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Removal of Dyes from Water Using Aluminum-Based Water Treatment Sludge as a Low-Cost Coagulant: Use of Response Surface Methodology

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Abstract: The aim of this research was to valorize waste (sludge) from a drinking water treatment plant as a coagulant in the removal of dyes (methylene blue and crystal violet) from water and to prevent environmental issues associated with sludge storage. To accomplish this purpose, the response surface methodology based on a central composite design with five levels was implemented. In order to enhance the efficacy of the coagulation–flocculation process, three key operational variables were considered for optimization: the pH, coagulant dosage (mg/L), and initial dye concentration (mg/L). To achieve this, a quadratic polynomial model was established. According to the mathematical model that has been developed, it is predicted that the highest efficiency for removing dyes is 94.44%. This maximum effectiveness is reached when the pH is adjusted to 12.04, the coagulant dose is set at 87.044 mg/L, and the dye concentration of MB is maintained at 2.955 mg/L. Conversely, the best dye removal of CV was attained at 100% under the following conditions: pH = 12.045, a coagulant dosage of 2.955 mg/L, and a dye concentration of 2.955 mg/L. The R2 (98.44% and 95.80% for MB and CV, respectively) validated both models. In this work, the coagulant was characterized by the surface charge, FTIR, BET, and SEM analysis.

Keywords: alum sludge; coagulation–flocculation; dyes; optimization and modeling; response surface methodology

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1. Introduction

A dye is a product capable, by definition, of dyeing a substance or set of substances in a durable manner. Dyes are widely used in industry to color a variety of products, such as textiles, leather, food, beverages, paper, inks, and paints. However, these pollutants have the following peculiarity: their function as industrial colorants requires them to retain their color, making them difficult to degrade [1,2]. The discharge of wastewater into the ecosystem is a major source of pollution and aesthetic disturbance to aquatic life [3,4]. This practice also generates a potential risk of bioaccumulation [5]. This can affect human beings through the transport of these substances (colorants) in the food chain. Some dyes can also cause allergies and cancer [6,7].

Thus, this water must be treated before being released into the environment using water treatment process methods. Several techniques are available for the treatment of wastewater containing the most important dyes: (i) physical methods such as adsorption on activated carbon, membrane filtration, or coagulation–flocculation can be used to treat colored effluents [2,3,8–11]; (ii) chemical methods: in this case, advanced oxidation processes are the most commonly used chemical treatment methods for colored effluents, while chemical oxidation processes involve the addition of oxidizing agents such as chlorine (Cl_2), oxygen (O_2), and hydrogen peroxide (H_2O_2) to the treated solution [3,7,12–14]; (iii) biological methods: these are based on microbial transformation, but the majority of these substances are stable and do not biodegrade easily. Nonetheless, research works have shown that dye biodegradation, whether total or partial, can be achieved biologically. However, it is important to stress that these techniques are not always suitable for industrial effluents due to their high concentration of pollutants, their toxicity, which can cause the death of microorganisms, or their low biodegradability [6,15–18].

However, most of these techniques have drawbacks, such as high costs, insufficient removal efficiency, and the production of large quantities of sludge [19,20]. Consequently, the application of alum sludge for dye removal could be identified as a sustainable management solution [21]. Alum sludge results from water treatment processes in drinking water treatment plants, where it is formed by adding aluminum salts to raw water to remove colloidal particles, cabbage- and clay-sized particles, color, and turbidity. Appropriately, water treatment sludge is derived from particles that settle out after the coagulation–flocculation process [21].

In the work presented here, sludge from the Oue El Athmania drinking water treatment plant, Mila, was used for the treatment of two dyes, methylene blue and crystal violet. Sludge was chosen as an alternative coagulant to other treatment processes for several reasons: (1) sludge offers a greater diversity of nutrients than any commercial fertilizer can provide; (2) the reduction in waste, and therefore the preservation of the environment, and the reduction in greenhouse gas emissions; (3) cost reductions either for their use as fertilizers or in the case of the recovery of the chemicals contained in the sludge [22,23]. For example, in Canada, aluminum sulfate is mainly used as a coagulant in water treatment and is also used in the fertilizer industry. The Canadian Fertilizer Products Forum has reported that aluminum sulfate or alum is used as a soil pH regulator in the lawn and garden industry due to the presence of aluminum. For this reason, aluminum sludge can be used in the fertilizer industry [24].

Water treatment sludge presents a valuable opportunity for wastewater treatment due to its richness in metal hydroxides. These sludges are abundant, readily available, and come at no cost. Furthermore, the ever-increasing production of water treatment sludge coincides with growing legislative and economic pressures to minimize waste and find beneficial uses for waste streams. As a result, recent years have seen a surge in research efforts exploring the potential to reuse water treatment sludge in various advantageous ways [25]. Several studies have explored the reuse of water treatment sludge (WTS) as a coagulant for wastewater treatment. The following is a breakdown of some key findings:

Chu investigated the feasibility of reusing WTS to treat textile wastewater, demonstrating its potential in this application [26]. Another study conducted by Moghaddam et al. investigated the use of WTS (Al-based WTS) to remove acid red 119 from an aqueous solution. This research highlights the potential application of WTS for dye removal from water [27]. Jangkorn et al. focused on the reuse of alum sludge as a coagulant for industrial wastewater containing mixed anionic surfactants [28]. Kang et al. examined the efficiency of using WTS in real animal farm wastewater treatment [29]. Their study evaluated the removal efficiencies of total suspended solids (TSS), phosphate ($PO4^{3-}$), and total organic carbon (TOC), providing valuable insights into WTS performance.

All of the studies cited above confirm the aluminum sludge performance in reducing dyes in water, but this requires the optimization and modeling of the coagulation–flocculation process to reduce the time wasted in experimental studies, while industries operate with continuous production of polluted water, as well as to perform an economic assessment study on the use of aluminum sludge on water treatment.

This research was carried out in three phases: (1) The first step was the characterization of the sludge powder using FTIR, SEM, zeta potential, BET, pH, TS, and TVS methods. (2) The second step was the optimization and modeling of the coagulation–flocculation process using the composite central design (CCD). In this section, three factors were considered (the pH, coagulant dose, and initial dye concentration) to assess MB and CV reduction. (3) The final step was the market analysis and cost evaluation of this coagulant in water treatment.

The innovative aspects of this study include the use of alum sludge to remove dyes (MB and CV) from the water. The originality aspects and novelty of this study compared with other publications concerning the use of aluminum-based water treatment sludge as coagulant includes the following: (i) The recovery and reuse of sludge from the Oued El Athmania plant to solve the environmental problems associated with the storage of this sludge since 2007. (ii) The development of mathematical models to facilitate the coagulation–flocculation process for waters with similar properties (methylene blue and crystal violet concentrations) (e.g., the textile industry), and eventually the replacement of the laboratory-scale experimental study by a modeling study using the models obtained, i.e., addition of coagulants and buffers (acid or base) without the pot-testing step (jar test optimization), using mathematical models only. The modeling study reduces the time lost during the experimental study, as the laboratory study lasts more than 25 days, while the plants operate continuously and permanently with a continuous production of polluted water. To avoid this problem, mathematical models were used. (iii) Finally, an economic assessment study on the coagulant (alum sludge).

2. Materials and Methods

The experimental procedures used in this study are illustrated in the following diagram (Figure 1):

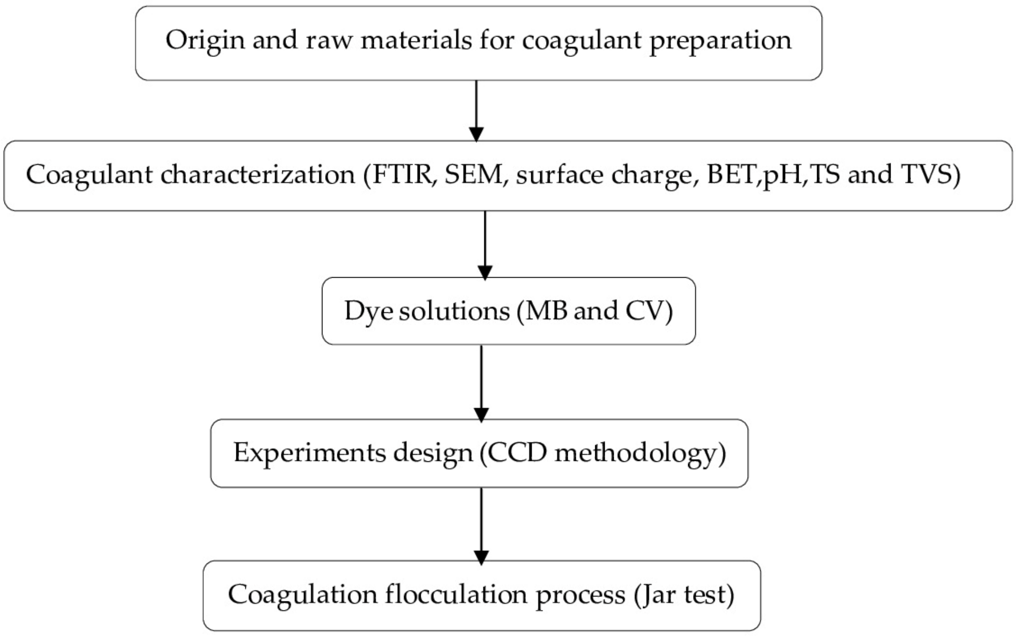


Figure 1. Flow chart of the experimental procedures.

