The Study of Removal of Remazol Red with Biomaterial Paras Stone and *Opuntia ficus-indica* by Coagulation-Flocculation

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Abstract: *The rapid progress of the textile industry sector has an impact on the environment by producing dye waste. The use of synthetic coagulants in processing textile industry waste containing azo dyes can cause residues that are detrimental to the environment. In this research, a technique for processing azo dye was done using natural coagulants. The use of natural coagulants provides several advantages, such as being eco-friendly, abundant, and cost-efficient. The potential of paras stone and* Opuntia ficus-indica *biomaterials as natural coagulants and flocculants for removing remazol red dye was thoroughly investigated under various conditions, including coagulant dose, the speed of coagulation, and the optimal initial pH of the test solution. The removal of remazol red dye was quantitatively analyzed using a UV-vis spectrophotometer at a wavelength of 520 nm. Findings from the research revealed that the removal efficiency of remazol red dye reached 96.70% with a coagulant dose of 2.75 g of paras stone and 2.00 g of* O. ficus-indica *at an optimal coagulation speed of 500 rpm and a pH of 4 for the testing solution. The results of this study provide an engineering perspective on optimizing operational parameters for removing remazol red in aquatic environments.*

Keywords: *dyes; industrial waste; environment; coagulation; flocculation*

■ INTRODUCTION

The textile industry contributes significantly to the global economy [1]. However, wastewater generated by the textile industry contributes to environmental pollution. One of the most commonly used synthetic dyes in the textile sector today is azo dye [2]. Producing azo dyes involves diazotizing aromatic primary amines with electron-rich nucleophiles, such as amino acids and hydroxy acids. Azo dyes account for approximately 70% of all synthetic dyes worldwide [3-4]. These dyes contain a –N=N– functional group that links two symmetric alkyl or aryl radicals and two asymmetric or non-azo radicals [5]. The quantity of azo dyes released into the environment ranges from 2 to 50% [6]. The discharged waste from the textile industry contains toxic, carcinogenic, and non-biodegradable azo dyes, threatening ecosystems. Increasing concentrations of these azo dyes can significantly harm the environment [7-8].

Several chemical and physicochemical methods for processing dye waste have been developed and utilized, including electrocoagulation, adsorption, and coagulation methods. The electrocoagulation method has limitations because it requires high energy and causes crusting on the electrodes. The adsorption method has the weakness of limited adsorption capacity. Meanwhile, the coagulation method is simple and effective in overcoming the problem of dye waste, so in this study, the coagulation method using biocoagulants was chosen. Removal of azo dyes via the coagulation-flocculation method is one of the most commonly used physicochemical processes. This method is very effective because it can remove up to 100% of the dye [9]. The coagulation-flocculation method consists of three steps, i.e., coagulation, flocculation, and filtration. In the first step, the coagulation process occurs by adding a coagulant, causing the small dye particles, which were initially mono-repulsive, to stop repelling each other and forming a microflow. The second step, flocculation,

involves particles that no longer repel each other, combining to form larger aggregates or flocs, also known as macro flocs. In the third step, a centrifugation technique is carried out to separate the solid from the liquid. In the next stage, the upper liquid (supernatant) resulting from the centrifugation process is obtained, which still contains small molecules so that it is easily separated from the dye through a filtering process [10].

Paras stone (PS) as a coagulant and *Opuntia ficus-indica* (OFI) as a flocculant resulted in a lower environmental impact, as both are natural materials and do not produce harmful by-products like synthetic coagulants and flocculants. Additionally, the costs are relatively low since these biomaterials are derived from waste that has not been previously reused. The PS coagulant has a positive charge, enabling it to attract negatively charged dyes. At the same time, the OFI flocculant contains polysaccharides that aid in floc formation and accelerate settling. Despite their advantages, PS coagulant and OFI flocculant also have drawbacks. Although these biomaterials are abundant, they are only available in specific regions, making them less accessible throughout Indonesia. Furthermore, the PS coagulant requires a longer settling time, so OFI flocculant was incorporated into this study to speed up the process. However, OFI has a short shelf life of approximately one month, and its effectiveness diminishes if used beyond this period.

The coagulation-flocculation method is a simple and effective technique for effluent removal in the textile industry, utilizing coagulants and flocculants. Synthetic coagulants used excessively can harm the environment, including the formation of chemical sludge, changing the pH of the water, higher cost than natural coagulants, and are dangerous to nature [11]. Several studies have explored the use of natural coagulants to treat dye waste. The natural coagulants can be used for treatment of textile waste wherever it is available in sufficiently and do not harm the environment [12]. Several studies on the removal of azo dyes via the coagulation-flocculation method have been carried out [9,13-14]. Bentonite as a coagulant and sodium alginate as a flocculant were able to remove rhodamine B, malachite green, methylene blue, and basic violet with efficiency 91.5, 98.2, 98.5, and 98.8% [15]. Similarly, PACl as a coagulant and bentonite clay as a flocculant successfully removed methyl red (98%) and crystal violet (99%) [16]. Bentonite combined with OFI as a flocculant achieved a removal efficiency of up to 98.99% for methylene blue [9]. Alum effectively removed industrial batik waste by 88.4% [17], while *Abelmoschus esculentus* removed textile industry waste with an efficiency of up to 93.57% [14]. In this research, the new potential of natural coagulants and flocculants from Lombok, Indonesia, has been studied. Removal of azo dyes using flocculation coagulation method using natural coagulants and flocculants from Lombok has been developed. PS is a natural coagulant from Central Lombok that is commonly used in making statues, tombstones, and wall decorations. The remains of carved statues and tombstones produce PS waste. This waste will be used as a natural coagulant to remove dyes in the textile industry. Rocks whose main composition is silica (SiO_2) generally consist of quartz minerals (quartz) or amorphous forms of silica, one of which is PS. PS is a type of stone that is classified as sandstone. In the process of formation, this stone is formed through sedimentation. SiO_2 sand contains 59% Si components. The presence of the silanol (Si–OH) and siloxane (Si–O–Si) groups contained in SiO_2 causes PS to have the potential as a natural coagulant [18-19]. OFI, as a natural flocculant, is a cactus plant from East Lombok. This plant is often left to dry and never used. OFI contains secondary metabolite compounds involved in the process. These compounds are flavonoid compounds such as quercetin and starch. Both of these active components can increase flocculation activity [20]. Therefore, this research modified PS as a natural coagulant and OFI cactus plants as a flocculant to treat waste using dye removal.

