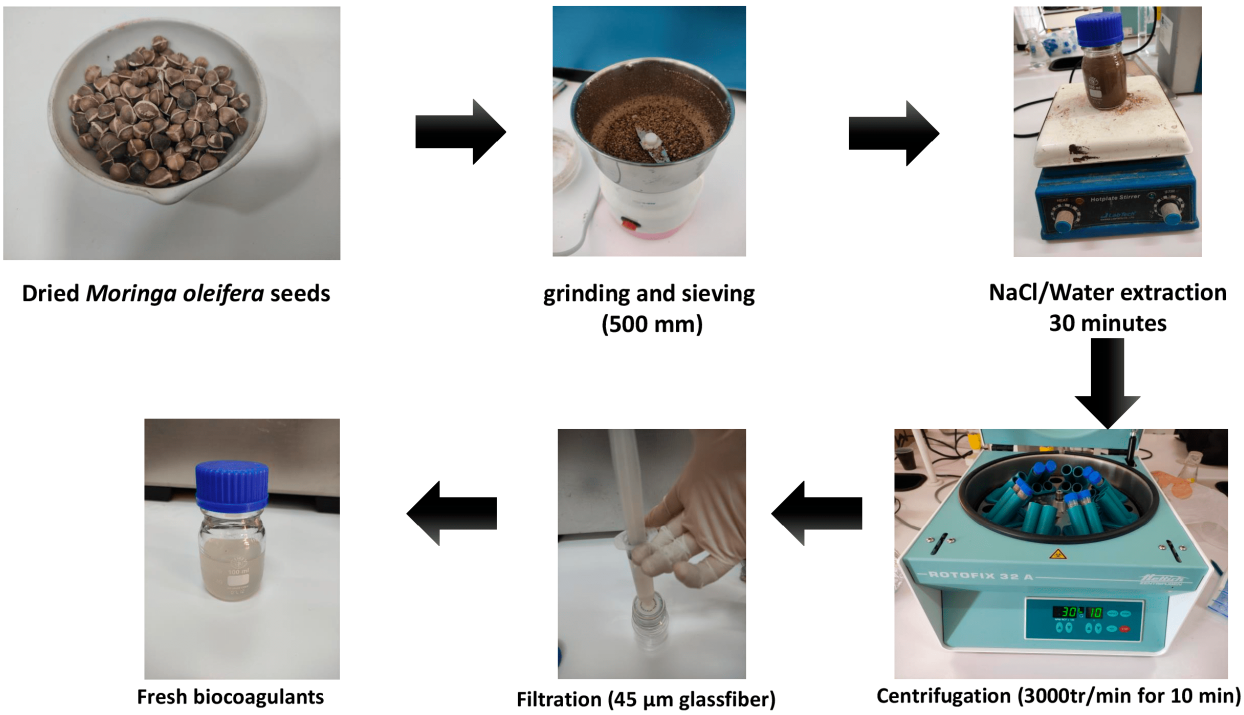
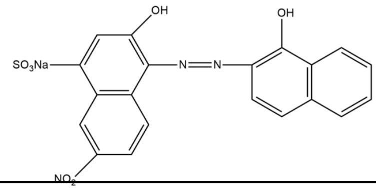


Figure 1. Preparation steps of the two coagulants (MOPS/MOPW).

Hydrochloric acid (HCl), sodium hydroxide (NaOH), sodium chloride (NaCl), aluminum sulfate octadecahydrate (AI $(SO_4)_3$ $18H_2O$), molecular weight: 342.15 g/mol (anhydrous basis) g/mol, purity: 98% were all from Sigma Aldrich Chemical Company, Burlington, Massachusetts, USA, MB11 (Table 1) was purchased from Biochem-Chemopharma, Cosne-Cours-sur-Loire, France.

Table 1. Characteristics of MB11 used in this study.

Characteristics	MB11	Chemical Structure
General name/synonyms	Mordant black 11/Eriochrome Black T	
Chemical formula	$C_{20}H_{12}N_3O_7SNa$	
Molecular weight (g/mol)	461.381	
Maximum wavelength absorbance (λmax)	535 nm	
Purity	Indicator grade	
Dye type	Anionic (azo) dye	

2.2. Preparation of the MB11 and Alum Solutions

In deionized water, a stock solution of MB11 dye with an initial concentration of 1000 mg/L was prepared. Using known concentrations of MB11 dye samples, the calibration curves were plotted. The absorption value was measured at 535 nm for pH = 6.5 (natural pH) (λmax). A stock solution of alum (1 g/L) was prepared using deionized water; it was then subsequently diluted to obtain solutions with the necessary concentrations.

2.3. Coagulation-Flocculation Experiments

Coagulation studies were conducted using jar-test equipment in 1 L beakers (VELP Scientifica Srl, Italy). Each beaker was filled with 200 mL of MB11 solution with varying concentrations and initial pH values (adjusted with 0.5 M HCl or 0.5 M NaOH) measured by a pH meter (Mettler Toledo, Columbus, OH, USA), along with varying amounts of freshly prepared MOP extracts (MOPS or MOPW) and alum. Each parameter's optimum value was determined using the one factor at a time (OFAT) approach. The mixture of MOPS/MOPW and alum with MB11 was agitated at 200 rpm for 3 min, followed by 30 rpm for 20 min; flocs were allowed to settle for 60 min. Afterwards, samples (20 mL) were extracted using a volumetric pipette 3 cm below the surface of the mixture and centrifuged (3000 rpm for 10 min). Using a spectrophotometer (Agilent Cary 60 UV-Vis, USA) at a wavelength corresponding to the maximum absorbance of 535 nm for MB11 dye, the final concentrations of the dye were measured. All studies were undertaken at room temperature (25 °C ± 2) and were repeated two times. The percent elimination of MB11 dye was determined using Equation (1):

$$\boldsymbol{Coagulation\ efficiency}\ (\%) = \frac{\boldsymbol{C_0 - C_f}}{\boldsymbol{C_0}} \times \mathbf{100} \tag{1}$$

where $\boldsymbol{C_0}$ and $\boldsymbol{C_f}$ represent the initial and residual dye concentrations, respectively.

3. Results and Discussion

3.1. FTIR Spectrum of MOP Seeds

Infrared spectral analysis (Thermo Fisher Scientific, Waltham, MA, USA) was used to identify the primary functional groups found in the seeds of MOP. As can be observed in Figure 2, the bandwidth peak at 3290 cm^{-1} may be ascribed to the O-H stretching in the fatty acids, protein, lignin, and carbohydrates units. Because of the seed's substantial protein composition, N–H stretching in amide bonding also makes a significant contribution to this region [28]. The peaks at 2921 cm^{-1} and 2852 cm^{-1} coincide with the asymmetric and symmetric bending of the C-H linkage in the CH_2 group, respectively. Because of the high intensity of these bands, they may be attributed to the primarily fatty component of the seed, which is present in large proportions comparable to the fraction of protein [29]. The C=O stretch of esters is represented at 1744 cm^{-1}, while the O=C-O-C stretch at 1231 cm^{-1} represents another type of ester. The absorption at 1650 cm^{-1} and 1538 cm^{-1} correspond to the C=O stretch and N-H bending of amides, respectively [30]; these results confirm the proteinaceous profile of MOP seeds.