2.1. Origin and Raw Materials for Coagulant Preparation

The raw material for preparing the coagulant was obtained from the drinking water treatment plant of Oued El Athmania, Mila (36°14′35.40″ N; 6°17′6.00″ E), exactly after the settling process. This plant uses aluminum sulfate as a coagulant and polyelectrolyte as a flocculant in the treatment chain after the pre-ozonation (pre-oxidation) process.

Alumina sulfate ionizes in water according to the following equilibrium reaction:

$$Al_2(SO_4)_3 \quad \leftrightarrow \quad 3SO^{2-}{}_4 + 2Al^{3+} \tag{1}$$

Aluminum ions react with hydroxyl ions in water to form aluminum hydroxide, as follows:

$$H_2O \quad \leftrightarrow \quad H^+ + OH^- \tag{2}$$

$$2Al^{3+} + 6OH^- \quad \leftrightarrow \quad Al(OH)_3 \tag{3}$$

The settling step was used to capture the total suspended solids (TSS) and for the elimination of organic matter and algae [30,31]. Although the final quality of the water after treatment still complies with Algerian standards, there is a problem with the decanted sludge, which is stored untreated in the plant. After a limited storage period, this sludge can be a source of environmental problems. Based on this drawback, this sludge has been valorized and used as a coagulant for dye removal in water (MB and CV).

In this study, coagulant powder (sludge) was prepared in several stages:

- Drying by placing the dehydrated sludge in an oven at 105 °C for 24 h.
- Grinding using a domestic grinder.
- Sieving using a vibrating sieve shaker, and finally, the powder form of the coagulant with homogeneous granulometry (148 µm).

2.2. Coagulant Characterization

The zeta potential of the coagulant powder was realized at a variable pH from 1 to 12, initially by mixing 0.01 g of the powder with 25 mL of NaCl (0.01 M) and then after adjusting its pH between 1 and 12 using NaOH (0.1 M) and HCl (0.1 M). In addition, the solutions obtained were stirred at 150 rpm for 24 h, after which the pH values were measured using a multi-parameter instrument (Jenway model 3540, Cam-lab, Cambridge, UK). The pH (final–initial) curve was plotted as a function of the initial pH. The point of zero charge (pHpzc) was determined by the intersection point of the resulting curve: final Ph–initial pH = 0 [32–34].

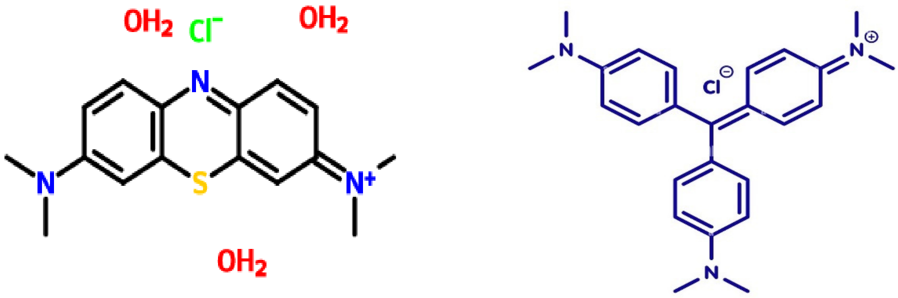
Fourier transform infrared spectrophotometry (FTIR) enabled us to identify the functional groups present in a molecule as well as to characterize its structure. In this study, the spectrum obtained from the Shimadzu Model HI 98713 (Kyoto, Japan) was used. The scanning electron microscopy (SEM) image of the sludge powder was determined using a scanning electron microscope (Hitachi TM 3400, Hitachinaka, Japan). The surface area of the AS was evaluated by the Brunauer–Emmett–Teller method (Quantachrome Instruments Corporate Headquarters, Boynton Beach, FL, USA). The pH, total solids (TS), and total volatile solids (TVS) of the sludge were determined by standard titrimetric methods [35].

2.3. Dye Solutions

Methylene blue (MB), a cationic dye with the formula $C_{16}H_{18}ClN_3S$ (see Figure 2a) and molar mass of 319.85 g/mol, was procured from Sigma Aldrich (St. Louis, MO, USA). It is also known as methylthioninium or tetramethylthionine chloride. It generally comes in the form of crystals or solid powders, which dissolve easily in water to form a blue solution.

Crystal violet is a cationic dye, also known as Basic Violet 3, belonging to the class of triphenylmethane dyes with a cationic based on the presence of $+N(CH_3)_2$ groups. The chemical structure is shown in Figure 2b; its chemical structure is $C_{25}N_3H_{30}Cl$ and molar mass is 407.979 g/mol. Crystal violet is very harmful if ingested or even inhaled [36].

For the experiment, all methylene blue and crystal violet solutions were prepared after the dilution of the stock solution, which was prepared in distilled water at a concentration of 1 g/L for each dye.



(**a**) (**b**)

Figure 2. Structure of (**a**) MB [37] and (**b**) CV [38,39].

2.4. Experimental Design

An experimental design was constructed. The influence of the three parameters, the pH, coagulant dosage, and initial dye concentration, on the MB and CV removal in water was considered. To carry out these experiments, the 5-level centered composite design (CCD) was used. The CCD is a second-order plane of symmetry composed of the following two parts: a 2k factorial with three central points and an axial part. The partial factor points provide the main linear effect and all pairwise iterative effects. In addition, residuals and standard errors can be calculated when the addition of the central points is taken into account. The pivot point is used to estimate the main quadratic effect [40,41].

Complete central composite designs have the following characteristics:

- ➢ They require an experiment number (N) according to the relationship N = 2k + 2k + nc, where k is the factor number and nc is the replica number of the central point.
- ➢ α depends on the number of variables and can be calculated by the relation $\alpha = 2k/4$; for three variables, they are 1.68.
- ➢ All factors are studied in five levels ($-\alpha$, -1, 0, +1, + α).

Table 1 shows the levels of the variables, which are presented in real and coded values. The latter has been set at five levels: -1.68 ($-\alpha$), 1 (minimum), 0 (central), +1 (maximum), and +1.68 (+α).

Table 1. Factor levels.

Coded Values	Parameters		
	pH	Coagulant Dosage (mg/L)	Dye Concentration (mg/L)
−1.68	1.954	2.955	2.955
−1	4.000	20.000	20.000
0	7.000	45.000	45.000
+1	10.000	70.000	70.000
+1.68	12.045	87.044	87.044

MB and CV were analyzed by a UV-visible spectrometer (SHIMADZU UV 1201 model, Kyoto, Japan) at wavelengths of 664 nm and 591 nm, respectively.

Once the final matrix was obtained, Minitab 18.0 software (Minitab, LLC, State College, PA, USA) was used to analyze and optimize the design.

The analysis of the design allows us to perform the following:

- ➢ Obtain the mathematical model linking the response (dye removal) with the factors studied.
- ➢ Test the significance of the factor effects.
- ➢ Identify the optimal conditions.

2.5. Coagulation–Flocculation Process (Jar Test)

The Jar test is laboratory equipment used to determine the optimal conditions, namely, the pH, the coagulant dosage, and the initial dye concentration. We treated the water contaminated by the two dyes separately. Each beaker features a run of the matrix, which is presented in Table 2. The jar test was carried out according to the following steps [42–44]:

- Fill beakers to a constant volume with contaminated water.
- Add a mass of dye (see Table 2).
- Adjust the pH according to Table 2 using solutions of NaOH (1 M) and H_2SO_4 (1 M).
- Add the coagulant doses according to the test matrix.
- Coagulation for 3 min at 160 rpm.
- Flocculation for 20 min at 30 rpm.
- The settling phase involves leaving the beakers to settle for 30 min.

Table 2. Results of the CCD in terms of the MB and CV removal efficiency.

Standard Run	pH (X_1)	Coagulant Dosage (mg/L) (X_2)	Dye Concentration (mg/L) (X_3)	RMB(%)	RCV(%)
01	4.000	20.000	20.000	24.634	33.210
02	10.000	20.000	20.000	42.783	76.030
03	4.000	70.000	20.000	43.553	58.890
04	10.000	70.000	20.000	59.981	61.310
05	4.000	20.000	70.000	46.703	29.120
06	10.000	20.000	70.000	60.914	60.160
07	4.000	70.000	70.000	61.096	60.100
08	10.000	70.000	70.000	61.074	60.610
09	1.954	45.000	45.000	42.595	60.180
10	12.045	45.000	45.000	75.349	99.540
11	7.000	2.955	45.000	33.313	27.360
12	7.000	87.044	45.000	66.117	58.190
13	7.000	45.000	2.955	32.734	38.730
14	7.000	45.000	87.044	47.045	38.550
15	7.000	45.000	45.000	40.116	38.550
16	7.000	45.000	45.000	39.577	38.500
17	7.000	45.000	45.000	39.252	38.620
18	7.000	45.000	45.000	39.047	38.620
19	7.000	45.000	45.000	39.27	38.550
20	7.000	45.000	45.000	39.304	38.550

After the settling phase, the final concentration of each dye (MB and CV) was determined by measuring the absorbance of the CV and MB at 591 and 664 nm, respectively, using a UV spectrometer. The dye removal efficiency is given by the following formula [11,45]:

$$\text{Dye removal efficiency } (\text{R }\%) = \frac{(C_0 - C_r) \times 100}{C_0} \quad (4)$$