The novelty of this research lies in the use of biomaterials derived from Lombok Island, Indonesia, as well as the investigation of the physicochemical mechanisms involved in the flocculation and coagulation processes. This study focuses on the role of Si–OH and Si–O–Si groups in PSs in aggregating and stabilizing dye particles. Additionally, the secondary

metabolites of OFI play a key role in accelerating precipitation and enhancing flocculation activity. The research aims to optimize operational parameters, such as coagulant dosage, coagulation speed, and the initial pH of the test solution. The findings provide valuable insights into developing an environmentally friendly technology for dye wastewater treatment. So, in this research, we studied the effect of coagulant dose, coagulation speed, and initial pH of the test solution on the performance of PS and OFI in removing remazol red (RR) dyes. Characterization of natural coagulants and flocculants was carried out using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and scanning electron microscope (SEM) instrumentation.

■ EXPERIMENTAL SECTION

Materials

The materials used in this experiment include distilled water, sodium hydroxide (NaOH, > 99%, Merck), hydrogen chloride (HCl, > 37%), filter paper, universal pH (Merck, > 99%), aluminum foil, latex gloves, RR ($C_{19}H_{18}N_2O_{11}S_3$, > 99%), PS (powder), and OFI (gel).

Instrumentation

The instrumentations used in this research include a UV-vis spectrophotometer (Genesys 10S UV-visible), FTIR (Shimadzu 8400s), XRD (X'Pert3 Powder), and SEM (Hitachi PM3000). A UV-vis spectrophotometer is used to determine the concentration of a solution before and after coagulation-flocculation.

Procedure

Experimental setup

Fig. 1 illustrates the research setup conducted in a batch system. The coagulant PS was added to the RR test solution, followed by the addition of the flocculant OFI. The RR test solution was stirred using a magnetic stirrer. In the final stage, the test solution was filtered to obtain the separation of the RR dye with a UV-vis spectrophotometer.

Experimental method

OFI cactus taken in Jerowaru, East Lombok Regency. Cactus cladding was washed with distilled water and dried at room temperature. Next, the cactus cladodia was cut into small square pieces, and the white inner part (parenchyma) was taken (Fig. 2) [21]. The parenchyma layer was crushed and then centrifuged at 40 rpm. The gel-like supernatant was collected and stored at 4 °C [13].

PSs were collected in Central Praya, Central Lombok Regency. Small pieces of PS were washed with distilled water and dried at room temperature. Next, the PS was pulverized and sieved with a size of 100 mesh. A total of 50 g of 100 mesh size PS was added with 100 mL of distilled water, stirred for 2 h at 240 rpm, and then dried at 100 °C for 6 h. The dried PSs were stored in a desiccator [9].

