
Research article

Valorization of chestnut shell waste as a biocoagulant for turbidity removal: Optimization via Box-Behnken Design

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Abstract: In this study, the influence of solid–liquid extraction conditions on the coagulation performance of a chestnut shell (*Castanea sativa*)-derived biocoagulant was systematically investigated. Extraction pH, chestnut shell mass, and extraction time were evaluated using response surface methodology based on a Box–Behnken design. The extracted tannins were subsequently chemically modified via the Mannich reaction to introduce positively charged groups and evaluated for turbidity removal from synthetic water through coagulation–flocculation jar test experiments using kaolin suspension as model turbid water. Statistical analysis indicated that the proposed model was not statistically significant (ANOVA, $P = 0.531$), and none of the evaluated extraction variables showed significant individual effects ($P > 0.05$). However, the quadratic effect of extraction time approached significance ($P = 0.068$), suggesting a possible nonlinear influence on turbidity removal. However, extraction time showed evidence of a potential nonlinear influence on turbidity removal, suggesting the existence of an optimal extraction range. Despite the limited predictive capability of the model, the synthesized coagulant demonstrated high efficiency, achieving turbidity removal rates of up to 96% under optimal experimental conditions. Moreover, its performance was directly comparable to that of aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$), a conventional metal-based coagulant, when tested under identical operational conditions. Collectively, these results demonstrate the potential of chestnut shell-derived coagulants as effective and sustainable alternatives to metal-based coagulants for wastewater treatment applications, contributing to agricultural residue valorization and circular economy principles.

Keywords: bio-based materials; coagulation; response surface methodology; tannins; wastewater treatment.

1. Introduction

Water is an essential resource for human life, ecosystems, and industrial development; however, its availability and quality are increasingly threatened by population growth, industrial expansion, and climate change [1,2]. In response to these challenges, the United Nations established the 2030 agenda for sustainable development, in which sustainable development goal 6 (SDG 6) aims to ensure universal access to safe water and sanitation, and the sustainable management of water resources [3]. Despite these efforts, water pollution remains major concern because of the excessive withdrawal of water resources and pollution associated with inadequate sanitation practices [4].

Among the various indicators of water quality, turbidity is of particular importance. This parameter is associated with the presence of suspended and colloidal particles, such as clay, silt, finely divided organic and inorganic matter, plankton, and other microscopic organisms [5]. High turbidity can hinder water treatment by clogging filters, increasing the demand for chemical disinfectants, and blocking ultraviolet irradiation, while also affecting consumer perception, since visible cloudiness in water often raises concerns about its cleanliness and safety [6].

To address these challenges, coagulation–flocculation remains one of the most applied methods to treat wastewater due to its operational simplicity, efficiency, and wide availability of coagulant–flocculant agents [7,8]. This process involves the destabilization of colloidal particles followed by their aggregation into larger flocs, which can be easily removed by sediment [9]. It is also valuable for its effectiveness in removing suspended particles, organic content, and other contaminants, such as fluoride [10]. It should be noted, however, that the efficiency of coagulation–flocculation depends on factors, including coagulant type and dose, temperature, pH, the quality of the water being treated, and hydrodynamic parameters like mixing speed and time [11].

Despite its widespread use, conventional coagulation–flocculation process relies on inorganic coagulants such as aluminum sulfate, ferric sulfate, and ferric chloride, which presents several drawbacks, including sludge containing residual metals, sensitivity to operational conditions, and potential environmental and health risks [6]. The presence of these residues in treated water is linked to neurotoxic and carcinogenic effects, with studies associating them with diseases including Alzheimer’s and Parkinson’s disease, as well as several forms of cancer [11].

In this context, increasing attention has been directed toward the development of natural coagulants derived from renewable resources. Among these materials, tannins have emerged as promising alternatives due to their availability biodegradability, and low cost [8].

Tannins are water-soluble phenolic compounds found in bark, seeds, leaves, and comestibles, such as grapes and walnuts [12]. They can display a wide variety of molecular weights and are distinguished by their ability to precipitate proteins from aqueous solutions [13]. Derived from agricultural residue products, these tannin materials are not only readily available and low cost but also provide safer treated water with reduced concentrations of toxic residual metals [8,10].

Recently, bio-based materials have received increasing attention for wastewater treatment due to their renewability, biodegradability, and potential to replace conventional chemical coagulants. Plant-based coagulants derived from agricultural residues and tannin-rich biomasses have demonstrated

promising performance for turbidity and contaminant removal while promoting waste valorization and circular economy strategies. These advances have encouraged the exploration of new biomass sources for sustainable water treatment applications [9,10].

Within this framework, chestnut shells (*Castanea sativa*) represent a particularly attractive raw material, because of their high tannin content, which makes them an excellent candidate to produce natural coagulants [14]. Portugal is one of the leading producers of chestnuts in Europe, generating large amount of shell residues as byproducts of the food industry [14]. Although these residues are sometimes used for energy recovery or soil conditioning, a significant portion is discarded, representing a missed opportunity for value-added applications [14].