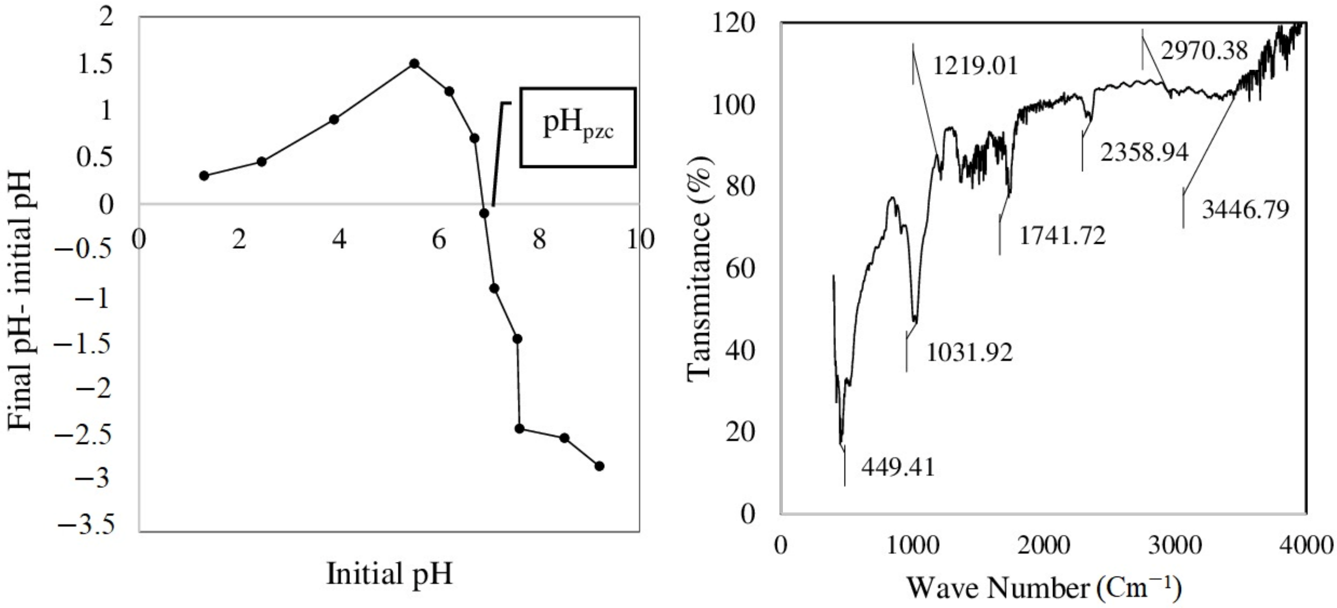
where C_0 is the initial dye concentration (mg/L) and C_r is the residual dye concentration (mg/L).

3. Results and Discussion

3.1. Coagulant Characterization (Sludge Powder)

3.1.1. Surface Charge and FTIR Characterization

The pHpzc is a good indicator of the surface charge of a material (sludge). Figure 3a shows the pHpzc of powdered sludge. The pHpzc value was 6.9. In this study, when the pH of the water was >pHpzc, the coagulation of cationic dyes such as MB and CV was favorable [32]. This confirms that the surface charge was negative and positively charged if, below this value, the main mechanisms are the adsorption and bridging of the dyes in the water [46].



(**a**) (**b**)

Figure 3. Surface charge (**a**) and infrared spectrum (**b**) of the sludge.

Figure 3b shows the infrared spectrum of the powder coagulant (sludge powder), showing several peaks. The peak at 3446.79 cm^{-1} corresponds to O-H bond (phenols, alcohols, and carboxylic acids) stretching, as well as the -NH group stretching [47].

In addition, average C-H bond stretching was observed at 2970 cm^{-1}, indicating the presence of alkanes [48]. The peak at 2358 cm^{-1} was attributed to O=H stretching, indicating the presence of carboxylic groups [49]. A localized peak is observed around 1741 cm^{-1}, which is attributed to the elongation vibrations of the C=O bond [50]. The C-H bending bands appeared in the ranges of 1275 to 1000 cm^{-1} [51]. The peaks at 1031 cm^{-1} and 449 cm^{-1} are assigned to the C-O [52] and Si-O-Si [53] bonds, respectively. It can be concluded that the sludge used is suitable as a coagulant for dye removal (RMB and RCV) in water. This is due to the presence of pronounced O-H bonds, indicating that the ions contained in the water treatment sludge form various soluble species, such as $Al(OH)^{2+}$ or $Al(OH)^{3+}$ [48,54]. Since they are adsorbed on the surface of the dye, they act as coagulants.

3.1.2. SEM Characterization

The sludge surface morphology is shown in Figure 4 at three magnifications: (a) 5 µm, (b) 10 µm, and (c) 100 µm. The microstructure of the sample, characterized by the presence of pores, explains the adsorbent capacity of this material (sludge). The sludge has an amorphous structural configuration, which favors the coagulation–flocculation process for the dye removal from the water [48,51,53].

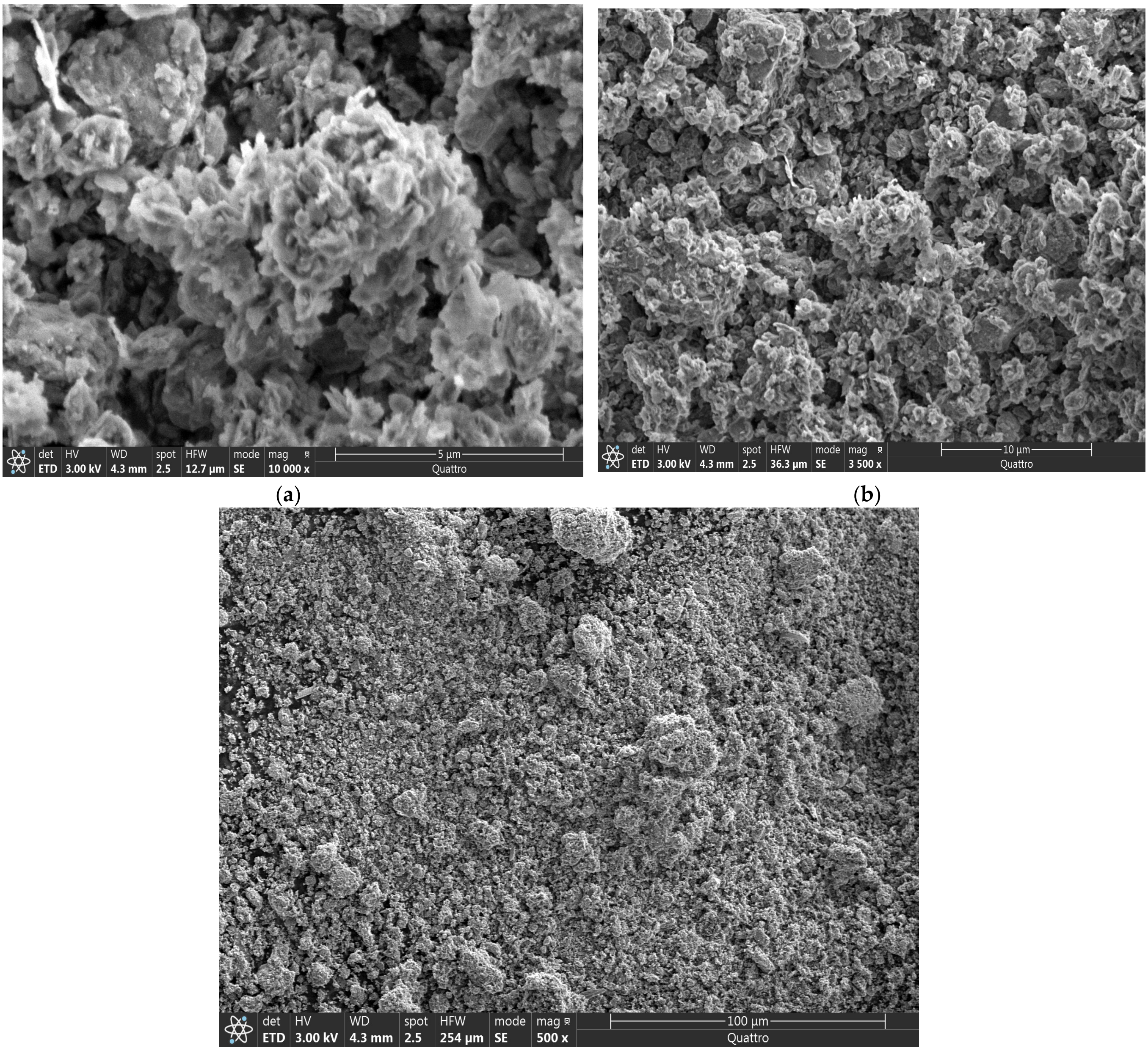


Figure 4. SEM analysis of powder sludge: (**a**) 5 µm, (**b**) 10 µm, and (**c**) 100 µm.

3.1.3. BET Surface Area Analysis

The BET analysis was used to measure the surface area (S_{BET}), the pore volume (V_p), and the pore diameter (pd) of the AS. This analysis shows that the S_{BET}, pd, and V_p were 89.041 m^2/g, 28.074 Å, and 0.553 cc/g, respectively. The obtained results confirm that the coagulant (AS) has a large surface area, which implies a high number of vacant sites, which vaporizes the coagulation of the methylene blue and crystal violet dye in water [55].