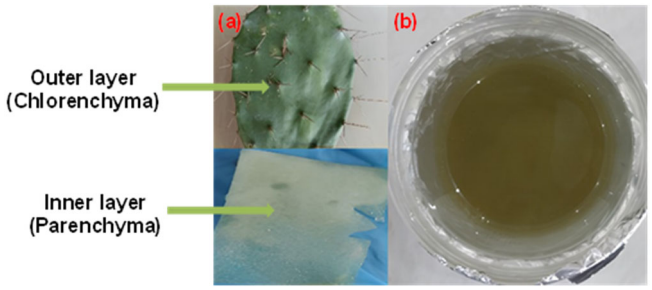

Fig 2. (a) Longitudinal section of a cladode of OFI and (b) OFI gel

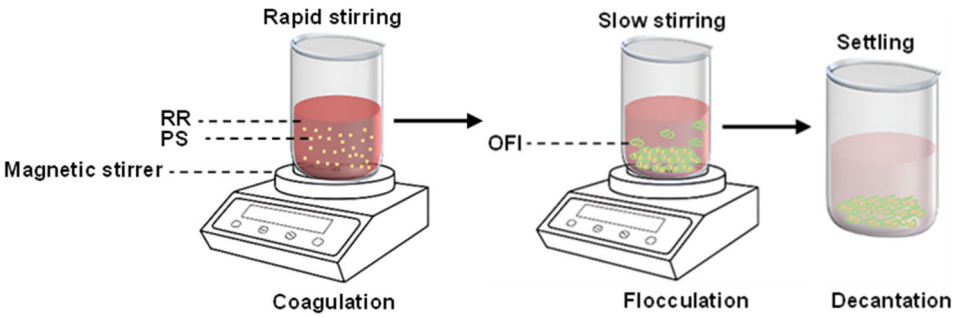

Fig 1. Experimental setup for coagulation and flocculation

RR stock solution (100 mg/L) was prepared and stored in a room with minimal light to prevent degradation. The RR test solution (30 mg/L) was diluted with 100 mL of distilled water (pH 3, 4, 5, 6, 7, 8, and 9). Then, the coagulation and flocculation process consisting of five stages is conducted. The first stage is the coagulation (fast stirring). The dyes contain small particles or colloids. Because of their small size, they are difficult to separate and repel each other.

In the coagulation process, a coagulant is added so that the particles that were repelling stop repelling each other, and the resulting flocs are small (micro flocs). Coagulation was carried out with a dose of PS coagulant (1.25, 2, 2.75, 3.5, and 4.25 g) added to 100 mL of RR test solution (30 mg/L) with speed variation coagulation (400, 500, 600, 700, and 800 rpm) for 4 min, followed by a dose of OFI flocculant (2.00 g) at the final stirring. Second stage, flocculation, the particles that have not repelled each other in the coagulation process begin to combine to form larger clumps or flocs (macro flocs). Flocculation was carried out with a dose of OFI flocculant (2.00 g) at a slow speed for 20 min. In the third stage, the 30 min of standing aims to bring the sediment down to facilitate the process of taking the test solution. The fourth stage, centrifugation, aims to separate liquids and solids to reduce the remaining particles. Centrifugation is carried out for 5 min at a speed of 40 rpm. In the fifth stage, filtering is done using filter paper. Then, the absorbance is measured using a UV-vis spectrophotometer instrument. Absorbance to determine the final concentration of the test solution. Then, the azo dye removal calculation was carried out. Calculation of azo dye removal in the test solution was calculated using Eq. (1) [22];

$$\text{Removal efficiency } (\%) = \frac{C_0 - C}{C_0} \times 100\% \quad (1)$$

where the removal efficiency (%) is the removal of azo dyes removal of azo dyes, and C_0 and C (ppm) are the azo dye concentration at initial and final conditions, respectively.

Characterization using FTIR instruments to determine the functional groups of biomaterials of PS and OFI, SEM characterization to determine the morphology of biomaterials so that the size and shape of biomaterials are known while XRD characterization to identify crystallite material in PS and OFI. The preparation of OFI to be characterized is using cladding whose inner layer (parenchyma) is cut square into smaller sizes and then dried at room temperature and ground until smooth to get OFI in powder form [23]. The pulverized PS and OFI in powder form will be characterized by FTIR, SEM, and XRD.

Data analysis

All values are the mean ± the standard deviation (SD) of three independent measurements, which totaled n = 3. A one-way analysis of variance (ANOVA) test was used to examine the actual differences between the variants after the use of Microsoft Excel. The least significant difference (LSD) test followed by statistical significance with $p < 0.05$.

■ RESULTS AND DISCUSSION

In this study, the removal of azo dye has been examined using PS as a natural coagulant and OFI as a natural flocculant. The effectiveness of this method is determined by the %removal to achieve a value close to 100%. This outcome is influenced by several factors, including coagulant-flocculant dosage, coagulation speed, and the initial pH of the test solution used. The percentage removal of RR dye was carried out by measuring the absorbance of the test solution using a UV-vis spectrophotometer at a maximum wavelength of 520 nm. The complete calculation of the %removal value follows Eq. (1).

Effect of Coagulant Dosage

The optimal coagulant dose is the smallest amount of coagulant required to treat wastewater to the desired quality standard. Coagulant dosage is important when determining the best conditions for the coagulation-flocculation process. If the dose is not controlled appropriately, the coagulation-flocculation process is not only disturbed, but further processes, such as sedimentation and filtration, are also disturbed [24]. The effect of coagulant dose on %removal was studied with varying coagulant doses of 1.25, 2.00, 2.75, 3.5, and 4.25 g.

In Fig. 3(a), it is known that the higher the coagulant dose, the higher the removal rate of azo dyes, which is indicated by the %removal value up to a certain time. The increase in %removal is caused by the higher the coagulant dosage, the more active compounds contained in the biocoagulant, and a charge neutralization process occurs where wastewater particles usually have a negative charge and the coagulant has a positive charge so that these particles easily combine and form microflows. After that, the microflocs gather into larger flocs and form bridges whose function is to bridge between particles [25]. The azo dye, RR, is anionic because it contains sulfonate groups that are completely ionized. The negatively charged dye is added to the positively charged coagulant and neutralized during the flocculation process so that the coagulation-flocculation process can occur. In Table 1, azo dye removal decreased after a dose of 2.75 g. This is due to reduced inter-charge neutralization, and the binding capacity at this dose has decreased. In other words, the number of particles present is not enough to guarantee good coagulation. The removal rate of azo dyes, which is lower than the optimum coagulant dose, is caused by the re-stabilization of the particles due to repulsion between the biomaterial and the pollutant, thereby preventing floc formation [9,26]. The results of the research produced the following data.