However, due to their predominantly anionic nature, chemical modification is often required to enhance their performance as coagulants. The Mannich reaction is one of the most widely used approaches for this purpose, allowing the introduction of cationic functional groups into the tannin structure [15]. Previous studies have demonstrated that this modification significantly improves the coagulation performance of chestnut shell tannins by introducing quaternary ammonium groups that promote charge neutralization [15,16].

Although chestnut shell tannins have recently been investigated as sustainable coagulants, previous studies have mainly focused on their extraction, chemical modification, and application in water and wastewater treatment [15–17]. In contrast, the influence of solid–liquid extraction conditions on the coagulation performance of the resulting cationized extracts remains poorly understood. Since extraction parameters directly affect tannin yield and composition, understanding their influence is essential for improving coagulant performance and establishing more efficient and reproducible production processes. Such knowledge is also fundamental for the development of standardized production protocols and for supporting the future scale-up and practical implementation of chestnut shell-derived coagulants.

Therefore, this study addresses this knowledge gap by systematically evaluating how solid–liquid extraction conditions influence the coagulation performance of the resulting chestnut shell-derived biocoagulant. Specifically, extraction pH, chestnut shell mass at a fixed solvent volume, and extraction time were investigated using response surface methodology (RSM) based on a Box–Behnken design. Following extraction, the tannins were cationized through the Mannich reaction, and the resulting coagulants were evaluated in terms of turbidity removal. Thus, the main contribution of this study lies in establishing a direct relationship between upstream extraction conditions and the downstream coagulation performance of the cationized chestnut shell extract. In addition, the performance of the developed biocoagulant was directly compared with conventional aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$) under identical operating conditions to assess its competitive potential.

2. Materials and methods

A simplified overview of the experimental steps used in this study to produce, modify, and test the chestnut shell coagulant is shown in Figure 1. The process includes alkaline extraction of tannins, chemical modification through Mannich reaction, and performance evaluation on turbidity removal.

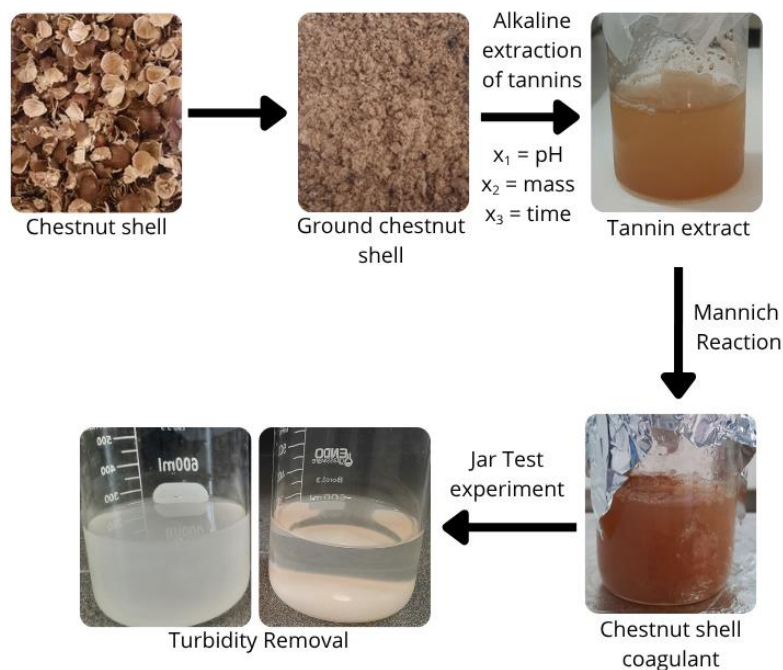


Figure 1. Overview of the methodological approach developed for extraction, modification, and coagulation testing.

2.1. Preparation of the coagulant

Chestnut shells (*Castanea sativa*) were obtained from a local market in Bragança, Portugal. Upon collection, the shells were visually inspected, and damaged or contaminated materials were discarded. To prepare the coagulants, the shells were initially washed thoroughly with distilled water to remove impurities, and subsequently dried in an oven at 60 °C, following procedures commonly reported for lignocellulosic biomass preparation [13,14,18,19] (Figure 2).



Figure 2. Chestnut shell after peeling.

The dried material was grounded to obtain a fine particulate material (Figure 3) and placed in an oven at 60 °C for another 24 h.



Figure 3. Ground chestnut shell.

The extraction of tannins was performed by mixing 5, 6, or 7 g of ground chestnut shells with 100 mL of 0.05 M NaOH (Sharlab S.L., Barcelona, Spain) solution, according to the Box-Behnken experimental design. Tannins were extracted using an alkaline solution, since alkaline conditions can depolymerize tannins and enhance their solubility, leading to greater extraction efficiency [18].

