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THE EFFECT OF PARAS STONE GREEN COAGULANT PREPARATION AND TEST SOLUTION CONCENTRATION ON AZO DYE REMOVAL

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ABSTRACT

Paras Stone, a volcanic clay rich in silica (SiO_2) and widely used in Lombok, West Nusa Tenggara (NTB), for sculptures, tombstones, and decorative ornaments, produces significant residual waste during carving. This waste can be repurposed as a natural coagulant for wastewater treatment, though research on its local application remains limited. Azo dyes, particularly prevalent in the textile industry, are produced at an estimated 700,000 tons annually, with 10–15% discharged into wastewater streams, posing serious environmental risks due to their toxic and non-biodegradable nature. This study investigates the removal efficiency of Remazol Red azo dye using Paras Stone under three conditions: non-activated, physically activated, and chemically activated with HCl or H_2SO_4. Chemical activation involved immersing Paras Stone in 3 M HCl or 0.1 M H_2SO_4 solutions with stirring for 2 hours, then rinsing to neutral pH and drying. Coagulation–flocculation experiments were conducted in batch mode, consisting of a 4-minute and 20-minute coagulation phase. The results demonstrated that non-activated Paras Stone achieved the highest dye removal efficiency (95.50%), surpassing samples activated with HCl (91.57%) and H_2SO_4 (92.53%). ANOVA analysis confirmed these differences as statistically significant at the 95% confidence level. The optimum conditions were obtained with a coagulant dose of 2.75 g of Paras Stone and 2.00 g of *Opuntia ficus-indica* gel, applied at a Remazol Red solution concentration of 30 mg/L. The *O. ficus-indica* gel, prepared by extracting parenchyma tissue, grinding, centrifuging, and collecting the gel-like supernatant, was a natural flocculant that facilitated the formation of larger flocs and accelerated sedimentation. These findings indicate that non-activated Paras Stone offers an effective, low-cost, and environmentally sustainable alternative for removing azo dyes in textile wastewater treatment.

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INTRODUCTION

Synthetic dyes are widely used in various industries due to their ability to impart color to textiles, including traditional batik dyeing [1]. Globally, it is estimated that approximately 700,000 tons of synthetic dyes are produced annually, representing nearly 100,000 types of commercially available dyes [2]. Among these, azo dyes form the largest group, accounting for about 70% of organic dye production worldwide [4]. Structurally, azo dyes contain one or more azo groups (-N=N-), which are the fundamental chromophoric units responsible for coloration

[3]. The textile industry, particularly in batik production, is a major source of azo dye discharge, generating wastewater streams with high dye concentrations [5]. Approximately 10–15% of dyes used in textile processes are released into effluents [6].

Even at relatively low concentrations (10–50 mg/L), dyes are visible in water and can significantly reduce transparency and oxygen solubility, disrupting aquatic ecosystems [7]. Azo dyes and their biotransformation products, such as aromatic amines, pose toxic and carcinogenic risks [8], [9]. Their toxic, persistent, and non-biodegradable nature makes them particularly harmful to aquatic environments [10], [11]. When discharged into water, azo dyes hinder light penetration, suppressing the growth of algae and aquatic plants. In contrast, accumulation in aquatic organisms may produce toxic intermediates that threaten higher predators and overall ecosystem health [12].

In addition to environmental risks, azo dyes pose serious human health hazards. Exposure can occur through oral ingestion or skin contact [13]. Once inside the body, azo dyes are reduced by gut microflora into toxic amines, which can damage tissues in multiple organs. Similarly, bacteria residing on human skin can metabolize azo dyes into carcinogenic compounds [14].

Figure 1. Paras Stone

Paras Stone (Padas) is a type of volcanic clay rock, or more specifically, pyroclastic rock, whose mineral content consists mainly of glass minerals (non-crystalline) [15]. Paras Stone contains silica (SiO_2), aluminium oxide (Al_2O_3), and several other elements. The main elements in sandstone are SiO_2 (83.87%), Al_2O_3 (0.50%), CaO (10.65%), and Fe_2O_3 (0.17%) [15].

Table 1. Elemental components of Paras Stone [16].

Metallic elements	% relative mass
Si	67.539
Al	25.622
K	4.440
Fe	0.590
Cl	0.050

Previous research has shown that the high silica content of Paras Stone, approximately 67.54% (Table 1), makes it effective for removing pollutants from water. Paras Stone, a volcanic clay abundant in Central Lombok, West Nusa Tenggara (NTB), is traditionally used by local communities to produce statues, tombstones, and wall ornaments. However, the residual carving waste remains underutilized and is often discarded. This waste material has the potential to be repurposed as a natural coagulant. Similarly, the *Opuntia ficus-indica* (OFI) cactus, abundant in Lombok and well-adapted to arid soils and erratic climates [17]–[19], contains polysaccharide-rich mucilage that can function as a natural flocculant. The polysaccharide chains in OFI form bridges with colloidal particles, promoting the aggregation of larger flocs, which settle more rapidly in water [20], [21].

Several studies have investigated the use of Paras Stone for pollutant removal. For instance, Paras Stone has been reported to achieve a 96.70% removal efficiency of Remazol Red dye [16], an adsorption capacity of 7.80 mg/g for Rhodamine B, and adsorption capacities of 12.50 mg/g for Pb(II) and 12.49 mg/g for Cr(III) [22]. Furthermore, sandstone activated with sulfuric acid exhibited an adsorption capacity of 4.92 mg/g, while hydrochloric acid activation resulted in 4.97 mg/g for detergent waste removal [23]. To enhance its performance, Paras Stone can undergo physical activation, which removes trapped water molecules, improves the alumina–silica crystal structure, increases porosity, and expands surface area, or chemical activation, which removes inorganic impurities, cleans pore surfaces, and modifies structural composition [24], [25]. In this study, chemical activation was conducted using 3 M HCl and 0.1 M H_2SO_4, followed by washing, drying, and calcination.