Effect of Coagulation Speed

In the coagulation process, the speed of stirring is crucial for uniformly distributing the coagulant throughout the solution, which assists in neutralizing the repulsive forces between the coagulant particles and the contaminants. The effectiveness of rapid coagulant stirring is assessed at speeds of 400, 500, 600, 700, and 800 rpm for 4 min. The relationship between the coagulation speed and the percentage of synthetic dye removal achieved is outlined as follows.

As seen in Fig. 3(b) and Table 2, a greater speed of coagulation is linked to a higher percentage of dye removal, as demonstrated by the %removal values over

Table 1. Variation of coagulant doses in the removal of RR

Coagulant dosage (g)	Flocculant dosage (g)	%Removal
1.25	2.00	85.43
2.00	2.00	89.16
2.75	2.00	93.52
3.50	2.00	85.32
4.25	2.00	81.56

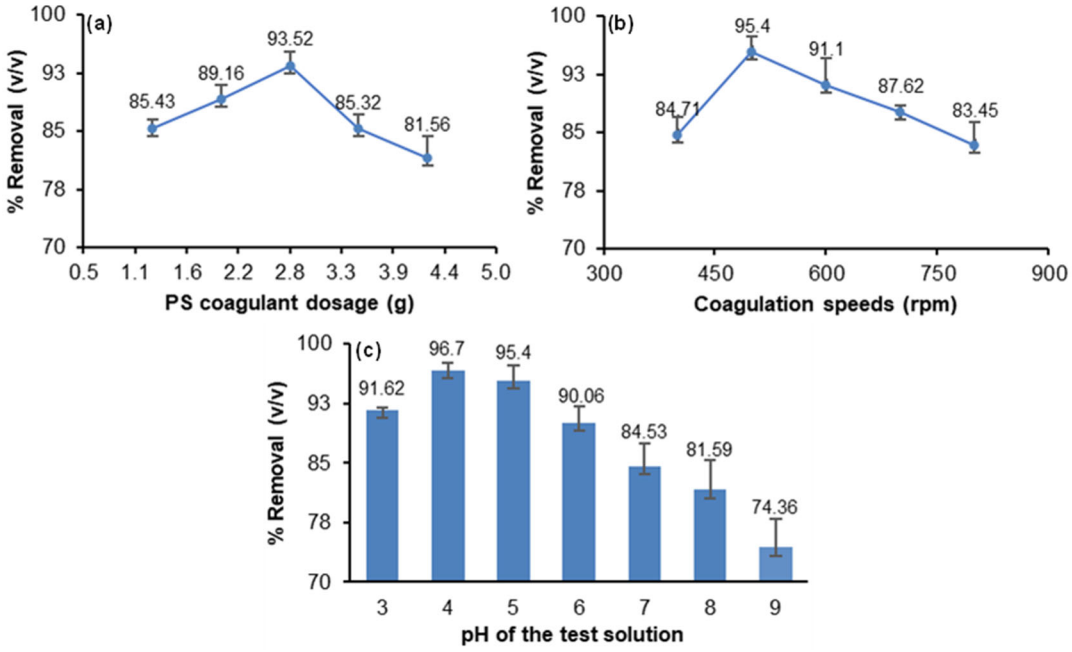

Fig 3. The effect of (a) coagulation dosage, (b) coagulation speed, and (c) initial pH on RR removal

Table 2. Variations in coagulation speed in removing RR

Coagulant dosage (g)	Flocculant dosage (g)	Coagulation speeds (rpm)	%Removal
2.75	2.00	400	84.71
2.75	2.00	500	95.40
2.75	2.00	600	91.10
2.75	2.00	700	87.62
2.75	2.00	800	83.45

time. The highest %removal recorded was 95.04% at a stirring speed of 500 rpm. An increase in %removal is crucial as it facilitates faster particle bonding and the development of larger aggregates, which can be separated from the dye with greater ease [7]. After reaching the optimal point, any stirring speeds ranging from 600 to 800 rpm led to a decrease in removal percentage because coagulation happens too quickly past a certain limit, resulting in the floc breaking apart into smaller particles that are more difficult to settle, thereby negatively influencing the dye removal rate [26].

Effect of Initial pH

The initial pH of the RR test solution is critical to the efficiency of the coagulation process, in addition to the coagulant dosage and coagulation speed. It has been stated that pH is an important component affecting the effectiveness of coagulants in dye removal, as this can have an impact on the production of hydrolyzed species. Previous studies have shown that OFI functions well in the 5–9 range, so in this study, the pH variation was chosen from very acidic to very basic, so the pH of the RR test solution used was from 3–9.

The electrostatic interaction occurs between the coagulant PS and OFI because surface biomaterials have a positive charge that can attract anions. On the other hand, the surface of RR has a negative charge, causing it to attract cations. The pH test solution is changed to an acid base with a pH variation of 3–9 to determine the optimum pH. The initial pH of the RR test solution was pH 5, and after adding natural biomaterials such as PS coagulant and OFI flocculant, the pH of the test solution remained at pH five even after varying the test solution to pH 3–9. The optimum pH obtained was 4 (Fig. 3(c)), and the removal of RR dye was around 96.70%. The absorption of dyes at pH 3 is lower than at pH 4, which means that pH also influences the azo dye removal process. The variation decreases as it reaches a maximum, as shown in Table 3. The decrease in pH 3 is because PS, as a coagulant, is not too affected by changes in environmental pH [17]. At pH 4, the silica species in PS is H_2SiO_3, which releases positively charged H^+ ions. At an alkaline pH, the silica species formed are SiO_3^{2-} and $HSiO_3^-$ [27]. RR can be attracted to the coagulant in an acidic pH because the H^+ ions released by the PS coagulant have a different charge from the sulfonate group on RR.