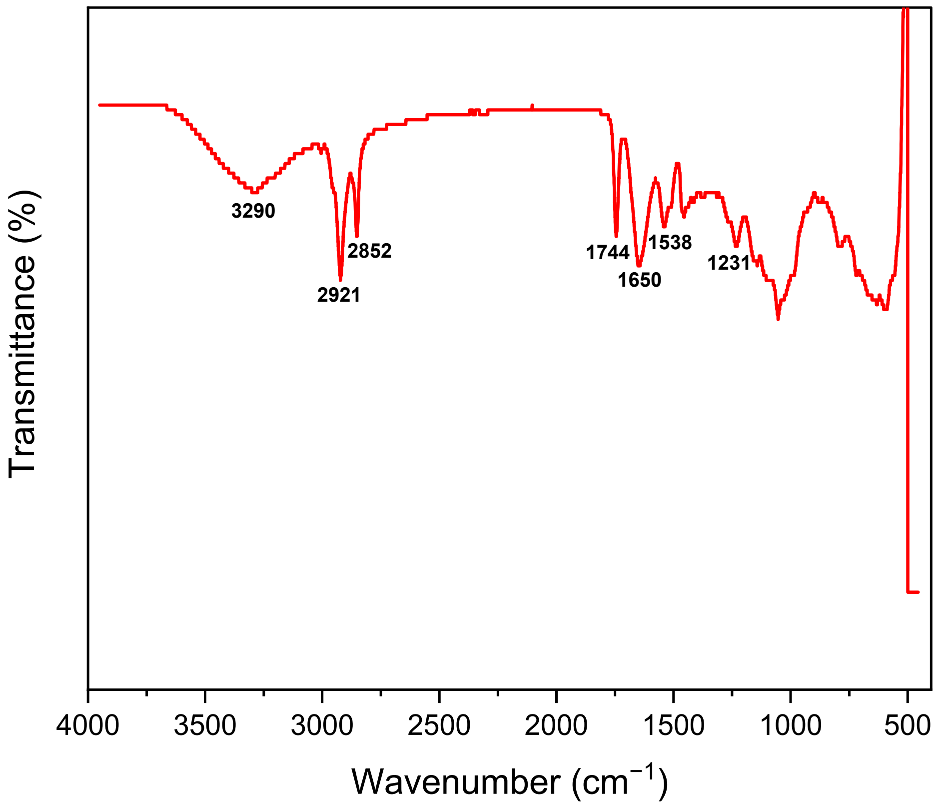


Figure 2. FTIR spectrum of MOP seeds.

3.2. *Effect of Coagulant Dosage*

In general, inadequate doses or overdoing would result in poor coagulating performances. Therefore, it is essential to identify the optimal dose in order to reduce dosing costs and sludge formation, as well as to achieve optimal treatment efficiency. Figure 3 illustrates the effect of the coagulants' dosages (100-600 mg/L) on the removal of MB11 using MOPW, MOPS, and alum coagulants. As demonstrated in Figure 3, there is a continuous elimination of MB11 when increasing coagulant dosages up to 400 mg/L and 500 mg/L for alum and MOPW/MOPS, with color elimination percentages of 98.65%, 80.12%, and 95.02%, respectively, these performances are relatively high compared to that of other bio-based materials for the removal of dye wastewaters (synthetic or real) (Table 2). The two biocoagulants exhibit similar color reduction patterns, as they are observed to increase and decrease constantly, indicating that both might follow adsorption and charge neutralization mechanisms to neutralize the anionic portion of the MB11 [31,32], resulting in an equivalent trend of color increase when overdosing occurs. The operating mechanism of alum may be described as follows: the introduction of this coagulant to the synthetic dye solution quickly hydrolyzes the salts, forming cationic species capable of gathering the negatively charged portion of MB11 and neutralizing it. Particle destabilization may then occur [33], entrapment is also a possible mechanism for this chemical coagulant. A clear difference in the coagulation efficiency between MOPW and MOPS is also observed through the whole pattern (Figure 3) and visually (Figure 4). This trend can be explained by the fact that water purification by *MO* seed coagulant is predominantly due to the activity of the seed's protein. The latter represents around 37% of the *MO* seed kernel content [34]. The primary causes of flocculation are basic polypeptides with molecular weights ranging from 6000 to 16,000 Daltons. The functional groups in the *MO* seed proteins' side-chain amino acids are expected to help with water clarification. Madrona et al. [35] established that these molecules found in *MO* do not dissolve properly in water without the addition of salt, thus, explaining the better coagulation efficiency when MOPS is used.

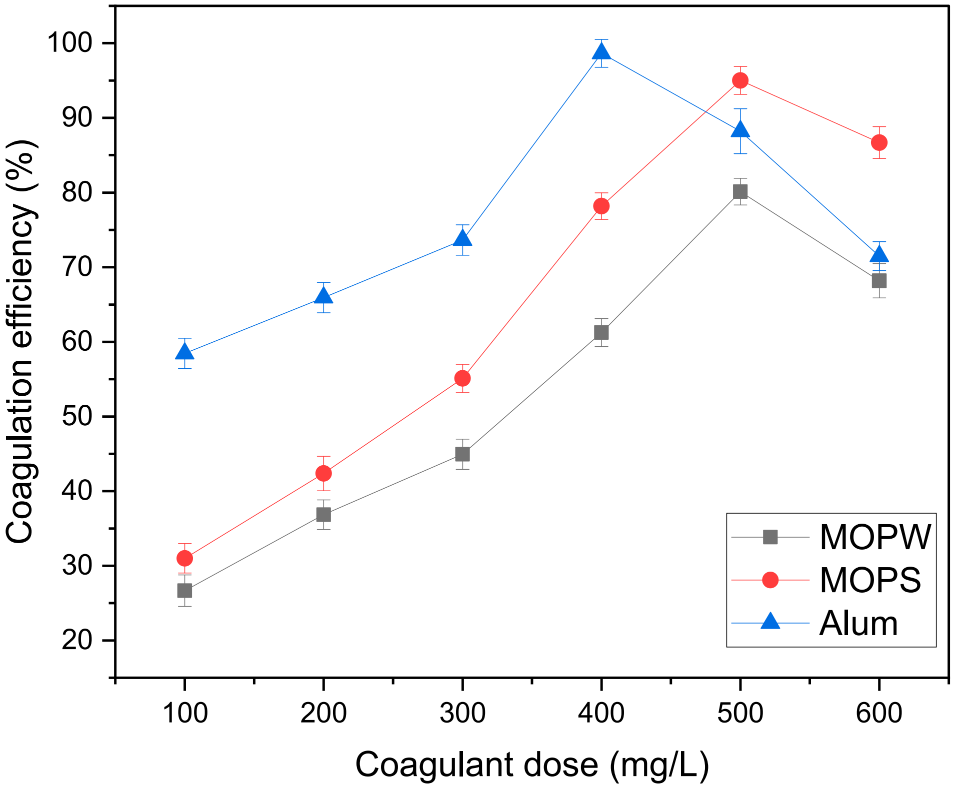


Figure 3. Effect of coagulant dose on coagulation efficiency (pH = 6.5, 1 M NaCl, 100 mg/L of MB11, 60 min of settling).