In this study, other sludge properties were measured, and the results obtained showed that the pH, TS, and TVS were 8.6, 1572.2 mg/L, and 1.36%, respectively.

3.2. Study of Dye Removal Using Sludge as a Coagulant

3.2.1. Statistical Analysis

The textile industry is one of the world's biggest consumers of water, and textile production also generates large quantities of wastewater. Textile wastewater can contain various pollutants, both organic and inorganic. Textile wastewater treatment is therefore an essential step in minimizing the environmental impact of this industry [9,56].

This study focuses on how the coagulation–flocculation process with aluminum-based sludge breaks down the cationic dyes methylene blue and crystal violet, which are often used in the textile industry.

The results obtained in this study are presented in Table 2. It can be seen that the maximum percentage reduction after the sludge treatment was 75.34 and 99.54% for MB and CV, respectively.

High-pH (alkaline) water is used because alkaline water is better suited to the coagulation–flocculation process, as it tends to contain more negatively charged ions that can interact with the dyes. OH- ions are present in very high concentrations, leading to the development of insoluble metal hydroxides ($Al(OH)_3$ and $Al(OH)_2$). These, in turn, dominate the flocculation process by sweeping [48,57], enabling a high coagulation efficiency under alkaline conditions (pH = 12.045). This sludge can be used as a coagulant, as it removes and reduces a significant percentage of the dyes (methylene blue and crystal violet) in water with different pH values from 2 to 12 [48].

The mathematical models (in real values) for this study are given below, as follows:

$$\text{RMB}(\%) = 18.8 - 5.47\,X_1 + 0.168\,X_2 + 0.653\,X_3 + 0.767\,X_1^2 + 0.00580\,X_2^2 + 0.00025\,X_3^2 - 0.0266\,X_1X_2 - 0.0340\,X_1X_3 - 0.00431\,X_2X_3 \quad (5)$$

$$\text{RCV}(\%) = 53.20 - 12.95\,X_1 + 0.697\,X_2 - 0.094\,X_3 + 1.6279\,X_1^2 + 0.00246\,X_2^2 + 0.00013\,X_2^2 - 0.1182\,X_1X_2 - 0.0228\,X_1X_3 + 0.00410X_2X_3 \quad (6)$$

3.2.2. Analysis of Variance (ANOVA)

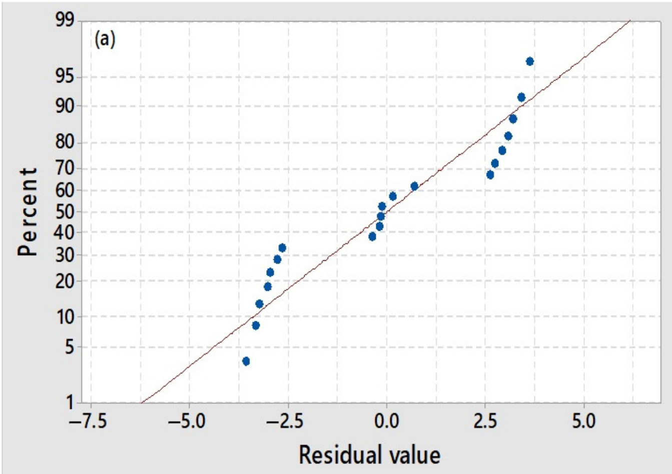
To determine the significance of curvature in the response, an analysis of variance (ANOVA) was used with a 95% confidence interval. The ANOVA results for dye removal are shown in Table 3. Both coefficients of determination (R^2) for the two dyes (MB and CV) are within an acceptable range. In addition, the coefficients of determination (R^2) are in agreement with the adjusted coefficients of determination (R^2adj). Thus, the R^2 and R^2adj values confirm the validity of the mathematical models for predicting dye removal (MB and CV).

Table 3. Analysis of variance (ANOVA) for the MB and CV removal efficiency (%).

Source of Variance	Degree of Freedom		Sum of Square (SS)		Mean Square (MS)		*p*-Value		R^2		R^2adj	
	MB	CV	MB	CV	MB	CV	MB	CV	MB	CV	MB	CV
Regression	9	9	3076.70	6001.91	341.855	666.38	0.000	0.000	95.80	98.44	92.02	97.03
Residual	10	10	134.83	95.36	13.483	9.54						
Total	19	19	3211.54	6027.27								

According to the ANOVA results (see Table 3), the *p*-value is less than 0.05 for each model. Examination of the residual curves reveals that the residuals follow a normal distribution [58]. This conclusion is supported by the observation that the points of the residuals align with Henry's curve (Figure 5a,b), as well as by the finding that the maximum errors were 3.61 and 3.94 for methylene blue and crystal violet, respectively (Figure 6a,b).

The CCD is then clearly well-adjusted in both models, and can therefore be used to optimize and model the flocculation–coagulation process for dye removal using alum sludge as a coagulant.



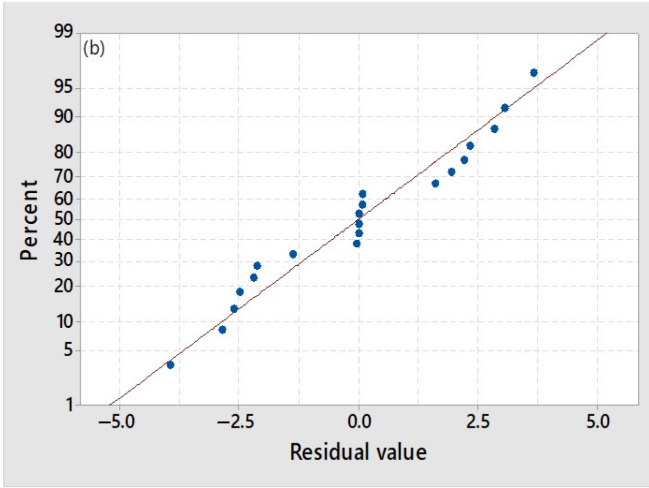
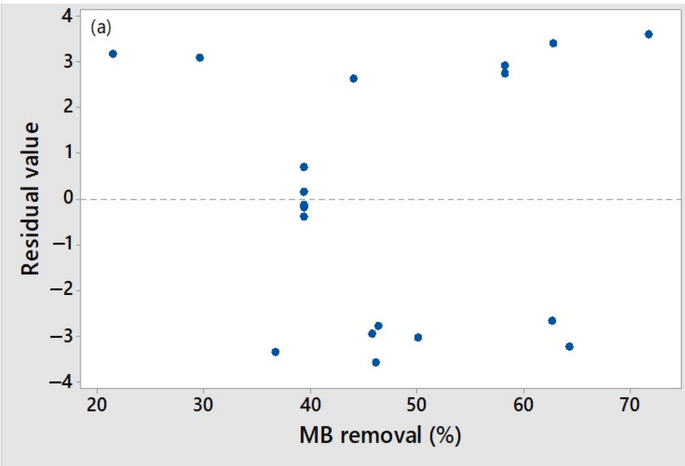


Figure 5. Distribution of residues on the Henry line (normal probability): MB removal (**a**) and CV removal (**b**).



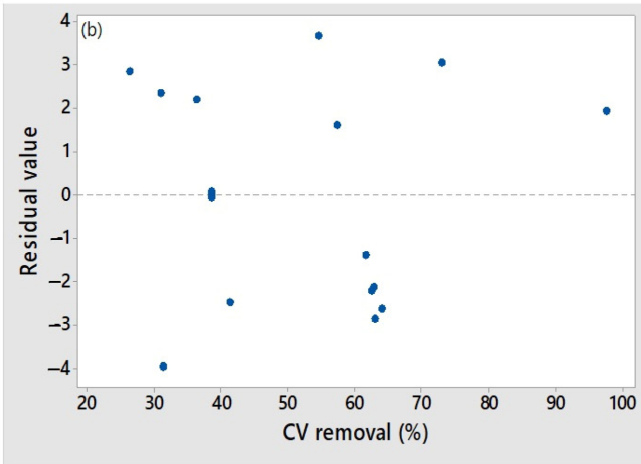


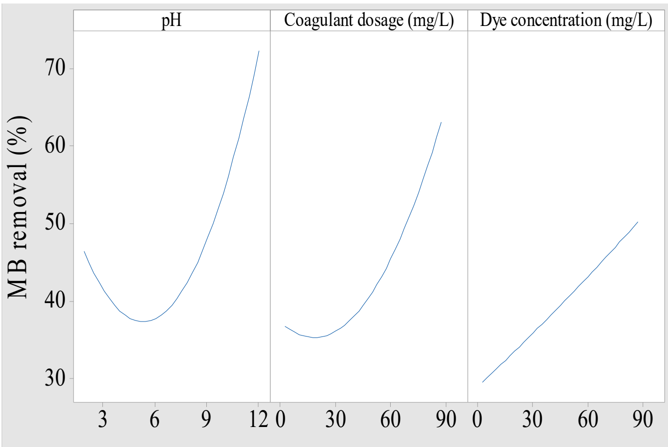
Figure 6. Plot of residual versus fitted value: MB removal (**a**) and CV removal (**b**).