Various methods have been applied to treat dye-containing wastewater, including coagulation–flocculation [26], electrochemical treatment, adsorption, oxidation, photocatalysis, and membrane filtration [27]. Among these, coagulation–flocculation is highly effective due to its stability, low cost, simplicity, and rapid sedimentation [34]. Numerous studies have applied this method for azo dye removal. For example, bentonite combined with sodium alginate successfully removed Rhodamine B (91.5%), Malachite Green (98.2%), Methylene Blue (98.5%), and Basic Violet (98.8%) [31]. Similarly, polyaluminum chloride (PACl) and bentonite clay achieved removal efficiencies of 98% for Methyl Red and 99% for Crystal Violet [32]. Bentonite coupled with OFI reached 98.99% removal efficiency for Methylene Blue [28], while alum removed 88.4% of batik wastewater [33], and

Abelmoschus esculentus removed 93.57% of textile effluents [30].

Natural coagulants and flocculants such as Paras Stone and O. ficus-indica offer a more sustainable alternative to synthetic agents, as they are abundant, low-cost, and environmentally friendly. Unlike chemical coagulants, they do not generate harmful by-products, and both materials can be sourced from local waste streams, minimizing costs [35]. Mechanistically, the positively charged surface of Paras Stone attracts negatively charged dye molecules, while OFI polysaccharides promote floc formation and accelerate particle settling. The OFI gel used in this study was prepared by extracting inner parenchyma tissue, grinding, centrifuging, and collecting the gel-like supernatant as a natural flocculant.

Given these considerations, this study investigates the removal efficiency of Remazol Red azo dye using both chemically activated and non-activated Paras Stone in combination with OFI gel. The research aims to determine the optimum operating conditions, particularly the concentration of dye solution and the effects of activation treatment, using batch-mode coagulation–flocculation experiments. The procedure consisted of a 4-minute coagulation phase, a 20-minute flocculation phase, and a 30-minute settling time.

METHODS

1. Materials and Equipment

The materials used in this experiment include hydrogen chloride (HCl, >37%), sulfuric acid (H_2SO_4, >99%) as chemical activators for Paras Stone, distilled water, filter paper, universal pH (Merck, >99%), aluminium foil, latex gloves, Remazol red ($C_{19}H_{18}N_2O_{11}S_3$, >99%), Paras Stone (powder) and *Opuntia ficus indica* (gel).

The equipment used in this research includes a UV-Vis Spectrophotometer (Genesys 10S UV-visible), an Oven (Memmert UN30), a centrifuge (Cencom II), a Centrifuge tube, a Magnetic stirrer, a 100 mesh sieve, and a stone mortar.

2. Preparation of Paras Stone and *Opuntia ficus indica*

Paras Stone was first crushed into small pieces, washed with distilled water, and dried at room temperature. The dried material was then heated at 100°C for 2 hours to remove residual moisture and stabilize its weight. Next, 50 g of 100-mesh Paras Stone was suspended in 100 mL of distilled water, stirred at 240 rpm for 2 hours, and oven-dried at 100°C for 6 hours. The dried Paras Stone (BP) was subsequently stored in a desiccator [36]. For *O. ficus-indica*, the cactus was cut into small square pieces, and the inner parenchyma (white tissue) was collected [37]. The parenchyma was crushed and centrifuged at 4000 rpm, and the resulting gel-like supernatant was collected and stored at 4°C. This viscous, whitish-transparent gel was used as a natural flocculant at 2.00 g per treatment.

3. Paras Stone Activation

A total of 30 g of Paras Stone was treated with 60 mL of 3 M HCl, while 50 g was treated with 100 mL of 0.1 M H_2SO_4. Each suspension was stirred at 500 rpm for 2 hours, with mass variations adjusted to the

concentration and volume of the respective acid solutions to ensure sufficient material for testing. The precipitates were filtered, rinsed with distilled water until neutral pH, and oven-dried at 100°C for 2 hours. Subsequent calcination was conducted at 550°C for 3 hours with a heating rate of 5°C/min, after which the samples were cooled in a desiccator for 30 minutes and weighed [16]. Treatment with HCl enhanced the silica-based matrix of Paras Stone, whereas H_2SO_4 introduced sulfate groups ($-SO_4$) on the coagulant surface, increasing its affinity toward anionic dyes such as Remazol Red.

4. Determination of % removal by the coagulation-flocculation method

In the first stage (coagulation), 2.75 g of Paras Stone coagulant was added to 100 mL of dye solution (10–50 mg/L) and stirred rapidly at 500 rpm for 4 minutes to destabilize dye particles. During the second stage (flocculation), 2.00 g of *Opuntia ficus-indica* gel was introduced, and the suspension was stirred gently for 20 minutes to facilitate floc formation. The third stage (settling) involved allowing the suspension to rest for 30 minutes for particle separation. The fourth stage (centrifugation) was performed at 4000 rpm for 5 minutes to separate the solids and liquids further. The final stage (filtration) employed plain filter paper to obtain the clarified supernatant. Absorbance of the filtrate was measured at 520 nm using a UV-Vis spectrophotometer, with distilled water as the blank. The final dye concentration (*C*) was determined, and the removal percentage was calculated accordingly.