The extraction process was carried out under constant agitation at room temperature. The extraction parameters (pH, chestnut shell mass, and time) were simultaneously varied according to the experimental design described in Section 2.1.1 to optimize the extraction of tannins.

After extraction, the solid residue was separated from the liquid via gravimetric filtration. The tannin extract was stored under refrigeration for subsequent applications.

Since tannins are predominantly anionic in aqueous solution, the extracted tannins were chemically modified via the Mannich reaction, a well-established method for introducing cationic functional groups into organic molecules [19]. This cationization method involves the reaction between a phenolic compound (tannin), an aldehyde (formaldehyde), and an amine source (ammonium chloride) [14]. First, formaldehyde (Labkem, Barcelona, Spain) and the ammonium chloride (Pronalab, Lisbon, Portugal) combine to form a reactive iminium species, which then reacts with an enol group on the tannin molecule [20], as shown in Figure 4.

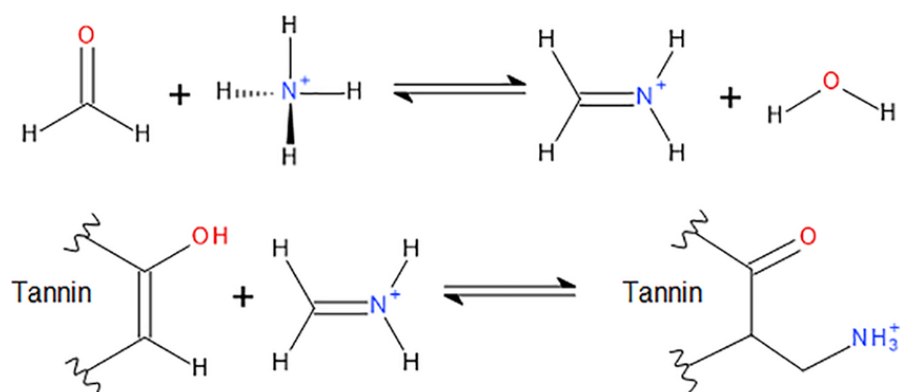


Figure 4. Representation of the Mannich reaction for tannin modification [19].

This modification introduces positively charged functional groups to the tannin structure, increasing its molecular weight, and enabling them to destabilize and neutralize negatively charged

colloidal particles frequently found in wastewater [19,21]. Therefore, the resulting water-soluble compound has good flocculating properties and can be used to remove suspended particles from wastewater [17,21].

Initially, the pH of the alkaline raw extract was adjusted to 6.0 by adding a hydrochloric acid (HCl) solution, since it is well established that the Mannich reaction with tannins occurs under acidic conditions, producing water-soluble amphoteric tannins with flocculating properties [21]. The Mannich solution was prepared by mixing ammonium chloride (NH₄Cl) and formaldehyde (37%), adopting the proportions to maintain a tannin:NH₄Cl:formaldehyde ratio of 1:1.25:3.75 [17]. The solution was heated at 120 °C for 2 h under continuous mixing to form the iminium ion required for tannin cationization [22].

Simultaneously, the tannin extract was heated to 55 °C under continuous stirring to ensure complete homogenization of the mixture. The Mannich solution was then gradually added to the extract, and the temperature was increased to 85 °C, maintaining these conditions until a rise in viscosity indicated successful cationization [17]. Finally, distilled water was added to the reaction mixture.

2.1.1. RSM

RSM was employed to optimize the extraction conditions of chestnut shell-based natural coagulants for wastewater treatment, since this method enables the assessment of linear, quadratic, and interaction effects among the studied variables, as well as the analysis of the response surface behavior within the experimental range [23].

To achieve this, a three-factor, three-level Box-Behnken design was adopted due to its efficiency in reducing the number of experimental runs while still allowing accurate evaluation of variable interactions and curvature effects [23].

The first variable (x_1) was the extraction pH, evaluated at levels 9, 10, and 11. The second variable (x_2) was the chestnut shell mass, defined at 5, 6, and 7 g. The third variable (x_3) corresponded to the extraction time, with values of 12, 24, and 36 h, as shown in Table 1.

Table 1. Summary of the factors, their codes, and levels utilized in the Box-Behnken Design for the optimization of tannin extraction.

Factor	Code	Levels		
		Low (-1)	Mid (0)	High (1)
pH	x_1	9	10	11
Chestnut shell mass (g)	x_2	5	6	7
Extraction time (h)	x_3	12	24	36

The experimental design consisted of 17 runs, including central point replicates to assess reproducibility and estimate experimental error. Turbidity removal efficiency (%) obtained through coagulation–flocculation experiments was selected as the response variable. Subsequently, analysis of variance (ANOVA) was performed using the statistical software Minitab® to determine which factors had the greatest influence on the coagulation efficiency.