Illustrations of Coagulation and Flocculation

The PS coagulant works through two mechanisms: charge neutralization and particle bridging via electrostatic interactions. Fig. 4 illustrates how the PS coagulant interacts with the sulfonate groups of RR. The coagulation process of RR dye occurs due to colloidal destabilization. The colloidal destabilization process

Table 3. Variations in the pH of the test solution in the removal of RR

Coagulant dosage (g)	Flocculant dosage (g)	Coagulation speed (rpm)	Initial pH	%Removal
2.75	2.00	500	3	91.62
2.75	2.00	500	4	96.70
2.75	2.00	500	5	95.40
2.75	2.00	500	6	90.06
2.75	2.00	500	7	84.53
2.75	2.00	500	8	81.59
2.75	2.00	500	9	74.36

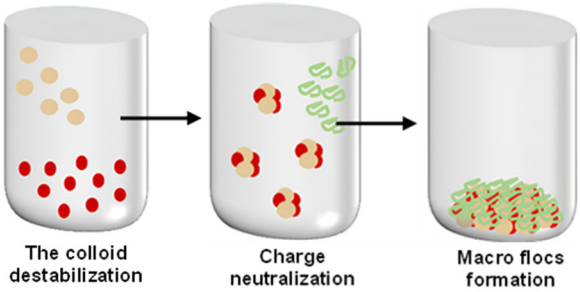

Fig 4. Illustration of coagulant-flocculant interaction with RR

begins with the charge difference between the sulfonate (SO_3^-) group in RR dye and PS, which releases positively charged H^+ ions. This charge difference causes charge neutralization, allowing the particles to bond. As a result, the micro flocs combine to form larger clumps of macro flocs [28]. The OFI flocculant mucilage contains polysaccharides as its main component. The primary and side chain groups of OFI polysaccharides form bridges in the polysaccharide-particle complex. Hydrophilic groups in polysaccharides, such as OH and COOH, form hydrogen bonds with neutral particles, facilitating flocculation. Polysaccharides act as binders, connecting colloidal particles into larger aggregates. The large flocs formed become heavier, allowing them to settle more quickly or be filtered [13,29].

FTIR Characterization

Coagulant-flocculant biomaterials

The results of the FTIR spectra characterization of the two biomaterials can be seen in Fig. 5. The characterization of the natural coagulant PS produces a peak at a wave number 1603 cm^{-1}, indicating the presence of an O–H group from the silanol group. Wavenumber of 1004 cm^{-1}, and there are the Si–O–Si group vibrations, which indicate the formation of a silica network [30-32]. The Si functional group in the application of SiO_2 functions as a natural coagulant because it has a porous shape, which is related to the surface area so that the greater the surface area of a material containing Si, the more capable it is of absorbing and act as a suitable coagulant in liquid waste removal [19,33].

In the natural flocculant OFI characterization, a peak at a wavenumber of 3500–3000 cm^{-1} indicates the presence of O–H bonds from the water solvent. At a wavenumber of 1620 cm^{-1}, it shows that there is asymmetric stretching of the C=O double bond in the carboxylate group. Wavenumber 1200–950 cm^{-1} shows the characteristics of polysaccharide bands and the presence of C–O bonds from alcohols and ether [23,31-32]. Polysaccharides were detected at the 1033 cm^{-1} band, indicating the presence of flocculant agents such as proteins and polysaccharides. This is attributed to the vibration of C–O–C and O–H bonds in polysaccharides [34]. These functional groups show the characteristics of bio coagulants/bio flocculants such as polysaccharides, proteins, carbonyl, carboxyl, hydroxyl, and amine groups, which can bridge the charge neutralization process in dye removal [15,35].

Coagulant-flocculant optimization results

The coagulants and flocculants produced under optimum conditions were characterized using FTIR spectrophotometry. The FTIR spectrum obtained was compared with the FTIR spectrum of the RR dye test solution. This is intended to ensure that the RR dye removal process has occurred. The coagulants and flocculants produced under optimal conditions were dried, and FTIR was characterized in the wavenumber range of 3500–500 cm^{-1}.

Fig. 6 shows the absorption at wavenumber 2093 cm^{-1} in the RR test solution under optimal conditions. The absorption shift occurred in the C=O and C–O groups, from wave numbers 1620 and 1200–950 cm^{-1}