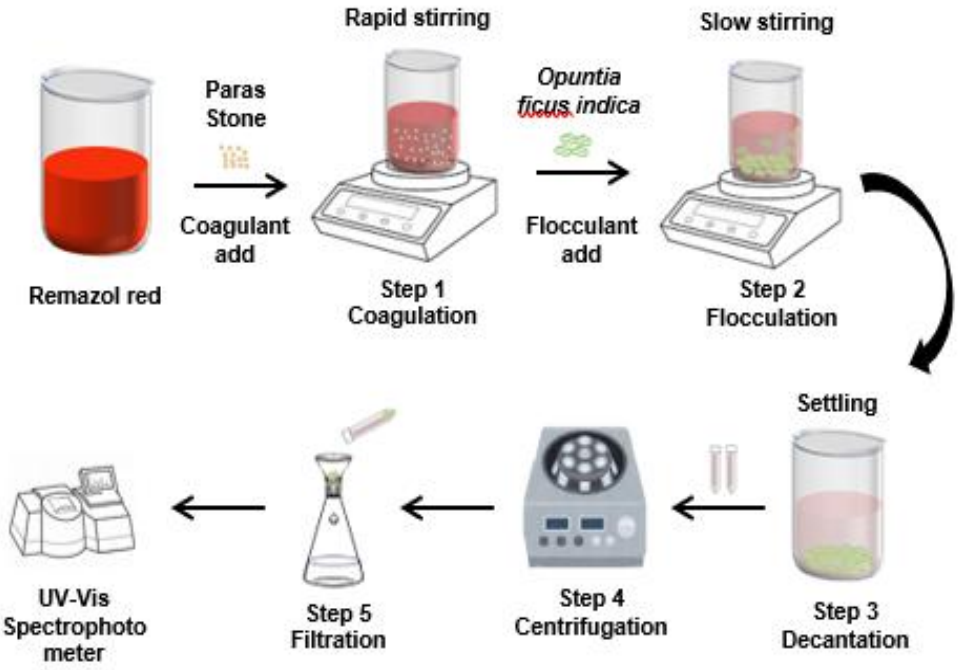

Figure 2. Schematic illustration of coagulation and flocculation of Remazol red with Paras Stone as Coagulant and *Opuntia ficus indica.*

Azo dye removal in the test solution was calculated using the following equation [38].

$$\textit{Removal Efficiency (\%)} = \frac{(Co-C)}{Co} \times 100\% \quad (1)$$

Information:

% = Removal of azo dyes

C_o = Azo dye concentration (mg/L)

C = Final concentration of azo dye (mg/L)

5. Data Analysis

All experimental results are presented as mean ± standard deviation (n = 3), obtained from three repeated measurements conducted under identical conditions for each treatment (i.e., not independent batches). Assumptions required for ANOVA, including normality (Shapiro–Wilk test) and homogeneity of variance (Levene's test), were verified, with all *p*-values exceeding 0.05. For transparency, the exact p-values for each test are reported in the Results section. Descriptive statistics were performed using *Microsoft Excel*, whereas one-way ANOVA and LSD post-hoc tests were conducted using *IBM SPSS Statistics 22*.

RESULT AND DISCUSSION

1. Effect of Acid Activation on Paras Stone

The acid concentration plays an important role in activating Paras Stone. Higher concentrations can increase the specific surface area, but at the same time pose a risk of damaging the mineral structure. Conversely, lower concentrations may result in a less effective activation process. In this study, crushed Paras Stone was immersed in HCl and H_2SO_4 solutions to activate the surface by dissolving certain minerals and impurities [39]. The calcination process following acid treatment aimed to remove residual moisture and eliminate organic matter from the Paras Stone. Heating at high temperature also helps to expand the surface structure by opening pores, thereby improving the material's ability to adsorb azo dyes. In addition, acid activation reduces the concentration of iron oxide and other metal oxides naturally present in the raw material. The mechanism of acid activation, in which H ions replace impurities (X), is illustrated in Figure 3 [40].

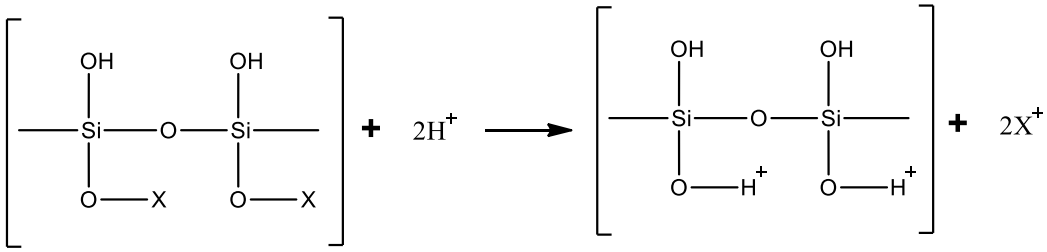

Figure 3. The acid activation process of Paras Stone [40].

Previous studies have also reported that acid activation increases the specific surface area of Paras Stone compared to untreated samples. For example, the measured surface area of non-activated Paras Stone was 16.66 m²/g, while activation with HCl and H_2SO_4 resulted in slightly higher values of 17.01 m²/g and 18.24 m²/g,

respectively [23]. These findings indicate that acid treatment does somewhat enhance surface area, although the increase is relatively small.

The efficiency of Remazol Red removal using Paras Stone—both acid-activated (HCl and H_2SO_4) and non-activated—is presented in Table 1. The results show that the highest dye removal was achieved with non-activated Paras Stone, reaching 95.40%. By contrast, the removal efficiency of the HCl-activated sample was 91.57%, and that of the H_2SO_4-activated sample was 92.53%. These results suggest that acid activation did not significantly improve dye removal efficiency. On the contrary, acid treatment may have altered surface functional groups and reduced the cation exchange capacity (CEC), an important factor in the electrostatic interaction mechanism. Since no direct CEC measurements were performed in this study, this explanation is proposed as a plausible hypothesis, supported by findings in related literature [41].

The mechanism of dye removal can also be explained by considering the chemical nature of the dye and the properties of Paras Stone. Remazol Red is an anionic dye requiring a positively charged coagulant to promote strong electrostatic interactions. As an aluminosilicate material, Paras Stone contains aluminum ions (Al^{3+}) in its structure. Due to isomorphic substitution, some of the Si^{4+} ions are replaced by Al^{3+}, which results in a net negative framework charge. This charge imbalance is compensated by the presence of exchangeable cations such as Na^+, K^+, and Ca^{2+}, which are located on the surface or within the structure. Under acidic conditions, these cations contribute to developing a positive surface charge, thereby enabling electrostatic interactions with negatively charged dye molecules. This charge-balancing mechanism explains why Paras Stone can function effectively as a coagulant for anionic dyes such as Remazol Red.