3.2.3. Effect of Main Factors on Dye Removal

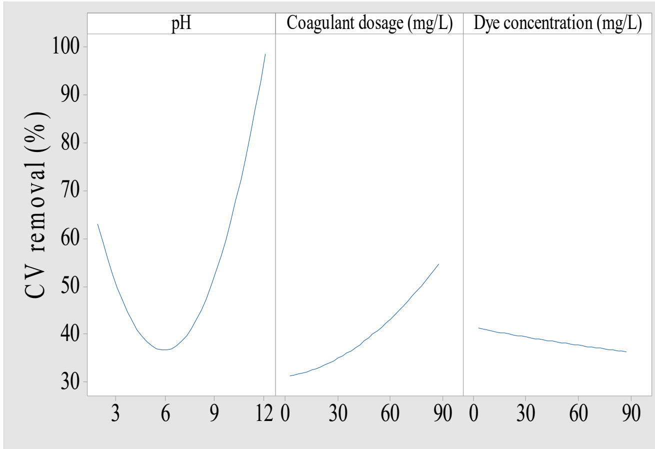
The effect of each factor (the pH, coagulant dosage, and initial dye concentration) on the efficiency of dye removal was studied and is shown in Figure 7a for methylene blue and in Figure 7b for crystal violet.

All factors studied influence the removal of methylene blue (RMB). An alkaline pH was found to offer maximum reduction, while increasing the dye concentration and coagulant dosage led to increased MB reduction (Figure 7a).

According to Figure 7b, it appears that an almost total reduction in the crystal violet concentration occurs at a pH of 12. Furthermore, increasing the coagulant dosage leads to an increase in the percentage reduction in crystal violet. However, it is important to note that the initial dye concentration (CV) has a negative effect on the removal of crystal violet (RCV). This means that, the higher the initial dye concentration (CV) in water, the lower the CV reduction yield using sludge as a coagulant.



(**a**)



(**b**)

Figure 7. Effect of the pH, coagulant dosage, and initial dye concentration on methylene blue removal (**a**) and crystal violet removal (**b**).

In this study, an acidification and alkalization treatment of chemical sludge from drinking water treatment plants was used to recover and solubilize aluminum (Al^{3+}) and improve the coagulation–flocculation performance. The results indicate that the yield of coagulation–flocculation concerning dye reduction was mainly due to the dissolution of aluminum in water. If the Al $(OH)_3$ precipitate was the dominant species within the sludge flocculation, i.e., dye reduction, this can be expressed as the dissolution of aluminum-containing coagulants (sludge) after the addition of a base (NaOH) or acid (H_2SO_4) according to Equations (7) and (8).

$$Al(OH)_3 + NaOH \leftrightarrow Al(OH)^{-}{}_4 + Na^+ \tag{7}$$

$$2Al(OH)_3 + 3H_2SO_4 \leftrightarrow Al_2(SO_4)_3 + 6H_2O \tag{8}$$

According to Equation (7), water treatment sludge becomes alkaline, in which case, the OH^- competes with the dyes (CV and MB) to coordinate with Al. Consequently, aluminum is more necessary for dye removal due to the competitive formation of $Al(OH)_4{}^-$.

According to Equation (8), water treatment sludge becomes acidic by adding acid. The presence of sulfate ions ($SO_4{}^2$) can act as an intermediate, promoting the hydrolysis/polymerization of aluminum and the aggregation of decomposed aluminum species, which may play a direct role in dye removal [59].

The effectiveness of aluminum coagulant recovery and dye removal is pH-dependent. When no material is consumed, an acid or base other than that required to dissolve Al^{3+} is necessary. The theoretical value for the recovery of Al^{3+} by the NaOH addition, i.e., 1.0 mol Al^{3+} dissolved/mole of H^+ added, can also be derived from Equation (7). The stoichiometry is 0.33 moles of dissolved aluminum (Al^{3+})/moles of added H^+, given by Equation (8).

3.2.4. Response Surface Plots (3D)

Theoretically, the response surface diagrams (3D) were used to determine the optimum zones for maximum dye reduction (MB and CV).

According to the response surface diagram (Figure 8a), it can be seen from the interaction graph between the pH and coagulant dosage that MB removal is maximal (about 74%) for a pH of 12 and a coagulant dosage of 50 mg/L. From the interaction graph between the pH and dye concentration (Figure 8b), it can also be seen that MB removal is maximal (about 72%) for a pH and concentration of 12 and 50 mg/L, respectively. Conversely, the interaction graph between the dye concentration and coagulant dosage shows that the MB removal is maximal (about 64%) for a dose of over 75 mg/L and a concentration of around 50 mg/L (Figure 8c).

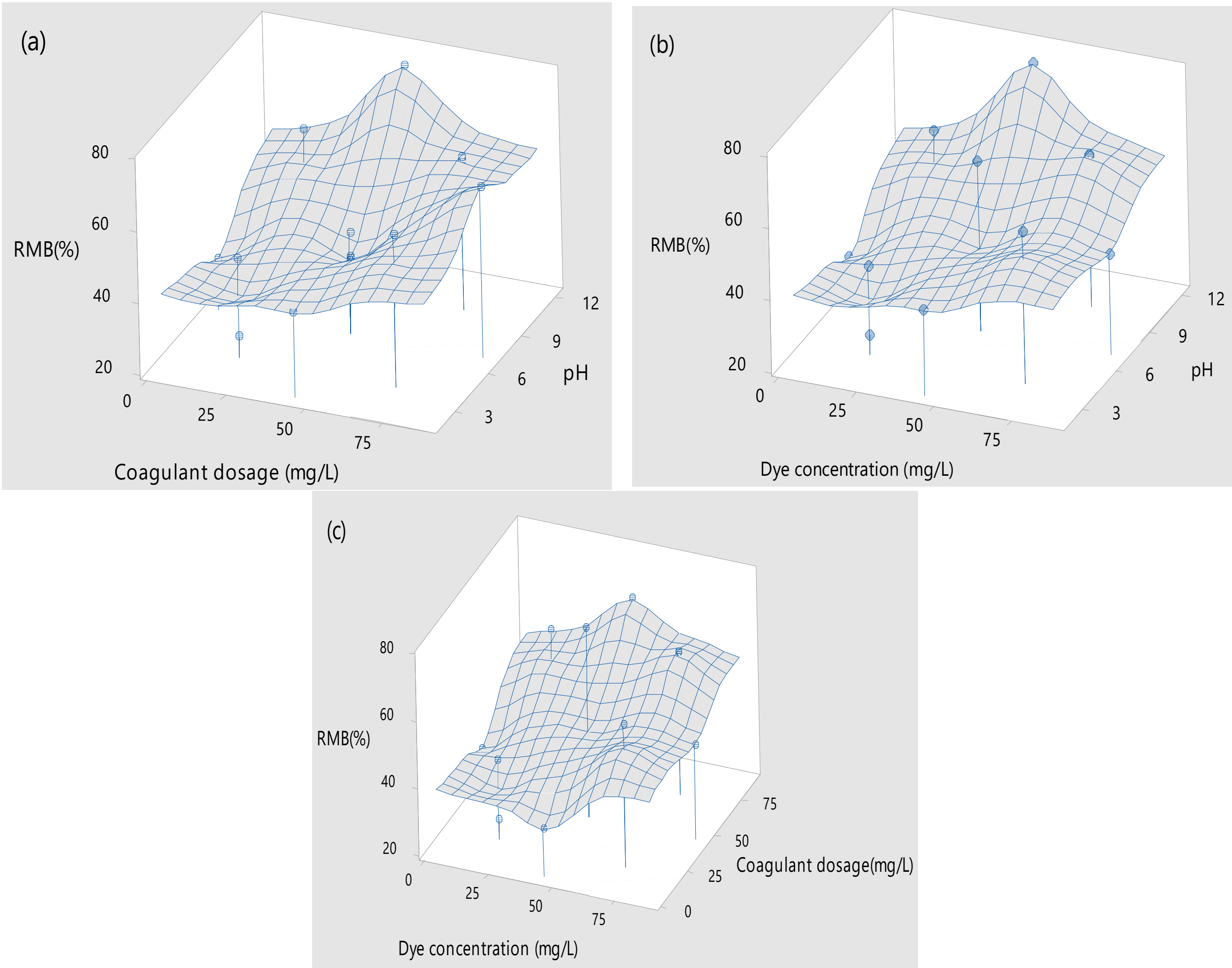


Figure 8. Surface plots (3D) for methylene blue removal as a function of (**a**) the coagulant dosage and pH at a constant dye concentration; (**b**) the pH and dye concentration at a constant coagulant dosage; (**c**) the coagulant dosage and dye concentration at a constant pH.

According to the analysis of the 3D response surface diagram for crystal violet reduction in water (Figure 9), the optimum zones observed were as follows:

- ➢ Interaction between the pH and coagulant dose (Figure 9a): CV reduction reaches its maximum level when a pH of 12 is combined with a coagulant dose of around 50 mg/L. This suggests that, at these specific pH and coagulant dose values, the best CV reduction is achieved (over 95%).
- ➢ Interaction between the pH and dye concentration (Figure 9b): This figure shows that the CV removal value is highest when the pH is set at 12 and the dye concentration is around 50 mg/L. This indicates that, for these particular pH and dye concentration values, the maximum CV dye reduction is around 97%.
- ➢ Interaction between the dye concentration and coagulant dosage (Figure 9c): The interaction graph reveals that the maximum CV removal (between 50 and 60%) is achieved for a coagulant dose of 75 mg/L and a dye concentration of around 25 mg/L or 75 mg/L.