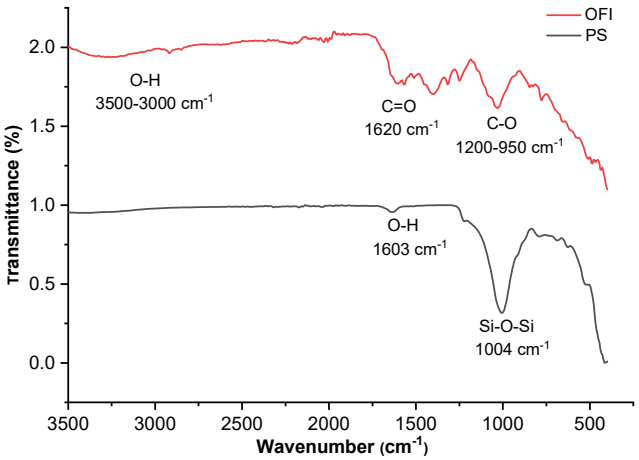

Fig 5. FTIR Spectra of PS and OFI

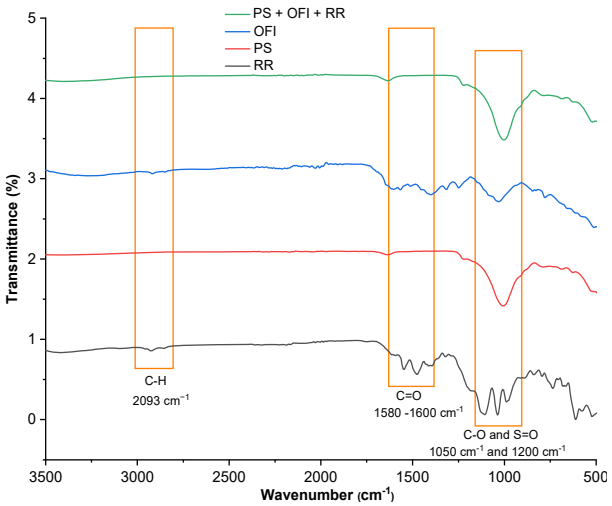

Fig 6. FTIR spectra of RR, PS, OFI, and (RR + PS + OFI) after coagulation-flocculation

to 1580–1600 and 1050 cm^{-1}. The absorption of the Si group was seen at wave number 1004 cm^{-1} in PS. After the coagulation-flocculation process in PS + OFI + RR, the absorption of the Si group was still detected. Absorption at wave number 1200 cm^{-1} occurred in the S=O deformation of sulfonic acid and sulfite. The characterization results of PS + OFI + RR after the coagulation-flocculation process showed that the sulfonate group was no longer present. Therefore, the removal of RR dye was successful [35-36].

The result of coagulant and flocculant characterization shows the results of FTIR characterization on PS before coagulation-flocculation showed there are the Si–O–Si group vibrations, while on OFI, the presence of O–H bonds from hydroxyl groups. There is asymmetric stretching of the C=O double bond in the carboxylate group, and C–O bonds from alcohols and ether are present. After coagulation-flocculation on PS + OFI + RR, the absorption of the Si group is still detected, a shift in absorption in the C=O and C–O groups, and the sulfonate group, which was initially detected in RR, but after coagulation-flocculation shows that the sulfonate group is no longer present. Thus, the removal of the RR dye was successful.

XRD Characterization

Coagulant-flocculant biomaterials

PS and OFI powders were crystallographically characterized using an XRD instrument. Characterization using XRD was carried out on biomaterials before the coagulation-flocculation process. The characterization results using XRD (Fig. 7) of the PS coagulant show a peak at 2θ of 26°, indicating the presence of amorphous SiO_2 and other phases appearing at different peaks. Similar to previous research, the peak at 2θ of 22° indicates the presence of SiO_2 [37], and the range of 26.34°–26.54° also indicates the presence of SiO_2 contained in PS [38]. Flocculant OFI shows visible peaks at 15° and 25°; at these angles, the crystal structure of OFI is complex and heterogeneous, making it suitable for the use as a flocculant. The components found in OFI include lipids, cellulose, proteins, and polysaccharides. Based on previous research, the cactus peaks at 15°, and its crystal structure is also complex and heterogeneous [34].

Coagulant-flocculant optimization results

The crystalline structure of the RR test solution and the precipitate produced from the coagulation and flocculation process was described through XRD analysis.

Fig. 8 of the RR test solution with the XRD pattern shows prominent peaks at 2θ around 30° and 40°, which may be related to the characteristic phases of the original dye solution. In contrast, the biocoagulant in the form of the PS + OFI + RR precipitate shows additional peaks or changes in peak intensity, indicating that new crystalline phases have altered due to the coagulation and flocculation process, with silica still present at 2θ of 26° degrees [36,39].