The visual results of the coagulation–flocculation experiment are shown in Figure 4, which depicts the color of the Remazol Red solution before and after treatment with both activated and non-activated Paras Stone under identical conditions (initial pH 4, 2.75 g Paras Stone coagulant, and 2.00 g *Opuntia ficus-indica* flocculant). The non-activated Paras Stone produced a clear and substantial reduction in color, with absorbance decreasing from 0.540 (before) to 0.024 (after), indicating very effective dye removal. In contrast, solutions treated with acid-activated Paras Stone remained faintly red, corresponding to higher residual absorbance values. This observation supports the finding that non-activated Paras Stone achieves superior removal efficiency under the same conditions.

The statistical analysis further strengthens these results. A one-way ANOVA followed by post-hoc testing demonstrated that the non-activated Paras Stone (mean = 95.50%) formed a distinct statistical group (‘b’), while the HCl-activated (91.57%) and H_2SO_4-activated (92.53%) samples clustered within the same group (‘a). Although the numerical differences in removal efficiency appear small, the statistical test confirms that the difference

between non-activated and acid-activated samples is significant at the 95% confidence level. Thus, the evidence clearly shows that non-activated Paras Stone performs better in removing Remazol Red dye than chemically activated samples.

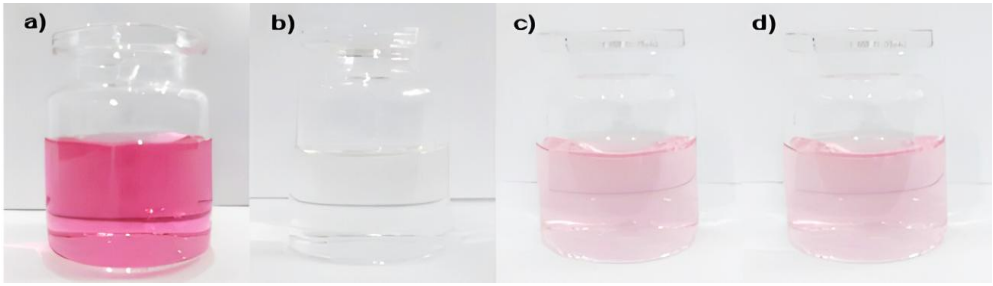

Figure 4. Color change of Remazol red test solution: a) before coagulation, b) after coagulation (without activation), c) after coagulation (3 M HCl activation), and d) after coagulation (0.1 M H_2SO_4 activation).

2. Dye Removal Efficiency at Varying Initial Concentrations

Remazol Red dye concentration was optimized for calibration at 10, 20, 30, 40, and 50 mg/L. The calibration curve followed the linear equation y = 0.018x with an R^2 value of 0.9998, indicating excellent linearity between absorbance and dye concentration (Figure 5). This calibration equation was subsequently applied to determine the concentration of Remazol Red in solution after the coagulation–flocculation process..

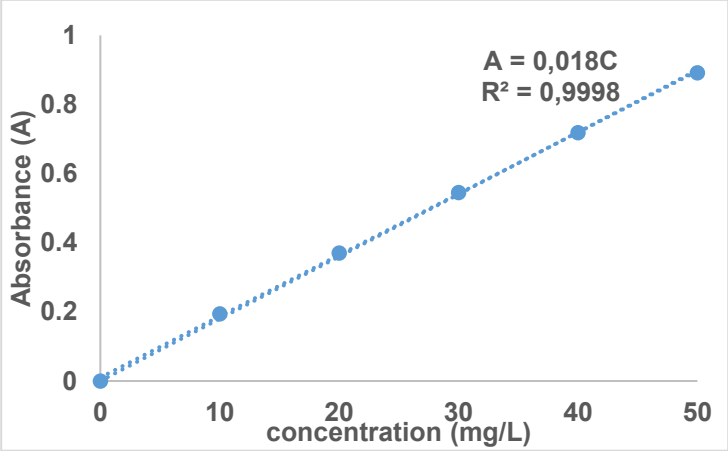

Figure 5. calibration curve equation

The initial dye concentration directly affects the number of colloidal particles in solution, which governs the extent of interaction with the coagulant. At an initial concentration of 30 mg/L, the balance between colloidal particles and the applied dose of Paras Stone was optimal, allowing effective charge neutralization and stable floc formation. This condition enhanced particle aggregation and maximized removal efficiency, confirming that dye removal strongly depends on both charge balance and the probability of particle collisions.

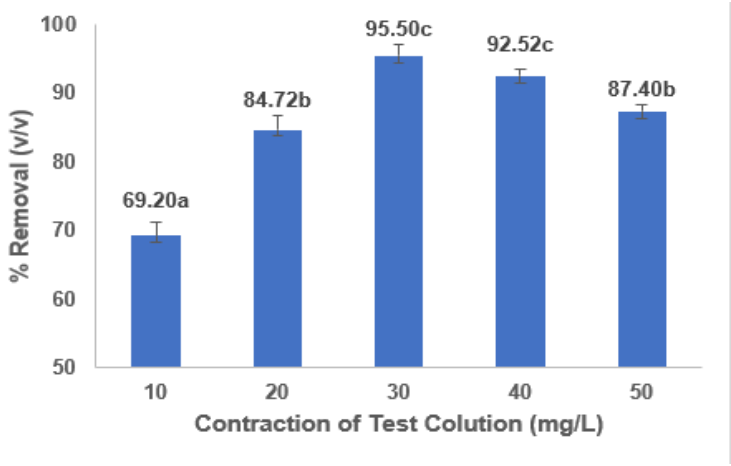

Figure 6. The effect of contraction of the test colution.