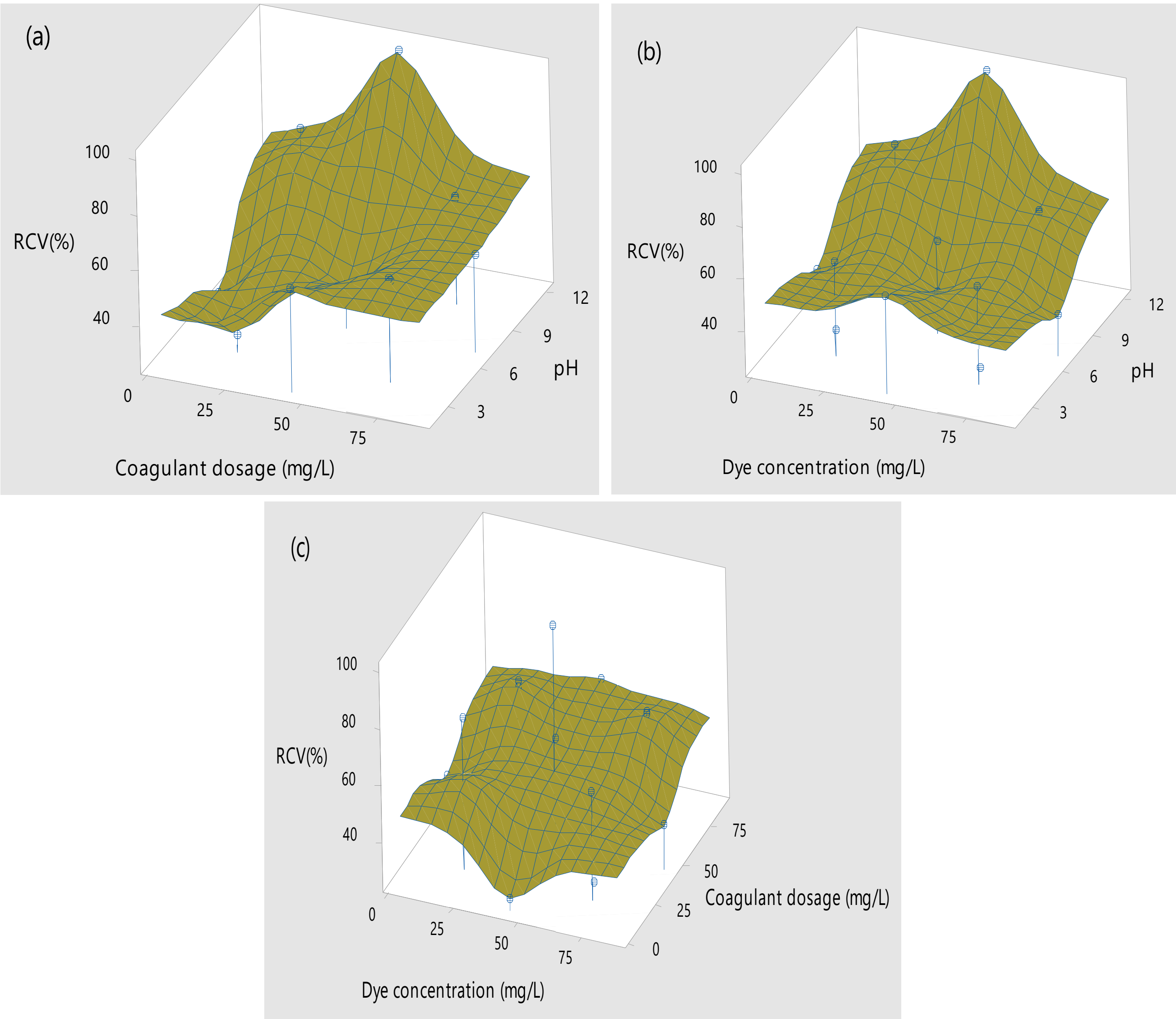


Figure 9. Surface plots (3D) for crystal violet removal as a function of (**a**) the coagulant dosage and pH at a constant dye concentration; (**b**) the pH and dye concentration at a constant coagulant dosage; (**c**) the coagulant dosage and dye concentration at a constant pH.

3.2.5. Optimization and Validation

The optimization results presented in Table 4 are applied to determine the combination of experimental factors that simultaneously optimize the responses (RMB and RCV). This is done by maximizing a desirability function. The response desirability is 0.92 for MB and 1 for CV. The optimum values for the three factors of the pH, coagulant dose, and dye concentration are (12.045 and 11.23), (87.049 and 4.484 mg/L), and (2.955 and 31.251 mg/L) for methylene blue and crystal violet, respectively. In this case, the predicted percentage removal in MB and CV was 94.44 and 100%, respectively. These optimization results validated the optimization conditions obtained in the laboratory. Experimental dye removal rates were 89.06% and 100% for MB and CV, respectively. As a result, both models developed were reliable and accurate in predicting the efficiency of the dye removal using alum sludge (AS) as a coagulant. This suggests that charge neutralization is not the only mechanism for dye particle removal. The AS apparently acts as a condensation nucleus, and the dye particles become entangled as the precipitate settles [39]. Theoretically, the AS could contribute to the trapping of dye particles, as shown in Equation (9).

$$Al(OH)_3 + \text{dye} \rightarrow \text{dye particles trapped in the AS} \quad (9)$$

Table 4. Optimization and validation.

Dye	Factors			Validation	
	pH	Coagulant Dosage (mg/L)	Dye Concentration (mg/L)	Y Predit * (%)	Y Experimental ** (%)
MB	12.045	87.044	2.955	94.444	89.06
CV	11.230	4.484	2.955	100	100

Notes: * The predicted dye removal (%). ** The experimental dye removal (%).

3.3. Economic Assessment

The industrial effluent treatment market is experiencing significant growth due to the growing awareness of the importance of sustainable water management and stricter environmental regulations. Traditional coagulants used in water treatment, such as iron and aluminum salts, are costly and can have a negative impact on the environment. The product presented here offers a sustainable alternative by using drinking water treatment plant sludge, a by-product that is already present in drinking water treatment plants, thus reducing the coagulant supply costs and minimizing the waste production. The potential market lies mainly in textile production plants to treat their rejects.

The cost of the coagulation–flocculation process includes the following: (1) the cost of the chemicals, i.e., aluminum sulfate and polyelectrolytes; (2) the cost of the treatment and the disposal of settled sludge. Therefore, the economic benefits of using sludge to degrade and remove colorants in water were examined from two perspectives: (i) the significant reduction in current and future sludge disposal costs in drinking water treatment plants; (ii) fresh coagulant (AS) savings in water treatment for the textile industry.

The approximate cost estimate for the coagulation–flocculation process by using AS as a coagulant for dye removal includes the following:

- The cost of the raw material. This study has shown that sludge is a reliable and readily available source in drinking water treatment plants. Thus, the cost of the raw material is very low or negligible because we have solved the problem of sludge stored in the plant; in addition, such a material is then economical compared to other dye treatment processes, such as microfiltration and advanced oxidation processes.
- The cost of the AS preparation. In this study, a simple and straightforward method was used to prepare this coagulant using a mill to obtain the powder form of the coagulant.
- The cost of the NaOH solution used to adjust the coagulation pH of the two dyes considered. A total volume of 2.1 mL (1 mol/L) and 2.4 mL (1 mol/L) was used to set the coagulation pH at 12.045 and 11.23, i.e., 96 and 84 mg NaOH were used to reduce MB and CV, respectively. According to the art-chemistry website, the cost of 1 kg NaoH was EUR 7.19 [60]; the cost of NaOH used to treat 1L of colored water was EUR 0.690 and 0.603 for MB and CV, respectively.

4. Conclusions

In the present work, a study was carried out to examine the feasibility of using sludge as a coagulant for dye removal (RMB and RCV). The results obtained in this study show that sludge is capable of reducing the concentrations of the various dyes.

The results obtained in this research can lead to the following conclusions:

- The infrared spectrum showed the presence of several functional groups responsible for the dye removal process, namely, the OH group. The pH of zero charge (pHpzc) was used to assess the surface charge of this material (AS). The pHpzc value was 6.9. In this study, when the pH of the water was >pHpzc, the coagulation of MB and CV was favorable. The coagulant (AS) has an amorphous structural morphology, which favors the coagulation–flocculation process.

- Powder sludge treatment of colored effluents is effective according to the results obtained for the two dyes used. The experimental results highlighted the optimization and modeling of the coagulation–flocculation process, and the pH, initial dye concentration, and coagulant dosage were used as factors influencing the reduction in MB and CV in water using the centered composite design (CCD) as the experimental method. The results show that the correlation coefficients, R^2 and R^2 adjusted, for MB and CV were 95.80%, 92.02%, 98.44%, and 97.03%, respectively. In this case, the maximum reductions were 89.06% and 100% % at the following optimal conditions: pH (12.045 and 11.23), initial dye concentration (2.955 and 31.251 mg/L), and coagulant dosage (87.049 and 4.484 mg/L) for MB and CV, respectively. It can be concluded that the three factors considered influence the dye removal efficiency. This study also shows that the two models obtained are reliable. Consequently, these uses can be applied to waters with properties similar to this study, such as industrial textile waters.
- The present work shows that the sludge can be used effectively as a low-cost coagulant for dye removal.

Finally, it can be concluded that the use of sludge can solve problems linked to environmental protection.

This study opens up new research perspectives on the development of aluminum-based water treatment sludge applicable to the treatment of industrial effluents (the elimination of heavy metals) and pharmaceutical effluents by the coagulation–flocculation process. It also includes experimental and economic studies on the use of these coagulants on an industrial scale.