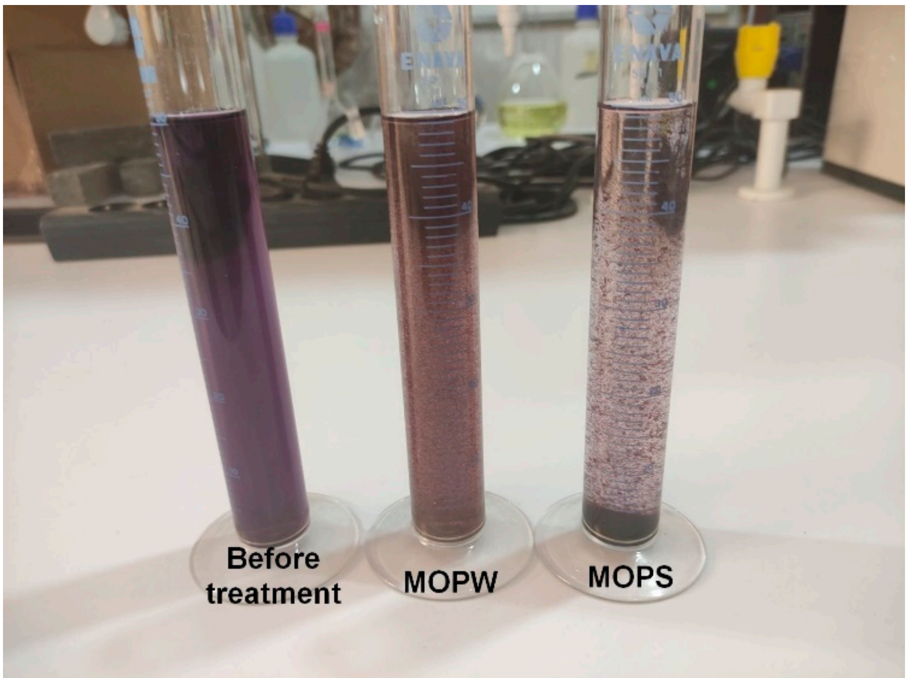


Figure 4. Discoloration process of MB11; blank and MOPW and MOPS (from **left** to **right**).

3.3. Effect of Initial pH

Because coagulants have their own suitable pH range that impacts the efficiency of their activities, it is a crucial parameter to consider. The pH range of 3 to 11 was selected for this investigation. As depicted in Figure 5, pH has little influence on the dye removal effectiveness of MOPW and MOPS, whereas a clear fluctuation is observed concerning the alum pattern. MB11 removal reduces with increasing pH, from 98.18%, 95.24%, and 85.12% at pH 6.5 to 89.18%, 87.32%, and 77.92% at pH 11 for alum, MOPS, and MOPW, respectively. Optimal performances of all coagulants were shown to occur at around pH 6.5. As mentioned in the previous section, *MO* is rich in protein content; these proteins have an isoelectric point in the range of pH 6.5–7.5 [36]. Consequently, this protein is cationic at pH < 6.5-7.5, which enables MOPS and MOPW to efficiently remove the anionic dye (MB11) across a broad pH range (from 3 to 6.5). This offers a significant advantage over alum as well as other natural coagulants, which are typically effective only within a limited pH range (Table 2). According to Tiaiba et al. [37], the dominant aluminum species at this pH range is Al^{3+}. The interaction between the cationic charges of Al^{3+} and the anionic charges of MB11 promotes a better coagulation efficiency; this is likely to explain the favorable coagulation efficiency occurring at this pH range. An investigation on the pH solutions' variation was also conducted for the three coagulants since the requirement for drinking water is between 6.0 and 8.5. The results are presented in Figure 6. As can be observed, no influence on the pH was recorded when MOPS and MOPW are applied to the synthetic dye solutions; this is likely owing to the fact that MOPS and MOPW do not hydrolyze efficiently in water due to their polymeric nature. Concerning alum, on the other hand, the final pH values are below the acceptable limit of drinking water, drastically decreasing with the increase of alum dosage (from 6.5 to 3.5 when the dosage increases from 200 to 600 mg/L). This may be the result of alum consuming water alkalinity during the hydrolysis; indeed, when alum is introduced to water, it first generates Al^{3+} and SO_4^{2-}, after which the Al^{3+} reacts with the OH in the water to form $Al(OH)_3$. As a consequence, consuming hydroxyl ions reduces the alkalinity and ultimately pH of the synthetic effluent. According to our findings, appropriate pH of wastewater discharge may be reached without the need for neutralization, representing a strong advantage to the use of *MO* as a replacement of chemical coagulants.

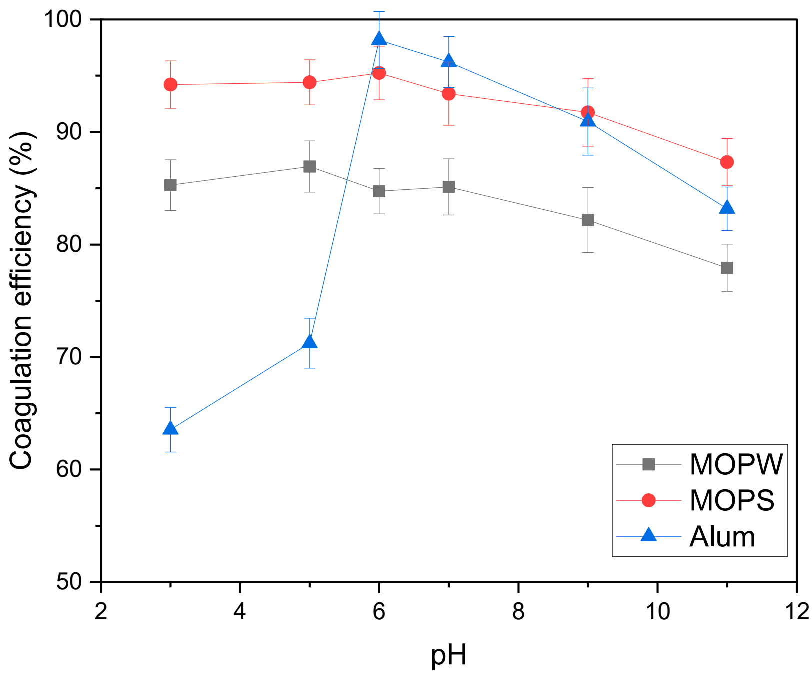


Figure 5. Effect of initial pH on coagulation efficiency (dose = 400 mg/L (alum), 500 mg/L (MOPW/MOPS), 1 M NaCl, 100 mg/L of MB11, 60 min of settling).

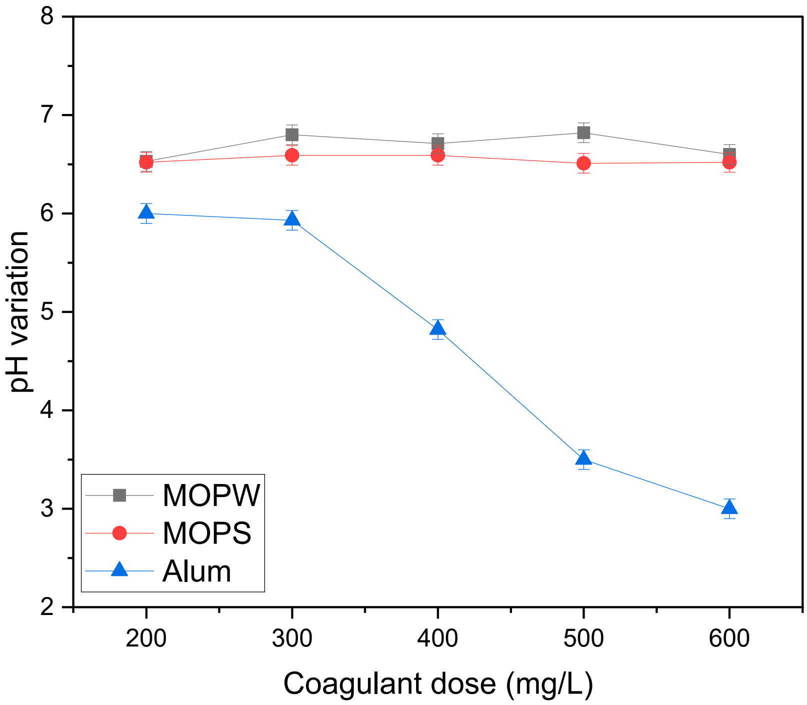


Figure 6. Effect of coagulant dose on the variation of pH's solution.