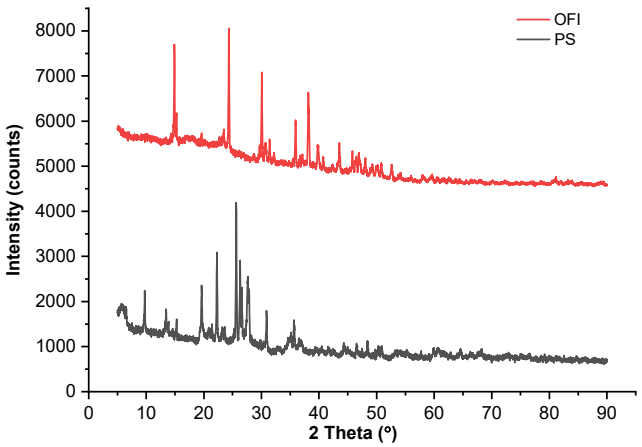

Fig 7. XRD of PS and OFI

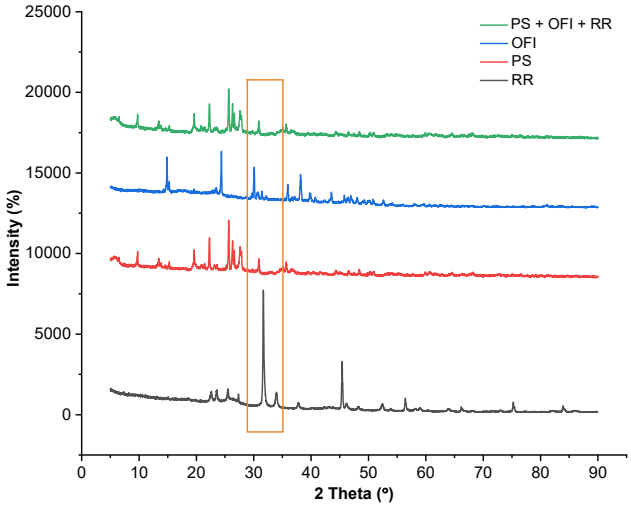

Fig 8. XRD pattern of RR, PS, OFI, and RR + PS + OFI after coagulation-flocculation

SEM Characterization

Coagulant-flocculant biomaterials

Further insight into the powder properties of PS and OFI was gained through the use of SEM. These techniques established the morphology of the material. Based on Fig. 9(a), the SEM characterization of PS at observation scales of 30 and 5 μm shows a rough and porous surface. The presence of pores was related to its function as a coagulant in dye removal. The PS in the SEM results has an irregular and abundant shape [40]. Fig. 9(b) observation scales 30 and 5 μm show the SEM characterization of OFI, indicating its heterogeneous and porous structure. The complex and irregular cactus contains fibrous tissue that functions to remove dyes from water and can even bridge dyes in water. The porous structure creates a broader contact surface between OFI and contaminants [41-42].

Coagulant-flocculant optimization results

Based on Fig. 10, the SEM characterization results show that RR has a microstructure, its shape resembling a cube, and is arranged in an orderly manner. At 30 μm magnification, it appears as small grains forming a cluster, but at 5 μm magnification, the particles are widely dispersed with a regular cubic shape. RR particles appear to have space between one particle and another because RR is an anionic compound, causing the particles to repel each other.

The characterization results of PS + OFI + RR after coagulation show the presence of small aggregates that may result from the electrostatic interaction between RR with the coagulant PS and the flocculant OFI. After the coagulation process, the shape of RR, which initially appeared as a cube and regular, now looks irregular. The irregular form of RR indicates that RR has already been