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Abbreviations

AS	Alum sludge
BET	Brunauer–Emmett–Telle
CCD	Central composite design
RSM	Response surface method
MB	Methylene blue
CV	Crystal violet
FAIR	Fourier transform infrared spectrophotometry
pH_{pzc}	Point zero charge
SEM	Scanning electron microscopy
R	Dye removal efficiency

FAIR	Fourier transform infrared spectrophotometry
pH_{pzc}	Point zero charge
SEM	Scanning electron microscopy
R	Dye removal efficiency
RCV	Removal of crystal violet
RMB	Removal of methylene blue
R^2	Coefficient of determination
R^2adj	Adjusted coefficient of determination
TOC	Total organic carbon
TS	Total solids
TSS	Total suspended solids
TVS	Total volatile solids
WTS	Water treatment sludge

References

1. Djelal, H.; Rigail, M.; Boyer, L. Les Effluents Industriels et Leur Traitement. *Manag. Avenir* **2008**, *20*, 275–288. [CrossRef]
2. Khalfaoui, A.; Hassen, M.A.; Kerroum, D. Isotherm and Kinetics Study of Biosorption of Cationic Dye onto Banana Peel. *Energy Procedia* **2012**, *19*, 286–295. [CrossRef]
3. Lemessa, F.; Simane, B.; Seyoum, A.; Gebresenbet, G. Assessment of the Impact of Industrial Wastewater on the Water Quality of Rivers around the Bole Lemi Industrial Park (BLIP), Ethiopia. *Sustainability* **2023**, *15*, 4290. [CrossRef]
4. Owhonka, A.; Fubara, E.F.; Justice, O.B. Wastewater Quality-It's Impact on the Environment and Human Physiology: A Review. *Int. J. Adv. Res. Innov.* **2021**, *9*, 43–58. [CrossRef]
5. Li, X.; Bao, L.; Wei, Y.; Zhao, W.; Wang, F.; Liu, X.; Su, H.; Zhang, R. Occurrence, Bioaccumulation, and Risk Assessment of Microplastics in the Aquatic Environment: A Review. *Water* **2023**, *15*, 1768. [CrossRef]
6. Hammami, S. Étude de Dégradation Des Colorants de Textile Par Les Procédés d'Oxydation Avancée. Application à La Dépollution Des Rejets Industriels. Ph.D. Thesis, Université de Marne la Vallée, Paris, France, 2008.
7. Mansour, H.B.; Boughzala, O.; Barillier, D.; Mosrati, R. Les Colorants Textiles Sources de Contamination de l'eau: CRIBLAGE de La Toxicité et Des Méthodes de Traitement. *Rev. Des Sci. L'Eau* **2011**, *24*, 209–238. [CrossRef]
8. Kasperchik, V.P.; Yaskevich, A.L.; Bil'Dyukevich, A.V. Wastewater Treatment for Removal of Dyes by Coagulation and Membrane Processes. *Pet. Chem.* **2012**, *52*, 545–556. [CrossRef]
9. Yao, S.; Fabbricino, M.; Race, M.; Ferraro, A.; Pontoni, L.; Aimone, O.; Chen, Y. Study of the Digestate as an Innovative and Low-Cost Adsorbent for the Removal of Dyes in Wastewater. *Processes* **2020**, *8*, 852. [CrossRef]
10. Alardhi, S.M.; Albayati, T.M.; Alrubaye, J.M. A Hybrid Adsorption Membrane Process for Removal of Dye from Synthetic and Actual Wastewater. *Chem. Eng. Process.-Process Intensif.* **2020**, *157*, 108113. [CrossRef]
11. Khalfaoui, A.; Khelifi, M.N.; Khelfaoui, A.; Benalia, A.; Derbal, K. The Adsorptive Removal of Bengal Rose by Artichoke Leaves: Optimization by Full Factorials Design. *Water* **2022**, *14*, 2251. [CrossRef]
12. Zou, H.; Ma, W.; Wang, Y. A Novel Process of Dye Wastewater Treatment by Linking Advanced Chemical Oxidation with Biological Oxidation. *Arch. Environ. Prot.* **2015**, *41*, 33–39. [CrossRef]
13. Szpyrkowicz, L.; Juzzolino, C.; Kaul, S.N. A Comparative Study on Oxidation of Disperse Dyes by Electrochemical Process, Ozone, Hypochlorite and Fenton Reagent. *Water Res.* **2001**, *35*, 2129–2136. [CrossRef] [PubMed]
14. Zaharia, C.; Suteu, D.; Muresan, A.; Muresan, R.; Popescu, A. Textile Wastewater Treatment by Homogeneous Oxidation with Hydrogen Peroxide. *Environ. Eng. Manag. J.* **2009**, *8*, 1359–1369. [CrossRef]
15. Xu, H.; Yang, B.; Liu, Y.; Li, F.; Shen, C.; Ma, C.; Tian, Q.; Song, X.; Sand, W. Recent Advances in Anaerobic Biological Processes for Textile Printing and Dyeing Wastewater Treatment: A Mini-Review. *World J. Microbiol. Biotechnol.* **2018**, *34*, 165. [CrossRef] [PubMed]
16. Ledakowicz, S.; Pa, K. Recent Achievements in Dyes Removal Focused on Advanced. *Molecules* **2021**, *26*, 870. [CrossRef] [PubMed]
17. Bhatia, D.; Sharma, N.R.; Singh, J.; Kanwar, R.S. Biological Methods for Textile Dye Removal from Wastewater: A Review. *Crit. Rev. Environ. Sci. Technol.* **2017**, *47*, 1836–1876. [CrossRef]
18. Paz, A.; Carballo, J.; Pérez, M.J.; Domínguez, J.M. Biological Treatment of Model Dyes and Textile Wastewaters. *Chemosphere* **2017**, *181*, 168–177. [CrossRef] [PubMed]
19. Sivarajasekar, N. Agriculture Waste Biomass Valorisation for Cationic Dyes Sequestration: A Concise Review Liquid-Liquid Extraction for Wastewater Treatment View Project. *Artic. J. Chem. Pharm. Res.* **2015**, *7*, 737–748.
20. Alsukaibi, A.K.D. Various Approaches for the Detoxification of Toxic Dyes in Wastewater. *Processes* **2022**, *10*, 1968. [CrossRef]
21. Abba, A.B.; Saggai, S.; Touil, Y.; Al-Ansari, N.; Kouadri, S.; Nouasria, F.Z.; Najm, H.M.; Mashaan, N.S.; Eldirderi, M.M.A.; Khedher, K.M. Copper and Zinc Removal from Wastewater Using Alum Sludge Recovered from Water Treatment Plant. *Sustainability* **2022**, *14*, 9806. [CrossRef]
22. Pierzynski, G.M. Plant Nutrient Aspects of Sewage Sludge. In *Sewage Sludge: Land Utilization and the Environment*; Clapp, C.E., Larson, W.E., Dowdy, R.H., Eds.; Wiley: Hoboken, NJ, USA, 1994; pp. 21–25.