Table 2. Comparison of natural coagulants' performances in the removal of color from water and wastewater.

Biocoagulant	Wastewater Type	Optimal Conditions		Color Removal Efficiency	References
		pH	Dose		
Opuntia ficus indica	Textile wastewater	7.25	40 mg/L	99%	[38]
Ocimum basilicum	Textile wastewater	8.5	1600 mg/L	69%	[39]
Papaya seed	Textile wastewater	2	570 mg/L	85%	[40]
Cassia fistula	Synthetic paint industry wastewater	8.4	160 mg/L	96%	[41]
Opuntia dillenii	Highly turbid lake water	-	1000 mg/L	15%	[42]
Moringa oleifera	Reactive yellow	6.5	60 mL	89%	[43]
Strychnos potatorum		6.5	60 mL	93%	
Okra mucilage	Textile wastewater	6	3.20 mg/L + 88.0 mg/L Fe^{3+}	93.57%	[44]
MOPW	MB11	≤6.5	500 mg/L	80.12%	**This study**
MOPS				95.02%	

3.4. Effect of Initial Dye Concentration

To assess the influence of the initial MB11 concentration on the coagulation efficiency, different dye concentrations were auditioned (100–350 mg/L). According to Figure 7, we can observe a significant drop in the coagulation efficiency when the dye concentration rises from 100 mg/L to 350 mg/L for both MOPW and MOPW, with a notable disparity in the removal efficiency of these two biocoagulants. This is imputable to the better protein extractability when salt is used. As previously stated, adsorption and charge neutralization of dye molecules are the key mechanisms of dye removal by MOPW and MOPS. As a result, a given quantity of coagulant may neutralize the charge of a certain amount of dye molecules. As the dye concentration increases, the quantity of coagulant in the solution is insufficient to neutralize the charge of all dye molecules; therefore, dye removal decreases. Similar trends have been reported by previous studies [45,46]. Concerning alum, raising the initial dye concentration from 100 to 350 mg/L reduced dye removal effectiveness from 97.54% to 84.18%. According to the findings, the initial dye concentration had a weak effect on dye removal effectiveness by alum. This can be attributed to the fact that alum may react in numerous ways, resulting in coagulation. When employed at relatively low dosages (<5 mg/L), charge neutralization (destabilization) is likely to be the principal mechanism involved. At larger doses (such as in this case), the predominant coagulation mechanism is believed to be entrapment, thus, the poorer influence on MB11 removal when dye concentration increases.

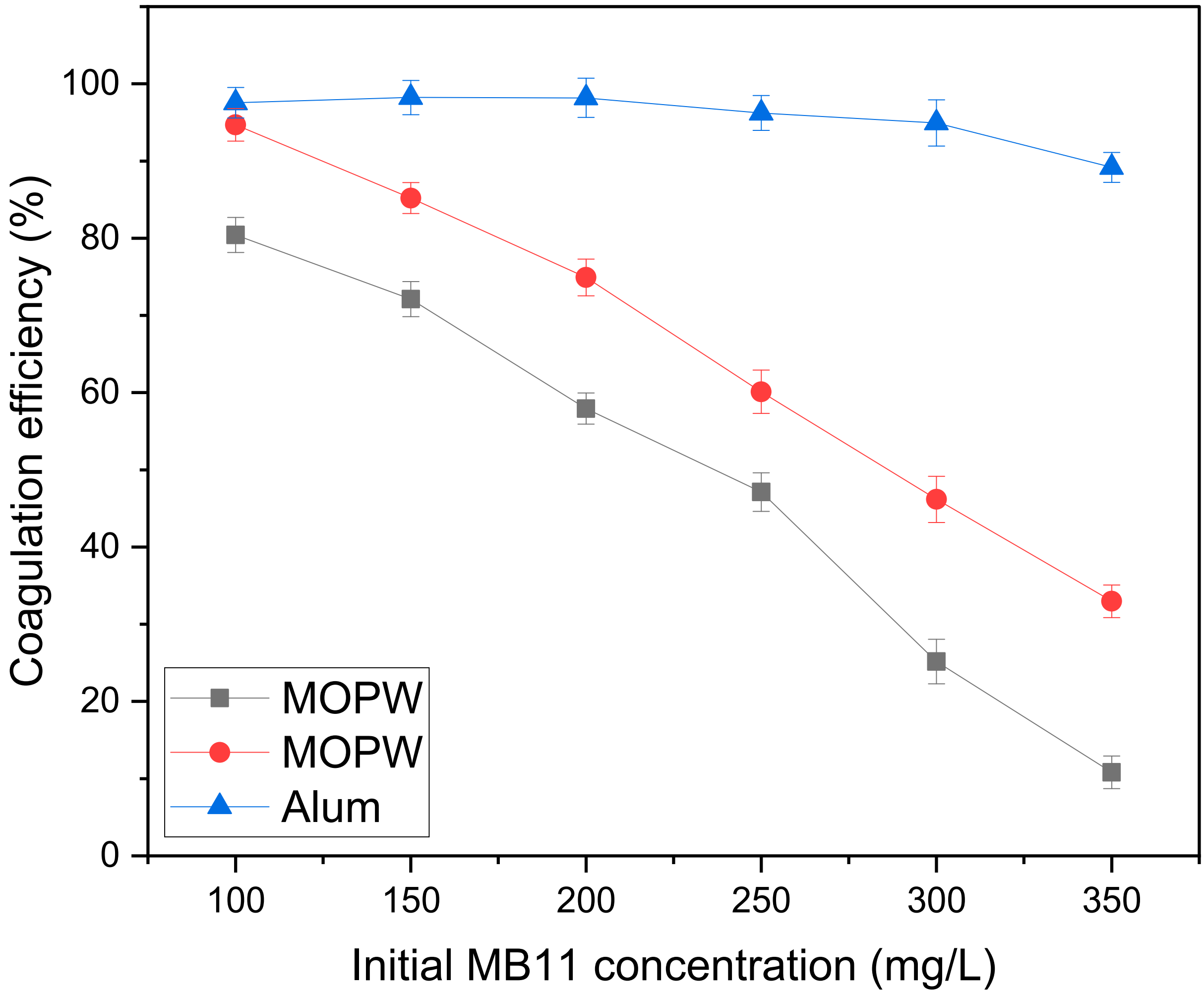


Figure 7. Effect of initial dye concentration on coagulation efficiency (%) (pH = 6.5, dose = 400 mg/L (alum), 500 mg/L (MOPW/MOPS), 1 M NaCl, 60 min of settling).