2.2. Preparation of synthetic water

Synthetic water was prepared using kaolin clay suspensions to simulate turbidity under controlled laboratory conditions. Synthetic water prepared with kaolin was used instead of real wastewater to ensure controlled and reproducible experimental conditions, as kaolin suspensions provide stable turbidity and minimize variations caused by the complex composition of real wastewater. A stock suspension was obtained by dispersing 5 g of kaolin in 1 L of deionized water [8]. To promote complete hydration and stabilization of the particles, the suspension was gently stirred at 30 rpm for 2 h, followed by a 24 h settling period [8,19].

2.3. Coagulation-flocculation experiments

Jar Test (Paralab-Equipamentos industriais de Laboratório, S.A., Portugal) was used to perform the coagulation-flocculation experiments at room temperature. In each 600 mL jar, 300 mL of kaolin suspension was placed, the pH was adjusted to 6, and 4.5 mL of the coagulant was added. The experiments were conducted with a rapid mixing of 3 min at 300 rpm, then a slow mixing for 20 min at 60 rpm [8]. Finally, the suspensions were allowed to settle for 90 min, and the final turbidity was measured using a turbidimeter (VWR TIR210, VWR International, Germany). The removal efficiency was evaluated based of the following Eq (1):

$$\text{Turbidity Removal (\%)} = \frac{T_i - T_f}{T_i} \cdot 100 \quad (1)$$

where T_i is the initial value of turbidity, and T_f is the turbidity value after treatment.

For comparative purposes, a 50 g L⁻¹ aluminum sulfate (Al₂(SO₄)₃) (PanReac AppliChem, ITW Reagents, Spain) solution was employed as a standard conventional coagulant under identical experimental conditions, including water type, settling time, and coagulant dosage. Jar Tests were performed using aluminum sulfate within comparable dosage ranges, and the resulting efficiency was assessed based on turbidity removal.

3. Results and discussion

3.1. Statistical analysis and process optimization (Box-Behnken design)

Jar Test experiments were performed using synthetic water prepared as previously described, following the experimental matrix defined by the Box-Behnken design, resulting in a total of 17 runs. ANOVA was used to statistically assess the impact of the extraction parameters on turbidity removal, with the corresponding results summarized in Table 2.

The ANOVA indicated that the model was not significant ($P = 0.531$). In addition, none of the linear factors evaluated (i.e., extraction time, pH, and chestnut shell mass) presented significant effects individually ($P > 0.05$), suggesting that these variables did not substantially affect turbidity removal within the studied conditions.

Even though the model showed a moderate R^2 of 64.26%, the adjusted R^2 value remained near zero, indicating weak predictive ability. Among the quadratic terms, time² had the smallest p-value ($P = 0.068$), which points to a potential nonlinear relationship between extraction time and turbidity removal,

implying that an optimal extraction time might exist.

Table 2. ANOVA results for turbidity removal through Box-Behnken design.

Source	Degrees of freedom	F-value	p-value
Model	9	1	0.531
Time	1	1.19	0.325
pH	1	0.08	0.792
Mass	1	0.91	0.385
Time ²	1	5.4	0.068
pH ²	1	0.18	0.692
Mass ²	1	0.33	0.588
pH*mass	1	0.24	0.643
pH*time	1	0.03	0.876
Mass*time	1	0.28	0.622
Lack of fit	3	17.46	0.055

The absence of overall model significance suggests that coagulation efficiency might be influenced by factors outside the selected domain, such as extract composition, or effectiveness of the Mannich reaction. Accordingly, the observed patterns should be interpreted as indicative of system behavior rather than as definitive optimization boundaries, and future research could narrow the experimental scope to more clearly determine the conditions that enhance coagulant performance.

It is important to emphasize that the extraction parameters investigated in this study were evaluated in terms of their downstream effect on coagulation performance rather than solely on extraction yield. Changes in extraction pH, solid loading, and extraction time may alter the amount and composition of tannin-rich compounds transferred to the liquid phase and, consequently, the characteristics of the material subsequently subjected to cationization. Therefore, the trends observed in turbidity removal reflect the combined influence of the extraction conditions on the properties and coagulation performance of the resulting cationized extract.

The coded coefficients for the turbidity removal model are shown in Table 3, and they help determine the effect of each extraction parameter assessed on turbidity reduction.