As shown in Figure 6, removal efficiency increased with concentration up to 30 mg/L, with a maximum efficiency of 95.50%. Beyond this concentration, efficiency declined because the number of dye particles exceeded the coagulation capacity of the Paras Stone coagulant. Statistical analysis supported this trend, revealing significant differences among concentration groups. For instance, removal efficiencies of 69.20% (a) and 84.72% (b) were significantly different, while 95.50% (c) and 92.52% (d) were not significantly different from each other but were significantly higher than 87.40% (b). These findings confirm that an initial concentration of 30 mg/L represents the optimum condition, where ideal charge neutralization and sufficient particle collision frequency occur to maximize dye removal.

Table 2. Removal of Remazol red dye at various concentrations of test solution (mg/L).

Concentrations (mg/L)	BP (g)	OFI (g)	Coagulation Speed (rpm)	initial pH of the test solution	% removal	SD	Errors (%)	Thoroughness (%)
10	2.75	2.00	500	4	69.20	2.04	2.95	97.05
20	2.75	2.00	500	4	84.72	1.94	2.29	97.71
30	2.75	2.00	500	4	95.50	1.54	1.61	98.39
40	2.75	2.00	500	4	92.52	1.04	1.13	98.87
50	2.75	2.00	500	4	87.40	1.05	1.20	98.80

Table 2 shows that at initial Remazol Red concentrations of 10 mg/L and 20 mg/L, the number of colloidal particles in solution was relatively low, which limited their interaction with the applied coagulant dose. As a result, the removal efficiency was suboptimal, since the available coagulant could not be fully utilized. In contrast, at higher initial concentrations of 40 mg/L and 50 mg/L, the number of colloidal particles exceeded the capacity of the fixed coagulant and flocculant doses. Under these conditions, the amount of coagulant was insufficient to neutralize all negative charges, leaving many dye particles dispersed in solution and reducing the overall efficiency of coagulation–flocculation.

a.

b.

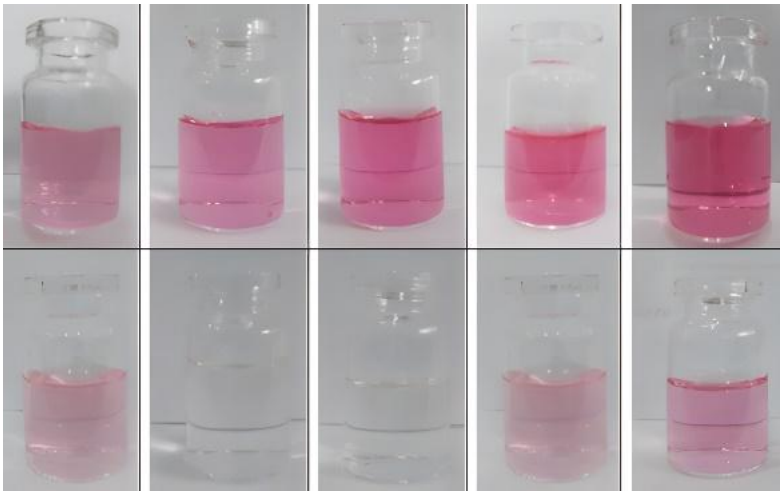

Figure 7. Colour change of Remazol red test solution at concentrations of 10, 20, 30, 40, and 50 mg/L, a) before coagulation and b) after coagulation.

As illustrated in Figure 7 and supported by the quantitative data in Table 3, the colour of the Remazol Red solution before treatment increased in intensity with concentration, which was also reflected in higher absorbance values. A deeper colour corresponds to more colloidal dye particles suspended in the solution. After treatment, the most significant colour change was observed at the initial concentration of 30 mg/L, which coincided with the lowest final absorbance value of 0.024, confirming maximum removal efficiency at this concentration.

The role of electrostatic interactions between the dye molecules and the Paras Stone coagulant can explain the removal mechanism. When the solution pH is below the point of zero charge (pH_pzc = 6.58), the surface of Paras Stone becomes positively charged. Under these acidic conditions, the positively charged coagulant surface is strongly attracted to the negatively charged sulfonate groups of Remazol Red, promoting effective coagulation. Conversely, when the solution pH exceeds 6.58, the surface of Paras Stone becomes negatively charged, which leads to electrostatic repulsion with the dye molecules and a subsequent reduction in removal efficiency [42].

Table 3. Absorbance of the Remazol red test solution before and after coagulation was measured at concentrations of 10, 20, 30, 40, and 50 mg/L.

Concentrations (mg/L)	Absorbance before coagulation (A_0)	Absorbance after coagulation (A)
10	0.182	0.056
20	0.361	0.055
30	0.540	0.024
40	0.712	0.053
50	0.902	0.014

3. Mechanism of Coagulation–Flocculation

Previous studies have shown that the surface chemistry of Paras Stone is influenced by pH, as illustrated in Figure 8. In the present work, the Remazol Red test solution was adjusted to pH 4, since earlier research identified this value as the optimum pH for Remazol Red removal [48]. The dominant silica species present at this pH is H_2SiO_3, which tends to release H^+ ions, producing a positively charged surface. Under alkaline conditions, however, silica species such as SiO_3^{2-} and $HSiO_3^-$ are predominant, generating negatively charged surfaces.

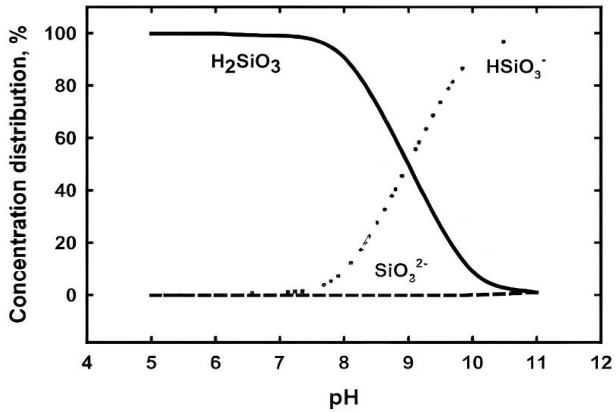

Figure 8. Distribution of silicate species on various pH [43].