3.5. Effect of Salt Concentration

The influence of salt concentration is also one of the most important factors affecting coagulant extraction. In order to study the effect of this parameter on coagulation efficiency, the NaCl concentrations were adjusted from 0.25 to 2 M, while fixing the other parameters at their optimum. Figure 8 illustrates the results. As can be seen, the increase in salt concentration results in an improvement in the coagulation efficiency, suggesting the extraction of more proteins (from 84.18% to 95.48%). Due to the dissolution of salt, the maximum density of charges might increase coagulation. In addition, it is hypothesized that the increase in protein solubility at higher NaCl concentrations was generated by salting phenomenon, in which the interaction between the oppositely charged ions of salts and the hydrophilic functional groups of proteins generates a double layer. Therefore, electrostatic interaction between protein molecules decreases, resulting in enhanced protein solubility [47]. MOPS extracted with higher NaCl concentrations lowers the efficacy of MB11 removal. This may be the "salting-out" effect, which is based on the idea that increasing the intensity of an attractive protein–protein interaction decreases its solubility at high concentrations [48]. Moreover, the addition of NaCl increases the amount of Na^+ available to compete with the protein molecule for reaction. As a result, the MOPS particle has less interaction to neutralize the negative charges of the dye [49], which diminishes the removal efficiency.

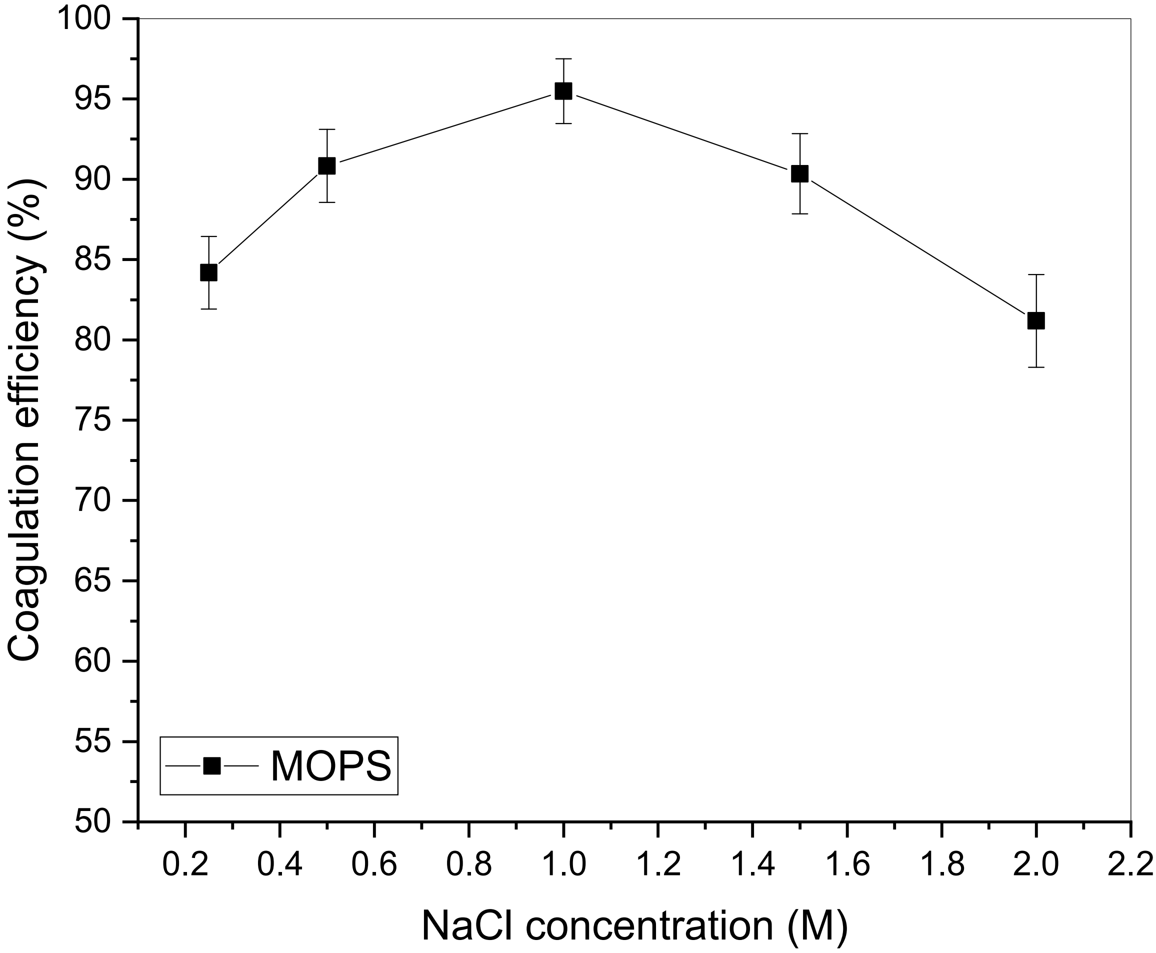


Figure 8. Effect of NaCl concentration on coagulation efficiency (%) (pH = 6.5, dose = 400 mg/L (alum), 500 mg/L (MOPW/MOPS), 100 mg/L of MB11, 60 min of settling).

3.6. Effect of Sedimentation Time

One of the crucial parameters of a treatment plant is the settling time. Due to its significant effect on the overall cost and coagulation efficiency of the purification process, its appropriate level must be investigated and established. In this study, the sedimentation time was chosen between 15 and 90 min. As depicted in Figure 9, it can be observed that the proportion of MB11 removed rises as settling time increases when the three coagulants were used. The removal effectiveness was high from 15 to 60 min; then, at a settling period of 60 min, equilibrium was reached. There was little or no substantial increase in MB11 removal beyond the equilibrium settling time (60 min). Concerning alum, the sedimentation of the flocs formed by the use of MOPW and MOPS is faster than that formed by using alum (45 min); this may be a good indication of the fact that larger flocs are formed when *MO* extracts are applied as biocoagulants. Both results show that once equilibrium is reached, no additional increase in settling time is required.