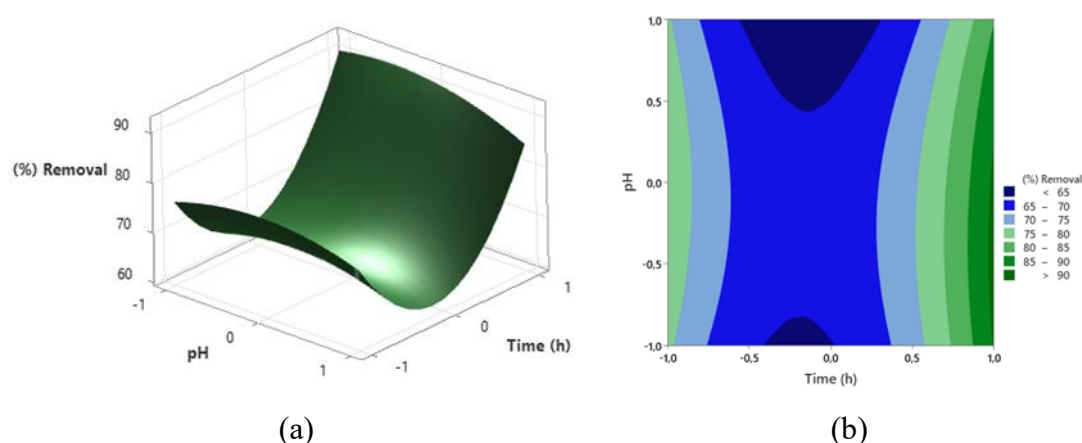
Although no statistically significant effects were confirmed, the positive coefficients obtained for time (5.87) and quantity (5.13) indicate a possible tendency for improved turbidity removal with increasing values of these variables. Contrarily, the negative coefficient associated with pH (-1.50) suggests that lower pH conditions may favor coagulation performance in the evaluated range.

Contour plots and three-dimensional response surfaces were generated from the RSM model to evaluate the combined effects of the independent variables and to better visualize their interactions on turbidity removal efficiency.

Table 3. Coded coefficients for turbidity removal using Box-Behnken Design.

Source	Coded coefficient	Standard error	t-value	p-value
Time	5.87	5.39	1.09	0.325
pH	-1.5	5.39	-0.28	0.792
Mass	5.13	5.39	0.95	0.385
Time ²	18.42	7.93	2.32	0.068
pH ²	-3.33	7.93	-0.42	0.692
Mass ²	-4.58	7.93	-0.58	0.588
pH*mass	-3.75	7.62	-0.49	0.643
pH*time	-1.25	7.62	-0.16	0.876
Mass*time	4	7.62	0.53	0.622

The response surface and contour plots for pH and extraction time (Figure 5) reveal a curved profile, indicating a nonlinear relationship between these variables. The highest turbidity removal (~96%) was observed at pH 9 and an extraction time of 36 h.

**Figure 5.** Response surface (a) and contour plot (b) of pH vs. extraction time for turbidity removal.

A region of reduced performance is observed at intermediate levels, where turbidity removal drops to approximately 60%. In contrast, higher removal efficiencies (~96%) are achieved toward the boundaries of the experimental domain, particularly at longer extraction times.

The observed curvature suggests that extraction time may affect the subsequent coagulation performance in a nonlinear manner, which is also consistent with the comparatively low p-value obtained for the quadratic time term ($P = 0.068$). Longer extraction periods may enhance solvent penetration into the lignocellulosic matrix and promote the transfer of tannin-rich compounds into the liquid phase [24,25]. This may increase the amount of phenolic material available for subsequent cationization through the Mannich reaction, potentially enhancing the formation of positively charged sites involved in colloidal destabilization [15,16]. However, prolonged exposure to alkaline conditions may also induce structural changes or degradation of phenolic compounds [25]. The balance between these phenomena may contribute to the nonlinear behavior observed for extraction time.

The better performance observed toward the lower extraction pH within the investigated

alkaline range may also indicate that moderate alkaline conditions provide a more favorable balance between tannin solubilization, and preservation of reactive phenolic structures required for subsequent cationization [24,25]. Nevertheless, because the individual effect of pH was not statistically significant ($P = 0.792$), this interpretation should be regarded as a mechanistic hypothesis rather than a confirmed effect.

The response surface and contour plots for chestnut shell mass and extraction time (Figure 6) also demonstrate a nonlinear pattern. The highest turbidity removal ($> 90\%$) was achieved using 6 g of chestnut shell and an extraction time of 36 h.

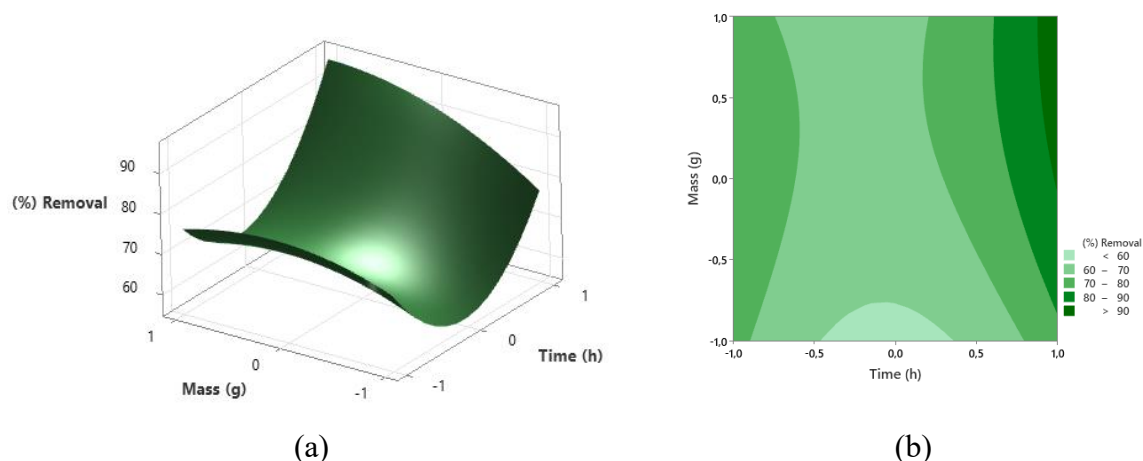


Figure 6. Response surface (a) and contour plot (b) of mass vs. extraction time for turbidity removal.