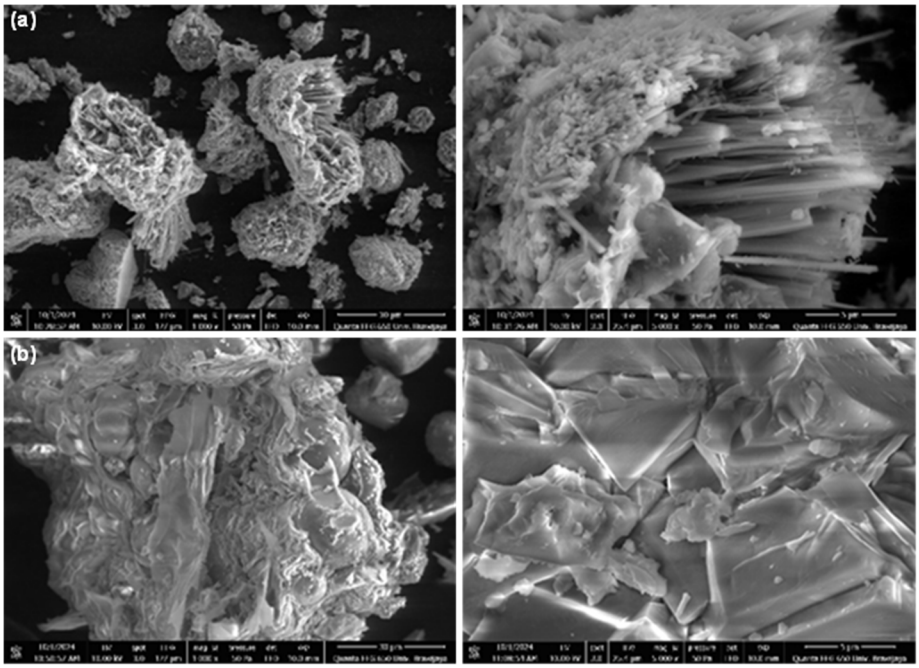

Fig 9. SEM images scale 30 and 5 μm of (a) PS and (b) OFI

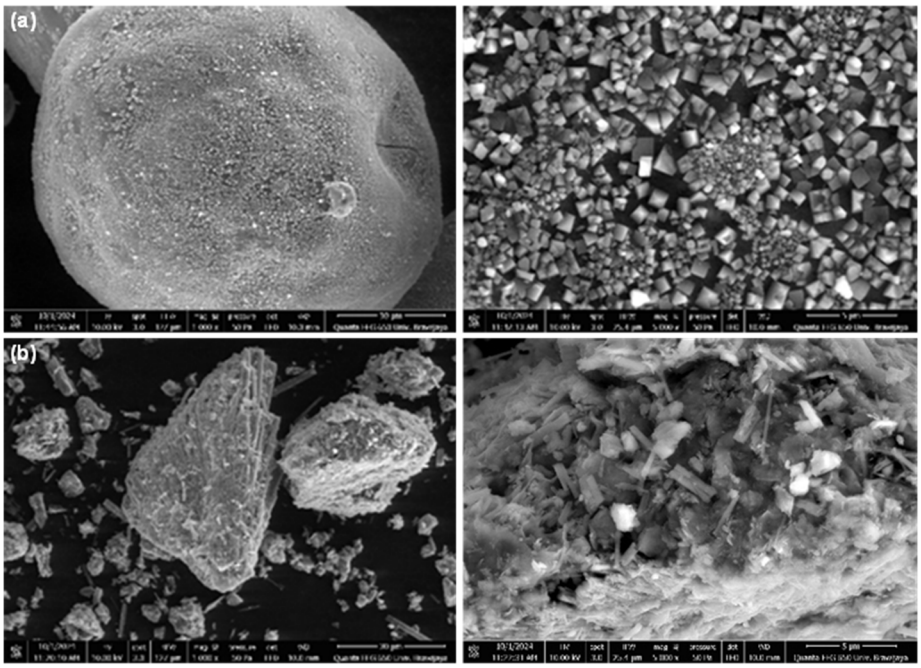

Fig 10. SEM images scale 30 and 5 μm of (a) RR and (b) PS + OFI + RR after coagulation-flocculation

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

Source of dye wastes	Coagulant	Flocculant	Optimum condition	%Removal	Ref
Methylene blue (MB)	Bentonite (B)	OFI	B 0.9 g; OFI 0.4 g, 180 rpm, 4 min, pH 7	98.99	[9]
Industrial textile	*Abelmoschus esculentus*	-	88.0 mg; 120 rpm, 30 min, pH 6	93.57	[14]
Rhodamine B (RB), malachite green (MG), MB, and Basic Violet 14 (BV)	B	Sodium Alginate (SA)	B 160 mg; SA 4 mg (RB and BV), B 160 mg; SA 160 mg (MB and MG), 300 rpm, 1 min, pH 9	91.50, 98.20, 98.50, 98.80	[15]
Methyl red (MR) and crystal violet (CV)	Polyaluminium chloride (PACl)	Bentonite Clay (BC)	PACl 25 mg; BC 600 mg (MR), PACl 75 mg; BC 800 mg (CV), 160 rpm, 1 min, pH 5 (MR); pH 12 (CV)	98.00, 99.00	[16]
Batik industry	Alum	-	1.5 g; 100 rpm 4 h, pH 8	88.40	[17]
Oil sands	OFI	-	1500 mg; 250 rpm, 1 min, pH 7	98.00	[23]
RR	PS	OFI	PS 2.75 g; OFI 2 g, 500 rpm, 4 min, pH 4	96.70	This study

bound to the coagulant and flocculant. RR also appears to be dispersed among larger structures, namely the structures of PS and OFI, indicating that the coagulation and flocculation processes have occurred because the coagulant and flocculant bind the particles of RR dye [43-44]. There are several inorganic elements in OFI, namely Na, Mg, K, and Ca. These inorganic elements help in the separation of RR dye [23].

Comparison with Previous Studies

Table 4 summarizes the results of previous studies on removing azo-type dye waste using the coagulation-flocculation method. RR is a type of azo dye containing an azo group. The summary of research results associated with the coagulation-flocculation method shows that the process generally achieves good results; namely, the average removal of dyes reaches more than

90%. The latest literature search summarizes research that several researchers have carried out, such as removing RR using PS coagulant and OFI flocculant, which have never been studied before. Therefore, this research continues regarding the capabilities of PS and OFI biomaterials using the coagulation-flocculation method to treat RR. Other authors report information about optimum conditions, which are linear in this research. It is recommended that this research be developed on various types of dyes and other natural potentials to be used as coagulants because more research is still needed on removing azo dyes.

■ CONCLUSION

The findings of the study indicate that natural coagulants can effectively replace synthetic ones. The electrostatic interaction occurs between the coagulant PS and OFI because surface biomaterials have a positive charge that can attract anions. On the other hand, the surface of RR has a negative charge, causing it to attract cations. The flocculation-coagulation process achieved a 96.70% removal rate of RR dye when using a PS coagulant at a dose of 2.75 g alongside a flocculant dose of 2.00 g from OFI, an optimal stirring speed of 500 rpm, and an initial solution pH of 4. Characterization results for the natural coagulants and flocculants indicate that the FTIR analysis of PS displays vibrations of the Si–O–Si group, while the OFI shows O–H bonds from hydroxyl groups, asymmetric stretching in the C=O bonds of the carboxylic group, and the presence of C–O bonds from both alcohol and ether. The XRD characterization of PS presents a peak at $2\theta = 26°$, whereas OFI displays peaks at $2\theta = 15°$ and 25°. The SEM characterization illustrates small aggregates, showing that the originally cuboidal and regular shape of RR has become irregular.

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■ CONFLICT OF INTEREST

The authors confirm that there are no known financial interests or personal relationships that may have influenced the findings presented in this paper.

■ AUTHOR CONTRIBUTIONS

Siti Hulwati and Vita Dwi Anggraini conducted the experiments, processed data, and wrote the manuscript. Qonitah Fardiyah supervised the experiments, analyzed data, and revised the manuscript. Barlah Rumhayati analyzed the data and provided advice on this research. All authors read and approved of the final manuscript.

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