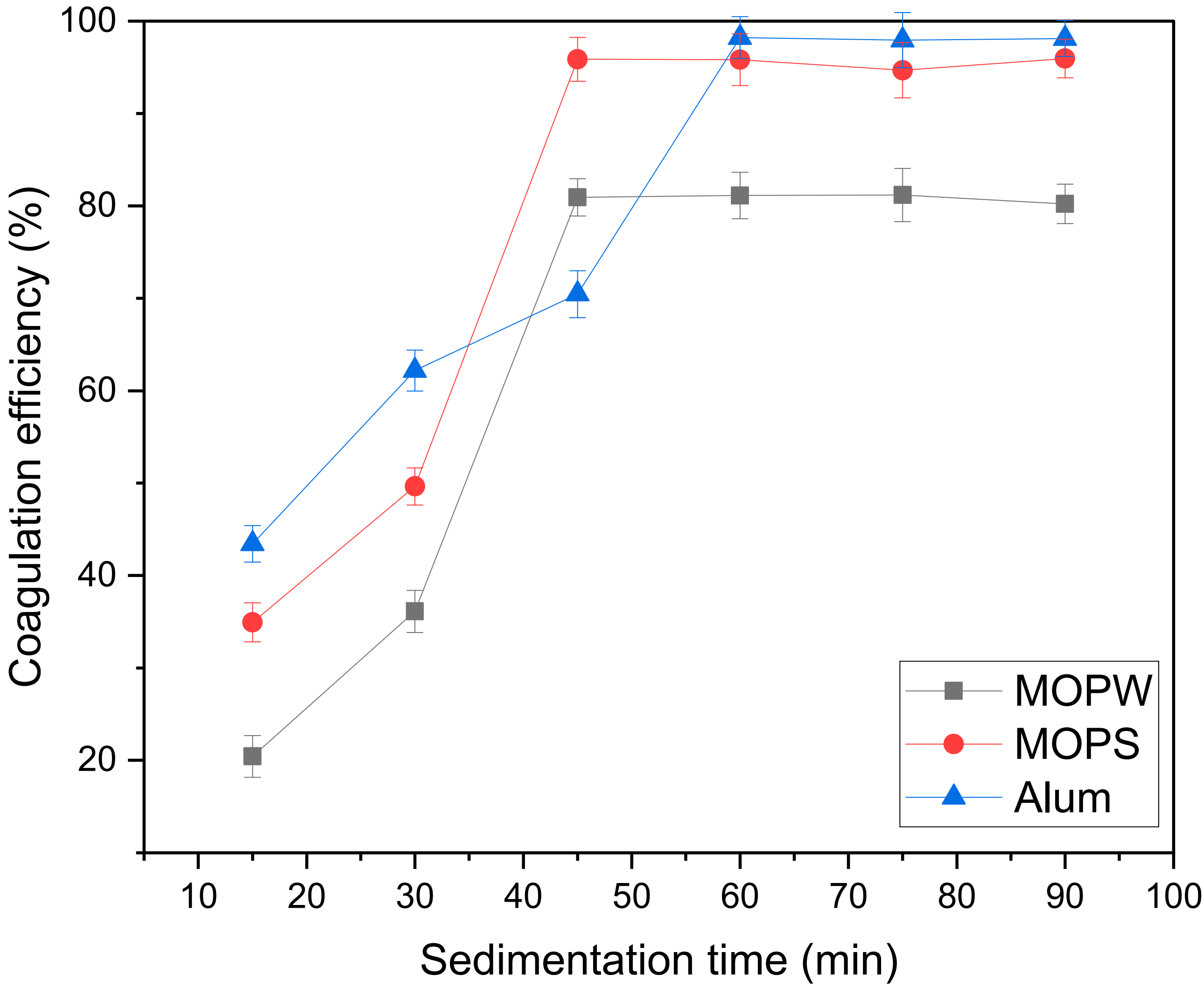


Figure 9. Effect of sedimentation time on coagulation efficiency (%) (pH = 6.5, dose = 400 mg/L (alum), 500 mg/L (MOPW/MOPS), 100 mg/L of MB11, 1 M NaCl).

4. Conclusions

This study examined the effectiveness of MB11 dye removal with naturally derived coagulants, MOPW and MOPS, as well as alum for comparative purposes. The primary outcomes obtained can be described as follows:

- The coagulant dose had a substantial impact on the effectiveness of MOPW and MOPS in removing MB11 dye. With an increase in dosage, the removal efficiency of both biocoagulants increased until the optimal dosage of 500 mg/L was recorded. Thereafter, an increase in coagulant dosage led to a decrease in dye removal efficiency, indicating that adsorption and charge neutralization might be the primary mechanisms occurring in this study.
- Within the pH range of 3 to 6.5, a minimal impact on the removal efficiency of MB11 was noticed when the biocoagulants were used. This was in contrast to alum, for which removal rates fluctuated significantly, indicating the versatility of biocoagulants to function effectively over a wide pH range. Tests on pH variations have shown that biocoagulants have a negligible effect on pH, enabling us to establish that the

neutralization step often needed when chemical coagulants are employed is no longer required.

➢ In contrast to MOPW and MOPS, increasing the initial concentration of MB11 had less of an effect on the proper functioning of alum as a coagulant. Indicating that distinct processes govern the coagulation-flocculation of this anionic dye.

➢ Despite the similar patterns of the two biocoagulants, MOPS outperformed MOPW. This was attributed to the proteinaceous structure of *MO*, which necessitates salt for increased extractability; nevertheless, this is not regarded as a disadvantage due to the accessibility and cost-effectiveness of NaCl salt.

➢ The removal efficiencies of MOPS and alum were comparable (95 and 98%), with decreased sedimentation time reported when the two biocoagulants were applied, indicating that the flocs generated by MOPS and MOPW may be larger and, hence, settle more quickly, which is a considerable advantage.

Based on the above findings, we can assume that *MO* extract is very efficient at eliminating MB11, with comparable performances to that of alum. In spite the higher dosage requirements (400 mg/L for alum and 500 mg/L for *MO* extracts to obtain an equivalent removal rate), reduced sedimentation times and pH stability were noticed when the biocoagulant was used. One of the constraints that exists, however, is the restriction of this plant to tropical environments, despite the fact that the species has been introduced successfully in numerous locations of Algeria, providing a positive outlook on the use of this biomaterial. Furthermore, additional investigation of the molecules responsible for the coagulation activity of *Moringa oleifera* and its possible isolation in reducing the quantity of organic matter associated with the raw *MO* extracts, which raises BOD and DOC levels in treated water, is required. Additionally, exploration of a synergistic usage of the *MO* extracts and the chemical coagulant in order to reduce the latter's use while benefiting from both of their advantages and minimizing their downsides might also be an interesting subject.

Author Contributions: Conceptualization, A.H., A.I., and L.M; methodology, A.H., A.I., L.M. and S.C.; validation, J.-C.B., A.A., A.A.A. and L.M; formal analysis, A.H., A.I. and S.C.; investigation, A.H.; resources, L.M., A.I. and M.K.; data curation, A.H., A.I., L.M. and S.C.; writing—original draft preparation, A.H. and A.I.; writing—review and editing, A.H., A.I., L.M., A.A., J.-C.B. and M.K.; visualization, A.H., L.M., J.-C.B. and A.A.A.; supervision, L.M., A.A. and J.-C.B.; project administration, L.M. and A.A.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors wish to thank all who assisted in conducting this work.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Bian, Z.; Liu, D. A Comprehensive Review on Types, Methods and Different Regions Related to Water–Energy–Food Nexus. *Int. J. Environ. Res. Public Health.* **2021**, *18*, 8276. [CrossRef] [PubMed]
2. Isik, Z.; Saleh, M.; M'barek, I.; Yabalak, E.; Dizge, N.; Deepanraj, B. Investigation of the Adsorption Performance of Cationic and Anionic Dyes Using Hydrochared Waste Human Hair. *Biomass Convers. Biorefinery* **2022**, 1–14. [CrossRef]
3. Sharma, V.T.; Kamath, S.V.; Mondal, D.; Kotrappanavar, N.S. Fe–Al Based Nanocomposite Reinforced Hydrothermal Carbon: Efficient and Robust Absorbent for Anionic Dyes. *Chemosphere* **2020**, *259*, 127421. [CrossRef] [PubMed]
4. Khan, F.S.; Mubarak, N.M.; Tan, Y.H.; Khalid, M.; Karri, R.R.; Walvekar, R.; Abdullah, E.C.; Nizamuddin, S.; Mazari, S.A. A Comprehensive Review on Magnetic Carbon Nanotubes and Carbon Nanotube-Based Buckypaper- Heavy Metal and Dyes Removal. *J. Hazard. Mater.* **2021**, *413*, 125375. [CrossRef]