Lower turbidity removal is observed at intermediate levels of both variables, while higher efficiencies ($> 90\%$) are obtained when greater biomass dosage is combined with extended extraction time. This pattern could result from the prolonged contact between the solute and the solvent, which enhances mass transfer [24].

Because the extraction solution volume was maintained constant at 100 mL, changing the chestnut shell mass from 5 to 7 g effectively modified the solid-to-liquid ratio of the extraction system. Increasing the biomass loading may increase the concentration of extractable tannin-rich compounds available in the liquid phase. However, at higher solid loadings, the amount of solvent available per unit mass decreases, which may limit solvent penetration and mass transfer from the solid matrix [24,25]. These competing effects may explain why the relationship between chestnut shell mass and final turbidity removal was not strictly linear. In this context, the observed coagulation performance results from the influence of the solid-to-liquid extraction conditions on the composition of the extract subsequently subjected to cationization.

The higher removal observed at longer extraction times may indicate that extended solid–liquid contact partially compensates for mass-transfer limitations associated with increased biomass loading, allowing more extractable compounds to migrate from the chestnut shell matrix to the alkaline solution.

The response surface and contour plots for pH and chestnut shell mass (Figure 7) exhibit a curved surface, suggesting a nonlinear interaction between these parameters. The best performance ($> 68\%$) was obtained using 7 g of chestnut shell at pH 9.

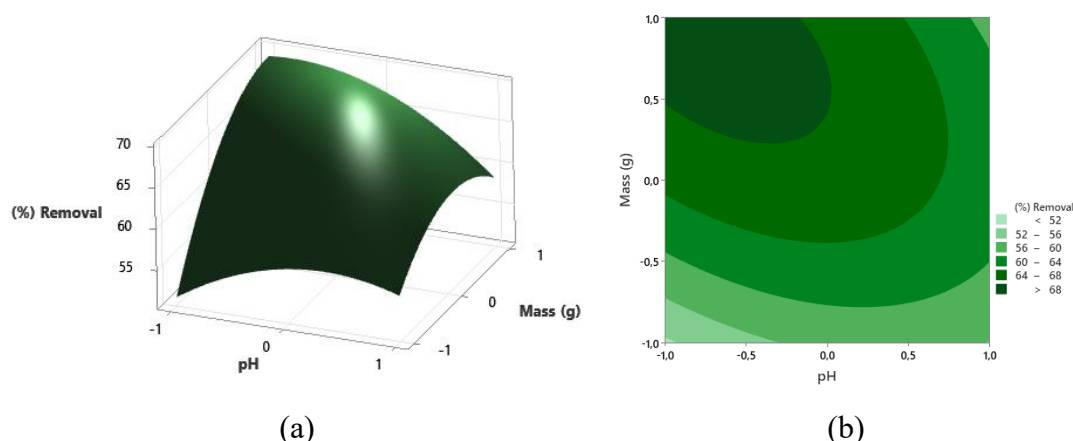


Figure 7. Response surface (a) and contour plot (b) of mass vs. pH for turbidity removal.

Higher turbidity removal (> 68%) is achieved at higher biomass dosages under lower pH conditions. The effect of pH is likely associated with its influence on tannin solubility and stability. Slightly alkaline conditions have been reported to improve extraction efficiency due to enhanced solubility, whereas highly acidic environments may lead to the formation of insoluble species [24]. Conversely, excessive alkaline conditions can promote degradation of the coagulant [25].

The response observed for pH and chestnut shell mass may reflect the combined effects of alkaline conditions and solid loading on the extraction of tannin-rich compounds. Under alkaline conditions, ionization of phenolic hydroxyl groups can enhance tannin solubilization and facilitate their transfer from the lignocellulosic matrix to the aqueous phase [24]. However, excessively alkaline conditions may also promote structural changes or degradation of phenolic compounds [25], potentially reducing the availability of reactive sites required for subsequent Mannich cationization. At the same time, increasing chestnut shell mass at a fixed extraction volume increases solid loading and may enhance the concentration of extracted compounds, although mass-transfer limitations may occur at higher solid-to-liquid ratios. Therefore, the observed response likely reflects a balance between tannin solubilization, biomass loading, and preservation of chemically reactive structures. Nevertheless, because neither pH nor mass showed statistically significant individual effects within the investigated range, these trends should be interpreted cautiously.