23. Pay, D.; Christopher, A.S.; Lica, R.-S.; Mark, R.; Akiça, B. *L'irrigation Avec Des Eaux Usées et La Santé*; CRDI, Ed.; Presses de l'Universite du Quebec: Québec, QC, Canada, 2012; ISBN 9782760531604.
24. The Canadian Fertilizer. 2024. Available online: https://fertilizercanada.ca/news-events/events/canadian-fertilizer-products-forum-5/ (accessed on 18 April 2024).
25. Sadri Moghaddam, S.; Alavi Moghaddam, M.R.; Arami, M. Coagulation/Flocculation Process for Dye Removal Using Sludge from Water Treatment Plant: Optimization through Response Surface Methodology. *J. Hazard. Mater.* **2010**, *175*, 651–657. [CrossRef] [PubMed]
26. Chu, W. Dye Removal from Textile Dye Wastewater Using Recycled Alum Sludge. *Water Res.* **2001**, *35*, 3147–3152. [CrossRef] [PubMed]
27. Sadri Moghaddam, S.; Alavi Moghaddam, M.R.; Arami, M. Response Surface Optimization of Acid Red 119 Dye from Simulated Wastewater Using Al Based Waterworks Sludge and Polyaluminium Chloride as Coagulant. *J. Environ. Manag.* **2011**, *92*, 1284–1291. [CrossRef] [PubMed]
28. Jangkorn, S.; Kuhakaew, S.; Theantanoo, S.; Klinla-or, H.; Sriwiriyarat, T. Evaluation of Reusing Alum Sludge for the Coagulation of Industrial Wastewater Containing Mixed Anionic Surfactants. *J. Environ. Sci.* **2011**, *23*, 587–594. [CrossRef] [PubMed]
29. Kang, C.; Zhao, Y.; Tang, C.; Addo-Bankas, O. Use of Aluminum-Based Water Treatment Sludge as Coagulant for Animal Farm Wastewater Treatment. *J. Water Process Eng.* **2022**, *46*, 102645. [CrossRef]
30. Anesthesia, N.; Be, S.; In, M.O.; In, L.; Appropriate, W.; Equipment, R.; Are, D.; Available, I.; Manage, T.O.; Ii, G.; et al. *Guidelines for Drinking-Water Quality, 4th ed: Incorporating the First and Second Addenda*; World Health Organization: Geneva, Switzerland, 2022; ISBN 9789240045064.
31. WHO. *Guidelines for Drinking-Water Quality*, 4th ed.; World Health Organization: Geneva, Switzerland, 2011; ISBN 9789241548151.
32. Padhiyar, H.; Thanki, A.; Kumar Singh, N.; Pandey, S.; Yadav, M.; Chand Yadav, T. Parametric and Kinetic Investigations on Segregated and Mixed Textile Effluent Streams Using Moringa Oleifera Seed Powders of Different Sizes. *J. Water Process Eng.* **2020**, *34*, 101159. [CrossRef]
33. Lopez-Ramon, M.V.; Stoeckli, F.; Moreno-Castilla, C.; Carrasco-Marin, F. On the Characterization of Acidic and Basic Surface Sites on Carbons by Various Techniques. *Carbon N. Y.* **1999**, *37*, 1215–1221. [CrossRef]
34. Benalia, A.; Atime, L.; Baatache, O.; Khalfaoui, A.; Fadia, A. Removal of Lead in Water by Coagulation Flocculation Process Using Cactus—Based Natural Coagulant: Optimization and Modeling by Response Surface Methodology (RSM). *Environ. Monit. Assess.* **2024**, *196*, 244. [CrossRef] [PubMed]
35. Federation, W.E. Standard Methods for the Examination of Water and Wastewater Standard Methods for the Examination of Water and Wastewater. *Public Health* **1999**, *51*, 940. [CrossRef]
36. Fosso-Kankeu, E.; Webster, A.; Ntwampe, I.O.; Waanders, F.B. Coagulation/Flocculation Potential of Polyaluminium Chloride and Bentonite Clay Tested in the Removal of Methyl Red and Crystal Violet. *Arab. J. Sci. Eng.* **2017**, *42*, 1389–1397. [CrossRef]
37. Gupta, K.N.; Kumar, R.; Thakur, A.K.; Khan, N.A. Treatment of Dyeing Wastewater Using Foam Separation: Optimization Studies. *Water* **2023**, *15*, 2236. [CrossRef]
38. Miyah, Y.; Lahrichi, A.; Idrissi, M.; Boujraf, S.; Taouda, H.; Zerrouq, F. Assessment of Adsorption Kinetics for Removal Potential of Crystal Violet Dye from Aqueous Solutions Using Moroccan Pyrophyllite. *J. Assoc. Arab Univ. Basic Appl. Sci.* **2017**, *23*, 20–28. [CrossRef]
39. Baatache, O.; Derbal, K.; Benalia, A.; Aberkane, I.; Guizah, Q.E.; Khalfaoui, A.; Pizzi, A. Valorization of Pine Cones (Pinus Nigras) for Industrial Wastewater Treatment and Crystal Violet Removal: A Sustainable Approach Based on Bio-Coagulants and a Bio-Adsorbent. *Water* **2024**, *16*, 260. [CrossRef]
40. De Paula, H.M.; Sangoi, M.; Ilha, D.O.; Sarmento, A.P.; Andrade, L.S. Dosage Optimization of Moringa Oleifera Seed and Traditional Chemical Coagulants Solutions for Concrete Plant Wastewater Treatment. *J. Clean. Prod.* **2018**, *174*, 123–132. [CrossRef]
41. Benalia, A. Extraction et Valorisation Des Produits Actifs Des Plantes Naturelles En Tant Que Bio Coagulants Utiles Dans l'amelioration de Qualite Des Eaux. Ph.D. Thesis, University of Constantine 3, El Khroub, Algeria, 2023.
42. Benalia, A.; Chaibraa, W.; Djeghar, S.; Derbal, K.; Khalfaoui, A.; Mahfouf, A.; Bouchareb, R.; Panico, A.; Pizzi, A. Use of Extracted Proteins from Oak Leaves as Bio-Coagulant for Water and Wastewater Treatment: Optimization by a Fractional Factorial Design. *Water* **2023**, *15*, 1984. [CrossRef]
43. Baatache, O.; Derbal, K.; Benalia, A.; Khalfaoui, A.; Bouchareb, R.; Panico, A.; Pizzi, A. Use of Pine Cone as Bio-Coagulant for Heavy Metal Removal from Industrial Wastewater: Use of Box—Behnken Design. *Ind. Crop. Prod.* **2024**, *210*, 118185. [CrossRef]
44. Benalia, A.; Baatache, O.; Derbal, K.; Khalfaoui, A. The Use of Central Composite Design (CCD) to Optimize and Model the Coagulation-Flocculation Process Using a Natural Coagulant: Application in Jar Test and Semi-Industrial Scale. *J. Water Process Eng.* **2024**, *57*, 104704. [CrossRef]
45. Khalfaoui, A.; Benalia, A.; Selama, Z.; Hammoud, A.; Derbal, K.; Panico, A.; Pizzi, A. Removal of Chromium (VI) from Water Using Orange Peel as the Biosorbent: Experimental, Modeling, and Kinetic Studies on Adsorption Isotherms and Chemical Structure. *Water* **2024**, *16*, 742. [CrossRef]
46. Chua, S.; Malek, M.A.; Chong, F.; Sujarwo, W.; Ho, Y. Red Lentil (Lens Culinaris) Extract as a Novel Natural Characterization and Performance Optimization Study. *Water* **2019**, *11*, 1686–1704. [CrossRef]
47. Oliveira, E.; Val, A.; Araujo, E.B. De Application of Lolium Multiflorum as an Efficient Raw Material in the Production of Adsorbent for Removal of Methylene Blue. *J. Carbon Res.* **2023**, *9*, 44.

48. Zainol, N.A.; Al Balqis Khalilullah, P.; Ghani, A.A.; Rashid, N.A.; Makhtar, S.M.Z. Turbidity Removal from Kaolin Synthetic Wastewater via Coagulation Process Using Sludge from Water Treatment Plant. *Int. J. Integr. Eng.* **2022**, *14*, 222–231. [CrossRef]
49. Okolo, B.I.; Adeyi, O.; Oke, E.O.; Agu, C.M.; Nnaji, P.C.; Akatobi, K.N.; Onukwuli, D.O. Coagulation Kinetic Study and Optimization Using Response Surface Methodology for Effective Removal of Turbidity from Paint Wastewater Using Natural Coagulants. *Sci. Afr.* **2021**, *14*, e00959. [CrossRef]
50. Elbariji, S.; Elamine, M.; Eljazouli, H.; Kabli, H. Traitement et valorisation des sous-produits du bois. Application à l'élimination des colorants industriels. *Comptes Rendus Chim.* **2006**, *9*, 1314–1321. [CrossRef]
51. Verma, S.; Prasad, B.; Mishra, I.M. Pretreatment of Petrochemical Wastewater by Coagulation and Flocculation and the Sludge Characteristics. *J. Hazard. Mater.* **2010**, *178*, 1055–1064. [CrossRef] [PubMed]
52. Adaobi, C.; Ighalo, J.O.; Iwuozor, K.O.; Dominic, O.; Ugochukwu, P.; Al-rawajfeh, A.E. Prediction and Optimisation of Coagulation-Flocculation Process for Turbidity Removal from Aquaculture Effluent Using Garcinia Kola Extract: Response Surface and Artificial Neural Network Methods. *Clean. Chem. Eng.* **2022**, *4*, 100076. [CrossRef]
53. Chahid, L.; Yaacoubi, A.; Bacaoui, A.; Lakhal, E. Valorization of Drinking Water Treatment Sludge (DWTS): Characterization and Applications as Coagulant and Sorbent for Olive Mill Wastewater (OMW). *J. Mater. Environ. Sci.* **2015**, *6*, 2520–2533.
54. Li, C.W.; Lin, J.L.; Kang, S.F.; Liang, C.L. Acidification and Alkalization of Textile Chemical Sludge: Volume/Solid Reduction, Dewaterability, and Al(III) Recovery. *Sep. Purif. Technol.* **2005**, *42*, 31–37. [CrossRef]
55. Laggoun, Z.; Khalfaoui, A.; Benalia, A.; Ghomrani, A.F.; Bouchareb, R.; Mahfouf, A.; Pizzi, A.; Panico, A.; Derbal, K. Applied Sciences Application of Response Surface Design for Optimization of Direct Red Dye Biosorption onto Cockleshells. *Appl. Sci.* **2023**, *13*, 12333. [CrossRef]
56. Imtiazuddin, S.M.; Mumtaz, M.; Khalil, A. Mallick Pollutants of Wastewater Characteristics in Textile Industries. *J. Basic Appl. Sci.* **2012**, *8*, 554–556. [CrossRef]
57. Benalia, A.; Derbal, K. Etude Expérimentale et Modélisation Du Processus de La Coagulation Floculation: Application Aux Eaux Destinée a La Consommation. Master's Thesis, University of Constantine 3, El Khroub, Algeria, 2015.
58. Ezemagu, I.G.; Ejimofor, M.I.; Menkiti, M.C.; Nwobi-okoye, C.C. Modeling and Optimization of Turbidity Removal from Produced Water Using Response Surface Methodology and Artificial Neural Network. *S. Afr. J. Chem. Eng.* **2021**, *35*, 78–88. [CrossRef]
59. Van Truong, T.; Tiwari, D.; Mok, Y.S.; Kim, D.J. Recovery of Aluminum from Water Treatment Sludge for Phosphorus Removal by Combined Calcination and Extraction. *J. Ind. Eng. Chem.* **2021**, *103*, 195–204. [CrossRef]
60. Art-Chimie Hydroxyde de Sodium Technique. Available online: https://www.art-chimie-online.com/ (accessed on 17 April 2024).