5. Kaur, Y.; Jasrotia, T.; Kumar, R.; Chaudhary, G.; Chaudhary, S. Adsorptive Removal of Eriochrome Black T (EBT) Dye by Using Surface Active Low Cost Zinc Oxide Nanoparticles: A Comparative Overview. *Chemosphere* **2021**, *278*, 130366. [CrossRef]
6. Cai, L.; Ying, D.; Liang, X.; Zhu, M.; Lin, X.; Xu, Q.; Cai, Z.; Xu, X.; Na, N. A Novel Cationic Polyelectrolyte Microsphere for Ultrafast and Ultra-Efficient Removal of Heavy Metal Ions and Dyes. *Chem. Eng. J.* **2021**, *410*, 128404. [CrossRef]
7. Wijannarong, S.; Aroonsrimorakot, S.; Thavipoke, P.; Kumsopa, C.; Sangjan, S. Removal of Reactive Dyes from Textile Dyeing Industrial Effluent by Ozonation Process. *APCBEE Procedia* **2013**, *5*, 279–282. [CrossRef]
8. Liu, Q.; Li, Y.; Chen, H.; Lu, J.; Yu, G.; Möslang, M. Superior Adsorption Capacity of Functionalised Straw Adsorbent for Dyes and Heavy-Metal Ions. *J. Hazard. Mater.* **2019**, *382*, 121040. [CrossRef]
9. Zhang, P.; Gong, J.-L.; Zeng, G.-M.; Deng, C.-H.; Yang, H.-C.; Liu, H.; Huan, S.-Y. Cross-Linking to Prepare Composite Graphene Oxide-Framework Membranes with High-Flux for Dyes and Heavy Metal Ions Removal. *Chem. Eng. J.* **2017**, *322*, 657–666. [CrossRef]
10. Waghchaure, R.; Adole, V.; Jagdale, B. Photocatalytic Degradation of Methylene Blue, Rhodamine B, Methyl Orange and Eriochrome Black T Dyes by Modified ZnO Nanocatalysts: A Concise Review. *Inorg. Chem. Commun.* **2022**, 109764. [CrossRef]
11. Zhang, Y.; Liu, X.; Xin, B.; Chen, S.; Huang, Q. Extracellular Biosynthesis of High-Purity γ-MnS by the Sulfate-Reducing Bacterium Anaerofilum Sp. through Selective Precipitation of a Mn^{2+}-Eriochrome Black T Chelate Complex. *Geomicrobiol. J.* **2016**, *33*, 194–198. [CrossRef]
12. Kakoi, B.; Kaluli, J.W.; Ndiba, P.K.; Thiong'o, G. Banana Pith as a Natural Coagulant for Polluted River Water. *Ecol. Eng.* **2016**, *95*, 699–705. [CrossRef]
13. Dayarathne, H.N.P.; Angove, M.; Aryal, R.; Abuel-Naga, H.; Mainali, B. Removal of Natural Organic Matter from Source Water: Review on Coagulants, Dual Coagulation, Alternative Coagulants, and Mechanisms. *J. Water Process. Eng.* **2020**, *40*, 101820. [CrossRef]
14. Owodunni, A.; Ismail, S. Revolutionary Technique for Sustainable Plant-Based Green Coagulants in Industrial Wastewater Treatment—A Review. *J. Water Process. Eng.* **2021**, *42*, 102096. [CrossRef]
15. Syed Zainal, S.F.F.; Aziz, H.; Mohd Omar, F.; Alazaiza, M. Influence of Jatropha Curcas Seeds as a Natural Flocculant on Reducing Tin (IV) Tetrachloride in the Treatment of Concentrated Stabilised Landfill Leachate. *Chemosphere* **2021**, *285*, 131484. [CrossRef]
16. Azamzam, A.; Rafatullah, M.; Yahya, E.; Ahmad, M.; Lalung, J.; Mahboob, A.; Siddiqui, M. Enhancing the Efficiency of Banana Peel Bio-Coagulant in Turbid and River Water Treatment Applications. *Water* **2022**, *14*, 2473. [CrossRef]
17. Bahrodin, M.; Zaidi, N.S.; Kadier, A.; Hussein, N.; Syafiuddin, A.; Boopathy, R. A Novel Natural Active Coagulant Agent Extracted from the Sugarcane Bagasse for Wastewater Treatment. *Appl. Sci.* **2022**, *12*, 7972. [CrossRef]
18. Hadadi, A.; Imessaoudene, A.; Bollinger, J.-C.; Assadi, A.A.; Amrane, A.; Mouni, L. Comparison of Four Plant-Based Bio-Coagulants Performances against Alum and Ferric Chloride in the Turbidity Improvement of Bentonite Synthetic Water. *Water* **2022**, *14*, 3324. [CrossRef]
19. Ueda Yamaguchi, N.; Cusioli, L.; Quesada, H.; Ferreira, M.; Fagundes-Klen, M.; Vieira, A.; Gomes, R.; Vieira, M.; Bergamasco, R. A Review of Moringa Oleifera Seeds in Water Treatment: Trends and Future Challenges. *Process Saf. Environ. Prot.* **2021**, *147*, 405–420. [CrossRef]
20. Ribeiro, J.V.; Vega, P.; Reis, A. Moringa Oleifera Seed as a Natural Coagulant to Treat Low-Turbidity Water by in-Line Filtration. *Rev. Ambient. Água.* **2019**, *14*, 1. [CrossRef]
21. Okuda, T.; Baes, A.U.; Nishijima, W.; Okada, M. Improvement of Extraction Method of Coagulation Active Components from Moringa Oleifera Seed. *Water Res.* **1999**, *33*, 3373–3378. [CrossRef]
22. Varsani, V.; Vyas, S.; Dudahagara, D. Development of Bio-Based Material from the Moringa Oleifera and Its Bio-Coagulation Kinetic Modeling–A Sustainable Approach to Treat the Wastewater. *Heliyon* **2022**, *8*, e10447. [CrossRef] [PubMed]
23. Flory Mkangombe, K.; Bernard, Z.; Hongbin, C. Study of Domestic Wastewater Treatment Using Moringa Oleifera Coagulant Coupled with Vertical Flow Constructed Wetland in Kibera Slum, Kenya. *Environ. Sci. Pollut. Res.* **2022**, *29*, 36589–36607. [CrossRef]
24. Johnson, U.K.; Imelda, N.N.; Geoffrey, M.M.; Caro, W.H.; Festus, M.; Josphert, K. The Effectiveness of Moringa Oleifera Seed Coagulant in Reducing the Turbidity and Modifying the Physico-Chemical Characteristics of Water. *Afr. J. Environ. Sci. Technol.* **2022**, *16*, 126–145. [CrossRef]
25. Tometin, L.; Nonfodji, O.; Chouti, W.; Dannon, M.; Aboubakari, A.; Fatombi, J. Use of Natural Coagulants in Removing Organic Matter, Turbidity and Fecal Bacteria from Hospital Wastewater by Coagulation-Flocculation Process. *J. Water Resour. Prot.* **2022**, *14*, 719–730. [CrossRef]
26. Eichhorn, C.; Weckmüller, S.; Urban, W. Natural Flocculant from a Combination of Moringa Oleifera Seeds and Cactus Cladodes (Opuntia Ficus-Indica) to Optimize Flocculation Properties. *Water* **2022**, *14*, 3570. [CrossRef]
27. Mohamed Noor, M.; Lee, W.; Azli, M.; Ngadi, N.; Mohamed, M. Moringa Oleifera Extract as Green Coagulant for POME Treatment: Preliminary Studies and Sludge Evaluation. *Mater. Today Proc.* **2021**, *46*, 1940–1947. [CrossRef]
28. Kachangoon, R.; Vichapong, J.; Santaladchaiyakit, Y.; Srijaranai, S. Green Fabrication of Moringa Oleifera Seed as Efficient Biosorbent for Selective Enrichment of Triazole Fungicides in Environmental Water, Honey and Fruit Juice Samples. *Microchem. J.* **2022**, *175*, 107194. [CrossRef]