The limited statistical significance of the model may be partially attributed to the inherent characteristics of the Box-Behnken Design, which reduces the number of experimental runs while still enabling response surface modeling. Although this design reduces the number of experimental runs while preserving response surface modeling capabilities, it also limits the degrees of freedom available for error estimation. Consequently, if the actual effects of the variables are small or the experimental variability is relatively high, the model may lack sufficient statistical sensitivity to reach significance.

Overall, the response surfaces indicate that extraction conditions should not be considered independently from the subsequent coagulation step. Although the statistical model did not establish significant individual effects or a robust predictive optimum, the observed trends suggest that extraction pH, solid loading, and extraction time may influence the characteristics of the tannin-rich extract and, consequently, the performance of the material after cationization. Thus, the relevance of these upstream extraction parameters lies in their potential downstream effect on biocoagulant performance rather than solely in their influence on tannin extraction itself.

3.2. Evaluation of coagulation performance and mechanisms

The coagulation-flocculation efficiency of the chestnut shell extract, chemically modified through the Mannich reaction, was assessed via Jar Test experiments by measuring its capacity to remove turbidity from kaolin water. Overall, the chestnut shell coagulant demonstrated high turbidity removal, with the best results reaching values between 93%–96% under optimal experimental conditions. In comparison, the control experiment (without the addition of a coagulant) achieved turbidity removal efficiencies of only 54%–57%, demonstrating that the addition of the biocoagulant substantially improved the coagulation-flocculation process. This strong performance can be attributed to the Mannich reaction, which introduces positively charged groups into the chestnut shell tannin structure, thereby destabilizing anionic suspended particles in water [26]. This performance is visually captured in Figure 8, which shows the kaolin water before and after the treatment.

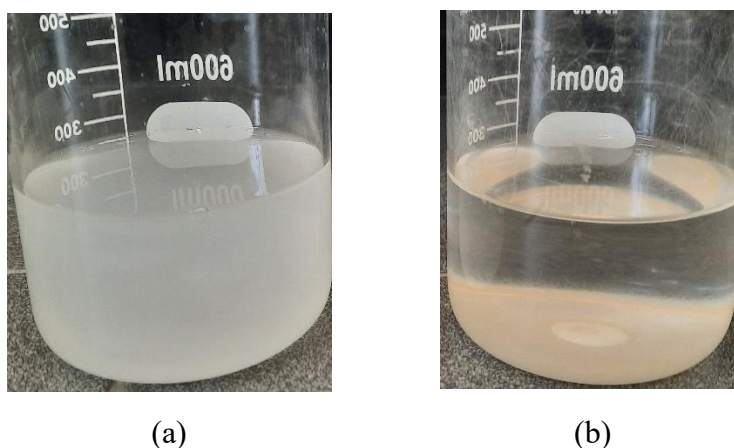


Figure 8. Kaolin water aspect before (a) and after (b) the coagulation-flocculation treatment.

In order to determine the practical relevance of the chestnut shell coagulant developed in this study, its efficiency was compared to that of an aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$) solution under identical experimental conditions.

As shown in Figure 9, aluminum sulfate achieved turbidity removal rates of 88%–96% within a settling time of 30 to 90 minutes. In comparison, the chestnut shell coagulant exhibited removal efficiencies of 92%–96% between 60 and 90 minutes of settling.

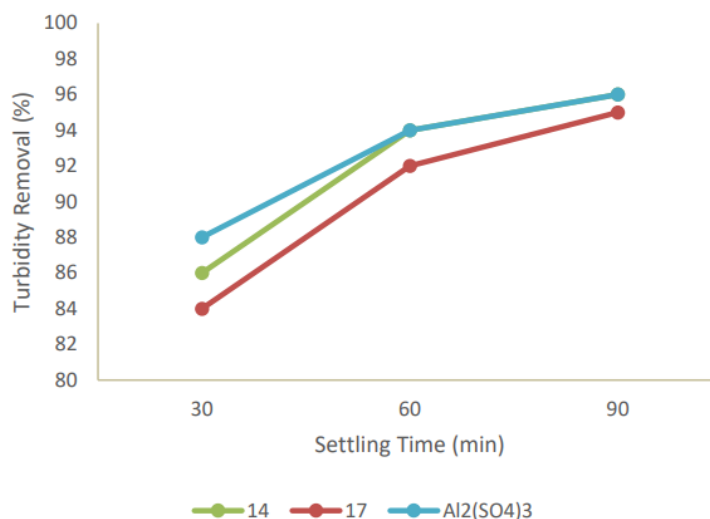


Figure 9. Comparison of turbidity removal between aluminum sulfate and chestnut shell coagulant (samples 14 and 17) at different sedimentation times (30–90 min).

This finding aligns with the literature, which indicates that settling time significantly influences coagulation performance. For instance, Zedan et al. [27] observed increased turbidity removal when the settling time was extended from 30 to 60 minutes using walnut seed extract.