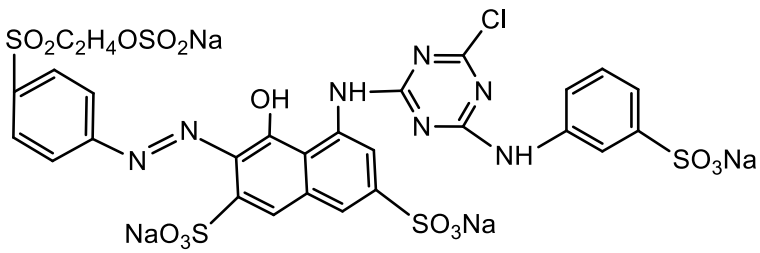

Figure 9. Structure of Remazol red [44].

The structure of Remazol Red dye is shown in Figure 9. The molecule contains an azo group (-N=N-) responsible for its characteristic colour and chemical reactivity. In addition, the presence of a sulfonate group (SO_3^-) makes Remazol Red highly soluble in water, a property that enhances its application in textile dyeing [2], [31], [32], [45]. However, the stability of the azo bond and its anionic nature make Remazol Red highly resistant to natural degradation, thereby classifying it as a persistent organic pollutant [46], [47].

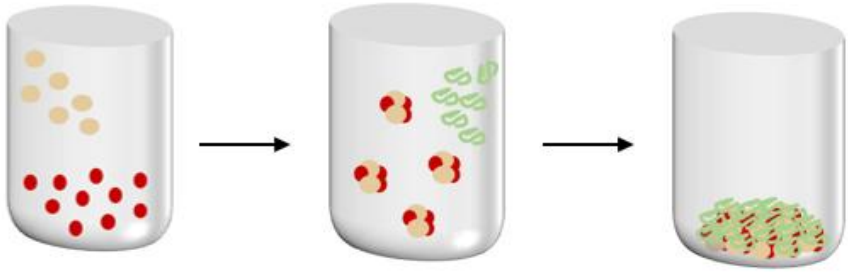

Figure 10. Electrostatic interactions between coagulant and Remazol red [48].

Electrostatic interactions between the Paras Stone coagulant and Remazol Red dye are illustrated in Figure 10. At acidic pH values, the positively charged Paras Stone surface interacts with the negatively charged sulfonate groups of Remazol Red, leading to strong electrostatic attraction and efficient removal. However, the dye and the coagulant surface at alkaline pH carry negative charges, resulting in electrostatic repulsion. Under such conditions, coagulation is ineffective, and dye removal is substantially reduced.

This is where the role of *Opuntia ficus-indica* (OFI) mucilage as a natural flocculant becomes critical. The mucilage contains polysaccharides as the main component, with linear chains and side branches that act as bridging agents between colloidal particles. These polysaccharides connect destabilized dye particles into larger flocs, which are heavier and settle more rapidly [20], [21]

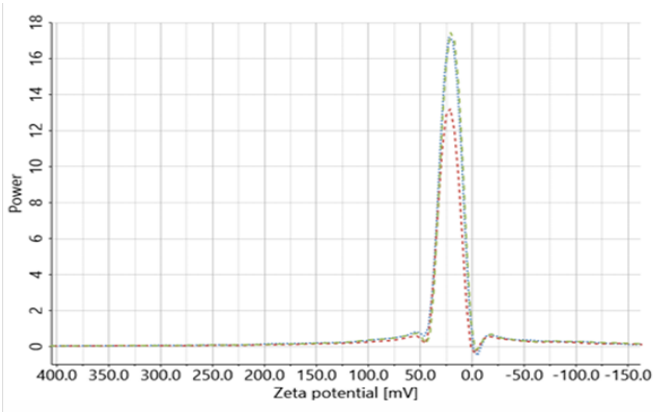

Figure 11. Zeta potential of the non-activated Paras Stone coagulant.

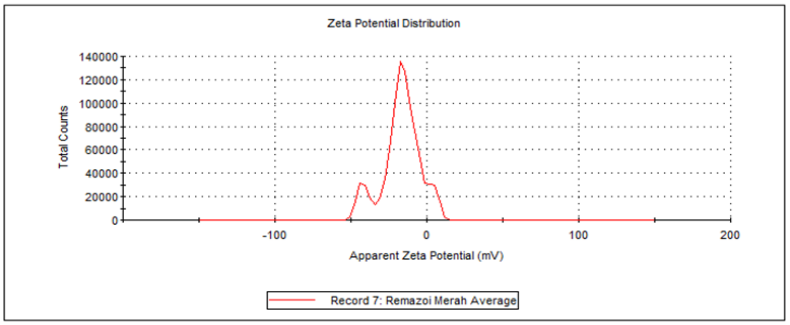

Figure 12. Zeta potential of the *Opuntia ficus indica* flocculant.

Zeta potential measurements were performed to validate the electrostatic mechanism further. The zeta potential of non-activated Paras Stone was +21.01 mV, whereas the Remazol Red dye solution had a zeta potential of –16.8 mV, measured at 25 °C (Figures 11 and 12). The difference in charge polarity confirms the electrostatic attraction between the positively charged coagulant and the negatively charged dye molecules. Zeta potential values beyond ±30 mV generally indicate high colloidal stability due to strong repulsive forces, which hinder aggregation. Since the values were moderate, the system was sufficiently unstable to allow effective particle aggregation and subsequent sedimentation.