29. Silva, K.; Filippov, L.; Piçarra, A.; Filippova, I.; Lima, N.; Skliar, A.; Marques Faustino, L.; Leal Filho, L. New Perspectives in Iron Ore Flotation: Use of Collector Reagents without Depressants in Reverse Cationic Flotation of Quartz. *Miner. Eng.* **2021**, *170*, 107004. [CrossRef]
30. Ezeamaku, U.; Chike-Onyegbula, C.; Iheaturu, N.; Onwuka, E.; Ezike, C.; Onuchukwu, S. Treatment of Lead Contaminated Wastewater Using Aluminium Sulphate and Moringa Oleifera as Coagulants. *Niger J. Polym. Sci. Technol.* **2018**, *13*, 82–92.
31. Zeng, H.; Tang, H.; Sun, W.; Wang, L. Strengthening Solid–Liquid Separation of Bauxite Residue through the Synergy of Charge Neutralization and Flocculation. *Sep. Purif. Technol.* **2021**, *285*, 120296. [CrossRef]
32. Lim, V.H.; Yamashita, Y.; Ogawa, K.; Adachi, Y. The Inhibitory Effects of Synthetic Polyacrylic Acid and Humic Substances on the Initial Stage of Colloidal Flocculation Induced by Polycationic Flocculant with Low Charge Density. *Colloids Surf. A Physicochem. Eng.* **2022**, *653*, 129930. [CrossRef]
33. Megersa, M.; Beyene, A.; Ambelu, A.; Asnake, D.; Tesfaye, B.; Firdissa, B.; Alebachew, Z.; Triest, L. A Preliminary Evaluation of Locally Used Plant Coagulants for Household Water Treatment. *Water Conserv. Sci. Eng.* **2016**, *1*, 95–102. [CrossRef]
34. Ndabigengesere, A.; Narasiah, K.S. Quality of Water Treated by Coagulation Using Moringa Oleifera Seeds. *Water Res.* **1998**, *32*, 781–791. [CrossRef]
35. Madrona, G.S.; Serpelloni, G.B.; Salcedo Vieira, A.M.; Nishi, L.; Cardoso, K.C.; Bergamasco, R. Study of the Effect of Saline Solution on the Extraction of the Moringa Oleifera Seed's Active Component for Water Treatment. *Water Air Soil Pollut.* **2010**, *211*, 409–415. [CrossRef]
36. Belbali, A.; Benghalem, A.; Gouttele, K.; Taleb, S. Coagulation of Turbid Wastewater with an Active Component Extracted from Moringa Oleifera Seeds. *J. Environ. Anal. Chem.* **2021**, 1–17. [CrossRef]
37. Tiaiba, M.; Merzouk, B.; Mazour, M.; Leclerc, J.; Lapicque, F. Study of Chemical Coagulation Conditions for a Disperse Red Dye Removal from Aqueous Solutions. *Membr. Water Treat.* **2022**. [CrossRef]
38. Bouatay, F.; Mhenni, M.F. Use of the Cactus Cladodes Mucilage (Opuntia Ficus Indica) As an Eco-Friendly Flocculants: Process Development and Optimization Using Stastical Analysis. *Int. J. Environ. Res.* **2014**, *8*, 1295–1308.
39. Shamsnejati, S.; Chaibakhsh, N.; Pendashteh, A.R.; Hayeripour, S. Mucilaginous Seed of Ocimum Basilicum as a Natural Coagulant for Textile Wastewater Treatment. *Ind. Crops Prod.* **2015**, *69*, 40–47. [CrossRef]
40. Kristianto, H.; Kurniawan, M.; Soetedjo, J.N.M. Utilization of Papaya Seeds as Natural Coagulant for Synthetic Textile Coloring Agent Wastewater Treatment. *Int. J. Adv. Sci. Eng. Inf. Technol.* **2018**, *8*, 2071. [CrossRef]
41. Solaiappan, V.; Sakthivel, S.; Karthick, R.; Gowsigan, V.S. A Sustainable Approach for the Treatment of Industrial Effluent Using a Green Coagulant Cassia Fistula vs. Chemical Coagulant. *Desalin. Water Treat.* **2020**, *195*, 189–197. [CrossRef]
42. Nougbodé, Y.A.; Agbangnan, C.P.; Koudoro, A.Y.; Dèdjiho, C.A.; Aïna, M.P.; Mama, D.; Sohounhloué, D.C. Evaluation of the Opuntia Dillenii as Natural Coagulant in Water Clarification: Case of Treatment of Highly Turbid Surface Water. *J. Water Resour. Prot.* **2013**, *5*, 1242–1246. [CrossRef]
43. Vijayaraghavan, G.; Rajasekaran, R.; Shanthakumar, S. Removal of Reactive Yellow Dye Using Natural Coagulants in Synthetic Textile Wastewater. *Int. J. Chem. Sci.* **2013**, *11*, 1824–1830.
44. Freitas, T.; Oliveira, V.M.; Souza, M.T.F.; Geraldino, H.; Almeida, V.C.; Fávaro, S.; Garcia, J. Optimization of Coagulation-Flocculation Process for Treatment of Industrial Textile Wastewater Using Okra (A. Esculentus) Mucilage as Natural Coagulant. *Ind. Crops Prod.* **2015**, *76*, 538–544. [CrossRef]
45. Mahmoudabadi, T.; Abbasi, F.; Jalili, M.; Talebi, P. Effectiveness of Plantago Major Extract as a Natural Coagulant in Removal of Reactive Blue 19 Dye from Wastewater. *Int. J. Environ. Sci. Technol.* **2019**, *16*, 7893–7900. [CrossRef]
46. Beltrán, J.; Sánchez-Martín, J.; Rodríguez-Sánchez, M. Textile Wastewater Purification through Natural Coagulants. *Appl. Water Sci.* **2011**, *1*, 25–33. [CrossRef]
47. Villaseñor, D.; Astudillo-Sanchez, P.; Real, J.; Bandala, E. Wastewater Treatment Using Moringa Oleifera Lam Seeds: A Review. *J. Water Process. Eng.* **2018**, *23*, 151–164. [CrossRef]
48. Kristianto, H.; Rahman, H.; Prasetyo, S.; Sugih, A.K. Removal of Congo Red Aqueous Solution Using Leucaena Leucocephala Seed's Extract as Natural Coagulant. *Appl. Water Sci.* **2019**, *9*, 1–7. [CrossRef]
49. Wahid, M.; Megat Mohd Noor, M.J.; Goto, M.; Sugiura, N.; Othman, N.; Zakaria, Z.; Mohammed, T.; Jusoh, A.; Hara, H. Recombinant Protein Expression of Moringa Oleifera Lectin in Methylotrophic Yeast as Active Coagulant for Sustainable High Turbid Water Treatment. *Biosci. Biotechnol. Biochem.* **2017**, *81*, 1–8. [CrossRef]