While aluminum sulfate exhibited a faster removal rate, the chestnut shell coagulant achieved a similarly high level of efficiency, suggesting its viability as a sustainable alternative. While conventional coagulants remain highly effective, natural alternatives offer advantages such as renewability, residue valorization, and reduced dependence on metal-based chemicals.

The high turbidity removal efficiency achieved in this study (up to 96%) can be attributed not only to the Mannich modification of the tannins, but also to the optimization of the extraction conditions. Previous studies have demonstrated that extraction parameters, such as pH, extraction time, and biomass-to-solvent ratio directly influence tannin yield and composition, affecting the availability of reactive phenolic groups and, consequently, the performance of the resulting coagulant [23,26]. By applying the Box–Behnken design, the present study identified extraction conditions that maximized the production of active compounds prior to chemical modification, contributing to the high coagulation efficiency observed. This result is consistent with previous reports on tannin-based coagulants, which highlighted that both extraction efficiency and cationization play complementary roles in determining coagulation performance [15,16,23].

The best-performing chestnut shell coagulant reduced the initial turbidity from 243 NTU to 9.6 NTU, corresponding to a turbidity removal efficiency of approximately 96.0%. Under the same experimental conditions, aluminum sulfate reduced the turbidity from 232 NTU to 8.4 NTU (96% removal), while the control experiment reduced the turbidity from 212 NTU to 91.8 NTU, corresponding to a removal efficiency of approximately 57%. All three values exceed the 0.5 NTU recommended by the World Health Organization for large municipal water supplies before disinfection, as well as the visible turbidity of 4 NTU, above which water appears cloudy to consumers [28]. However, the World Health Organization also acknowledges that small water supplies, particularly those with limited resources, may not be able to achieve such stringent targets [28]. In such contexts,

any substantial reduction in turbidity represents a meaningful improvement in water quality. Therefore, the near-equivalence between the chestnut shell coagulant (9.6 NTU) and aluminum sulfate (8.4 NTU) highlights its potential as a sustainable alternative.

Beyond the comparable turbidity performance, natural coagulants offer additional environmental advantages over metal-based salts, including less sludge generated, and the biodegradability of the produced sludge [29]. Consequently, these materials may provide long-term benefits due to their biodegradable nature and the potential to lower waste management costs associated with treatment residues [30].

It is important to note that, although the chestnut shell coagulant is derived from a renewable biomass source, the Mannich modification involves formaldehyde, which must be considered when evaluating its sustainability [20,21]. Recently, Tomasi et al. [14] demonstrated that the formaldehyde concentration in water treated with this coagulant was 1.05 mg L^{-1} , far below the World Health Organization acceptable limit of 2.6 mg L^{-1} . Moreover, the residual formaldehyde detected in the sludge was remarkably low ($46 \pm 2 \text{ } \mu\text{g g}^{-1}$) [14]. Nevertheless, identifying safer alternatives to formaldehyde remains essential in the development of these coagulants. Glyoxal, for instance, was explored as an alternative because of its high reactivity, low volatility, biodegradability, and low cost [31]. Beyond glyoxal, other alternatives, such as furfural and vanillin, can also be considered in future studies [31,32].

4. Conclusions

This study developed a natural coagulant based on chestnut shells through tannin extraction followed by chemical modification using the Mannich reaction. This study systematically evaluated the influence of solid–liquid extraction conditions on the coagulation performance of a cationized chestnut shell-derived biocoagulant. By varying extraction pH, chestnut shell mass, and extraction time, the work provides insight into how upstream processing conditions can influence the downstream turbidity-removal performance of the resulting coagulant.

Although the ANOVA revealed no statistically significant individual effects of the extraction variables within the narrow range studied, the empirical response surfaces revealed optimization tendencies, showing that longer extraction times and higher chestnut shell mass generally promoted better turbidity removal results. The synthesized coagulant showed high coagulation–flocculation performance, achieving turbidity removal efficiencies of up to 96% under the best experimental conditions. Notably, this performance was directly comparable to that of conventional coagulant aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$), showing that the chestnut shell coagulant can achieve the same level of turbidity removal as traditional metal salts.

These findings demonstrate the potential of chestnut shell-based coagulants as sustainable alternatives for wastewater treatment and suspended particle removal. Moreover, the study highlights the valorization of agro-industrial residues within the framework of circular economy practices, contributing to waste reutilization and reducing dependence on conventional chemical coagulants.

It is suggested that future studies investigate the application of the developed coagulant in real industrial effluents and in synthetic wastewaters containing organic matter. Additional research should evaluate total organic carbon (TOC), the potential impact of residual organic compounds on the treated effluent, sludge characterization, disposal and reuse, as well as pilot-scale studies to assess the feasibility of scaling the extraction and coagulant production processes.

Use of AI tools declaration

The authors declare that Artificial Intelligence (AI) tools were used only to assist with language editing and text refinement.

Conflict of interest

The authors declare that there is no conflict of interest regarding the publication of this article.

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