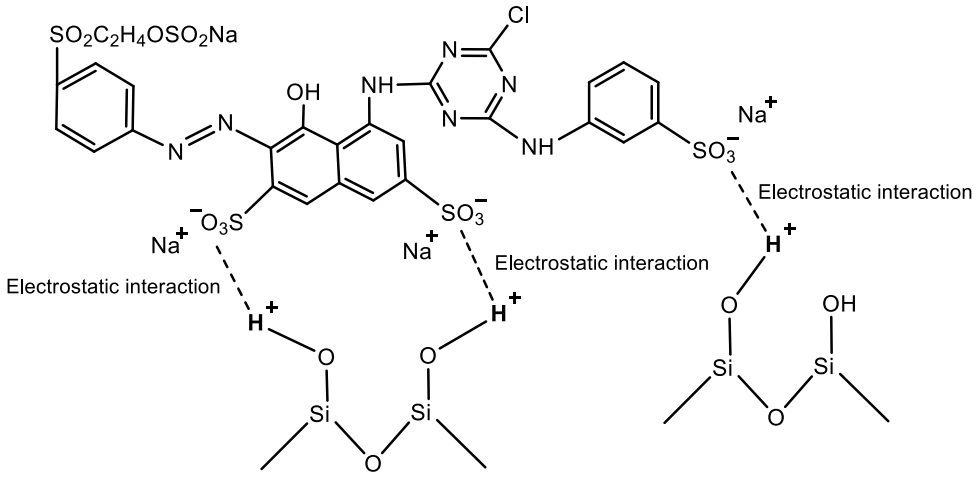

Figure 13. Reaction mechanism of Paras stone and Remazol red.

The proposed reaction mechanism is presented in Figure 13. Under acidic conditions (pH 4), the H_2SiO_3 species in Paras Stone releases positively charged H^+ ions, which interact electrostatically with the negatively charged SO_3^- groups of Remazol Red. This attraction facilitates dye destabilization and aggregation, which is further enhanced by the bridging effect of OFI polysaccharides. The schematic illustrates how the positively charged Paras Stone surface (+21.01 mV) interacts with the negatively charged dye molecules (–16.8 mV), corroborating both the zeta potential results and the experimental findings of dye removal efficiency.

4. Contribution of *Opuntia ficus indica* (OFI)

Opuntia ficus-indica (OFI), a member of the Cactaceae family, has been widely recognized as an effective natural bioflocculant for wastewater treatment due to the presence of mucilage-rich parenchyma tissue. The mucilage contains polysaccharides that provide exceptional flocculation properties through charge neutralization and particle bridging mechanisms. This study extracted and homogenized the inner parenchyma of OFI cladodes to produce a gel-type flocculant (Figure 14). The OFI gel effectively aggregated Remazol Red dye particles into larger flocs during the flocculation stage,

thereby enhancing sedimentation. The process achieved a removal efficiency exceeding 90%, significantly reducing sedimentation time compared with conventional flocculation systems.

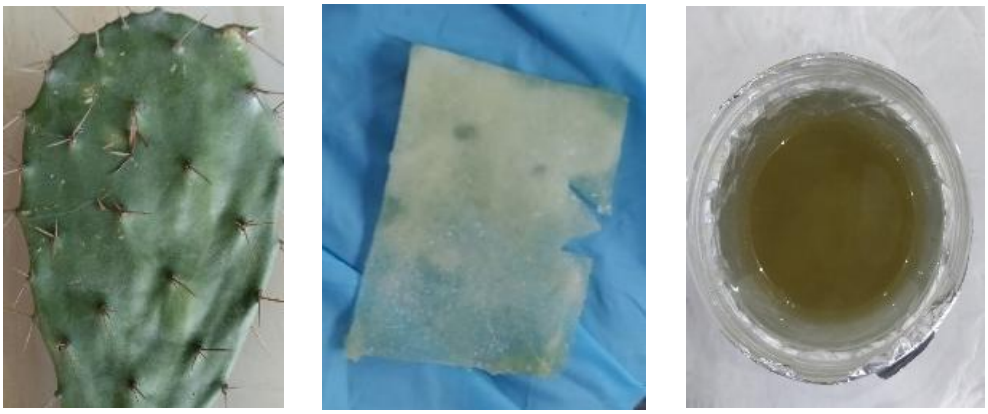

Figure 14. *Opuntia ficus indica.*

The application of OFI as a bioflocculant presents several advantages over synthetic alternatives. These include its biodegradability, non-toxic nature, and cost-effectiveness, particularly because OFI grows abundantly in arid and semi-arid regions without requiring intensive cultivation. The results of this study confirm that OFI provides a sustainable and environmentally friendly alternative for enhancing coagulation–flocculation processes, and holds significant promise for large-scale application in textile wastewater treatment.

Table 4. Comparison of various dye wastes processed via coagulation-flocculation.

Source of dye wastes	Coagulant	Flocculant	Optimum condition	% removal	Ref
Remazol red	Chitosan	-	0.300 g, pH 2	100%	[46]
Remazol red	Paras Stone (without activation)	OFI	PS 2.75 g; OFI 2 g, 500 rpm 4 min, pH 4	96.70%	[48]
Remazol red	Papaya Seeds (*Carica papaya* L.)	-	0.0260 mg, 950 rpm 5 min, pH 2	96.1%	[49]
Remazol red	Tamarind Seeds (*Tamarindus indica*)	-	500 mg, 350 rpm 5 min, pH 3	68.26%	[50]
Remazol red	Paras Stone (HCl and H_2SO_4 activation)	OFI	PS 2.75 g; OFI 2 g, 500 rpm 4 min, pH 4, 30 mg/L	95.50%	This study

Paras Stone and Opuntia ficus-indica (OFI) combined use offers clear environmental and economic advantages over conventional coagulants. Environmentally, this combination is non-toxic, biodegradable, and produces recyclable effluents, whereas conventional coagulants often generate toxic sludge with risks of metal accumulation. Paras Stone + OFI is economically highly cost-effective due to both abundant raw materials and local availability. Paras Stone is derived from residual stone carving waste in Lombok, while OFI grows naturally in arid areas and remains underutilized. Their preparation requires only simple physical treatments,

without hazardous chemicals or complex processing, reducing costs, energy input, and environmental impact.

According to Table 4, recent literature highlights numerous investigations into azo dye removal. Yet, the specific combination of acid- or base-activated Paras Stone with OFI flocculant for Remazol Red removal has not been systematically studied before. Earlier work reported high dye removal efficiencies with non-activated Paras Stone [48]. Although the Paras Stone + OFI combination showed slightly lower removal rates than chitosan, it demonstrated distinct practical advantages. Unlike chitosan, which requires complex and costly production, Paras Stone + OFI is low-cost, easily accessible, and sustainable for large-scale application. Moreover, Paras Stone + OFI exhibited superior performance compared with tamarind seed extract due to its higher silica pore structure and ion-exchange capacity. These findings suggest that coagulant selection should not only be based on removal efficiency but also consider economic feasibility and environmental sustainability.

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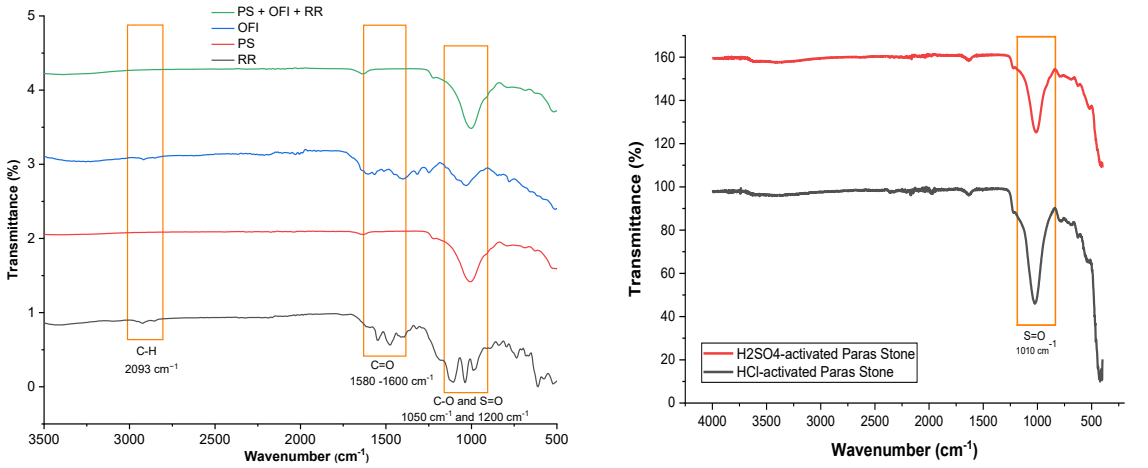

Figure 15. (a) FTIR spectra of Remazol red (RR), unactivated Paras Stone (PS), OFI, and Remazol red + unactivated Paras Stone + *Opuntia ficus indica* (PS + OFI + RR) after coagulation-flocculation [48]; (b) FTIR spectra of activated Paras Stone.

The FTIR characterization provides further evidence for the removal mechanism. As shown in Figure 15a, the spectrum of non-activated Paras Stone displays a peak at 1603 cm^{-1}, attributed to the O–H stretching vibration of silanol groups, and a band at 1004 cm^{-1} corresponding to Si–O–Si stretching, confirming the silica network structure. For OFI, a broad absorption band between 3500–3000 cm^{-1} corresponds to O–H groups, while a peak at 1620 cm^{-1} indicates asymmetric stretching of C=O in carboxylate groups. The region 1200–950 cm^{-1} is characteristic of polysaccharide bands and C–O vibrations from alcohols and ethers. After coagulation–flocculation (PS + OFI + RR), the Si–O–Si band at 1004 cm^{-1} remains detectable, but the sulfonate peak (~1200 cm^{-1}), which appeared in the pure Remazol Red spectrum, diminishes substantially. This disappearance indicates strong interaction between the sulfonate groups of Remazol

Red and the active sites of Paras Stone and OFI [48].

The superior dye removal observed with non-activated Paras Stone (95.50%) compared with HCl- or H_2SO_4-activated samples (91.57–92.53%) also aligns with the FTIR data. In acid-activated samples (Figure 15b), the intensity of the silanol O–H peak at ~1600 cm^{-1} decreases significantly, suggesting that acid treatment partially removes or protonates surface –OH groups. This modification may increase surface area (as seen in the sharper Si–O–Si bands, reflecting surface purification) but simultaneously reduces the cation exchange capacity (CEC), which is essential for effective electrostatic binding with anionic dye molecules. These findings highlight the critical role of silanol groups (–OH) in facilitating dye removal via ion-exchange and electrostatic interactions, explaining why unactivated Paras Stone outperformed its acid-activated counterparts

CONCLUSION

The results of this study indicate that non-activated Paras Stone is a highly effective and low-cost natural coagulant for textile wastewater treatment. In contrast, chemical activation with 3 M HCl and 0.1 M H_2SO_4 slightly reduced the removal efficiency compared to the untreated material. The coagulation–flocculation process using non-activated Paras Stone achieved a dye removal efficiency of 95.50% ± 1.61%, which was superior to that of the HCl-activated (91.57% ± 0.72%) and H_2SO_4-activated (92.53% ± 0.69%) samples. The maximum removal efficiency was observed at an initial Remazol Red concentration of 30 mg/L, attributed to strong electrostatic interactions between the positively charged H^+ ions from H_2SiO_3 in Paras Stone and the negatively charged SO_3^- groups of the dye molecules.

The integration of Paras Stone with *Opuntia ficus-indica* flocculant offers an environmentally friendly treatment system, as both materials are biodegradable, non-toxic, and derived from locally available renewable resources. Beyond demonstrating high removal efficiency, this approach also provides advantages in terms of sustainability and cost-effectiveness compared to conventional coagulants and flocculants.

Despite these promising results, the study was limited to a laboratory-scale system using synthetic Remazol Red dye solutions. Validation under real textile effluent conditions is necessary to confirm the practical applicability of this method. Future research should also explore process scalability, continuous-flow systems, and potential reuse or regeneration of the coagulant and flocculant to enhance economic viability.

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