# The Potential of Hybrid Polymer in Treating Textile Wastewater: Optimization of pH and Dosage Using Response Surface Methodology


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**Abstract.** The study aimed to evaluate the effectiveness of hybrid polymer ZOPAT compared to single polymers in treating textile wastewater. The research analyzed reduction of color, chemical oxygen demand (COD), turbidity, and suspended solids using jar testing. Response Surface Methodology (RSM) was employed to optimize the treatment, analyze variance, and create pertur-bation and desirability plots for multiple responses. The storage conditions of the hybrid polymer were also investigated. The results showed that ZOPAT was highly effective in reducing color, with a 93% reduction compared to other treatments. Additionally, turbidity and suspended solids were reduced by 100%, and COD was reduced by up to 80%. The RSM multi-response outcome showed a desirability plot of 0.592. The hybrid polymer required only 17.5 min for coagulation treatment, while the other treatments re-quired more than 40 min to achieve maximum effectiveness. The validation test showed that the optimization model's error rate was less than 1%. The study recommended that hybrid polymer solutions be stored in a cold room for up to 20 days to maintain consistency. The findings suggest that hybrid polymer is a highly effective coagulant for treating textile wastewater, with significant reductions in color, turbidity, and suspended solids. The use of RSM allowed for the optimization of the treatment, and the storage conditions were determined to ensure consistent results over time. Overall, the study's results have significant implications for the water treatment industry, with potential applications in treating wastewater in other industries.



**Keywords:** Hybrid polymer · Response Surface Methodology · Perturbation plot · Desirability plot · Storage conditions





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## 1 Introduction

Malaysia's textile and apparel industry is ranked eleventh in the country's manufacturing sector, with 84.1 million meters of cotton cloth exported in 2020 [1]. However, after the textile treatment process, the discharge is typically released into nearby rivers. This issue has been reported extensively in China and India, with textile contamination causing significant problems in rivers [2]. The concentration of textile effluent ranges from 10 to 250 mg/L [3], depending on the dye types, with the highest concentration reaching up to 7,000 mg/L in the reactive dye industry [4]. It is estimated that the production of 1kg of textile material requires 200 L of water [5], and studies indicate that approximately half of the dyes used in the textile industry end up as discharge wastewater containing organic and inorganic chemicals, dyestuffs, bleaching agents, finishing chemicals, starch, thickening agents, surface-active chemicals, wetting and dispersing agents, as well as metal salts [6]. This discharge contributes to high levels of pH, COD, BOD, color, suspended solids, turbidity, heavy metals, and other contaminants. As a result, it is crucial for wastewater treatment plants in every industry to be effective and systematic in their approach.

Currently, coagulation and flocculation are employed in primary treatment to separate gritty materials and suspended solids, and pH is an important factor that influences the effectiveness of coagulation. Typically, metal salts are used for coagulation, along with coagulant aids, which create larger flocs during slow mixing. The destabilization of charged particles allows flocs to form and settle during sedimentation. Inorganic, organic, and modified coagulants are commonly used today, but the effectiveness of inorganic coagulants is limited to a small pH range, typically between 5.5 and 7.5. To address this limitation, a hybrid coagulant has been developed that is effective over a wider pH range. In a study conducted by [7], a hybrid coagulant made of polyacrylamide and polymeric aluminum ferric chloride was found to be effective for the removal of Congo Red over a pH range of 6 to 9, and for the removal of Fast Turquoise Blue GL over a pH range of 4 to 7, with more than 90% removal achieved. The hybrid coagulant showed a high capability for adsorption bridging. Since pH is a critical factor in the coagulation process [8], it is important to determine the optimum conditions for coagulation, and the Response Surface Methodology is a useful analytical tool for achieving this.

Hybrid or modified coagulants have gained popularity in recent times due to their ability to enhance the efficiency of the coagulation and flocculation process. This is achieved by generating a high capacity of hydroxyl ions for charge neutralisation, as reported in literature [7]. The effectiveness of modified coagulants has been demonstrated in studies where they were able to reduce almost 90% of dye color [9] and more than 70% of organic compounds [8]. These coagulants can be composed of various combinations such as inorganic-inorganic, inorganic-organic, inorganic-natural, organic-organic, organic-natural and natural-natural polymers. Previous studies have explored the use of hybrid coagulants with zinc and various inorganic or organic polymers in the coagulation process [10–12].

The use of Zinc Oxide as a coagulant for pharmaceutical wastewater has been proven effective in reducing COD from 19,850 mg/L to 500 mg/L [13]. By modifying ZnO with an organic polymer such as polyacrylamide, longer chains can be produced, resulting in an abundance of binding sites. This modified ZnO has a broad pH range and high adsorption bridging capabilities [7]. Zhu et al. [11] discovered that blending polyacrylamide with iron and zinc as a coagulant base resulted in a higher floc growth rate (119.82 μm/min) and recovery factor (26.96) than non-hybrid versions. This hybrid also had a more significant effect on turbidity and dissolved organic nitrogen removal compared to non-hybrid versions such as polymeric Al-Zn-Fe and Polyaluminium chloride [9].

In this study, the various impacts of color, COD, turbidity, and suspended solids were examined using single polymers (zinc oxide, zinc oxide + acrylamide, acrylamide, tannin, and polyaluminium chloride (PACl)), as well as a hybrid polymer composed of zinc oxide, acrylamide, and tannin. The Response Surface Methodology - Central Hybrid Design (RSM-CCD) was employed to analyze the perturbation plot at the optimized pH and ZOPAT dose, as well as the impact of multiple responses on the desirability plot. Additionally, the effects of storage conditions at both cold room temperature (4–6°C) and room temperature (30°C) were studied, with a duration of up to 60 days.

## 2 Experiments

The method involved using zinc chloride ($ZnCl_2$), acetic acid ($CH_3COOH$), sulfuric acid ($H_2SO_4$), sodium hydroxide (NaOH), glycerol ($C_3H_8O_3$), and ethanol ($C_2H_5OH$) obtained from Qrec without any purification to synthesize zinc oxide. Tannin with a molecular weight of 1701.18 g/mol was procured from Shaanxi Kanglai Ecology Agriculture Co., Ltd. Cationic polyacrylamide with a molecular weight of 1 million g/mol was purchased from R&M chemicals. The raw textile wastewater was collected six times from textile industries in 2018, with an average pH of 11.25, turbidity of 150.58 NTU, COD of 2250 mg/L, color of 1724 Pt/Co, and suspended solids of 172.58 mg/L.

A homogeneous solution was created by blending zinc oxide, polyacrylamide, and tannin in different weight ratios (1:1:1) using 2% w/w. Glycerol was used as a stabilizer, and its effectiveness was confirmed in a previous study [14]. To reduce turbidity, color, COD, and suspended solids, one-factor-at-a-time experimentation was conducted. To achieve the highest removal efficiency, various ratios of ZnO, polyacrylamide, and tannin were tested to determine a suitable proportion of these ingredients. The best pH and ZOPAT dosage were also investigated.

In this study, a standard jar-test apparatus (Velp Scientifica JLT 6) equipped with six stainless steel paddles and a stirrer was used as the experimental setup. The reactor was a 1000 mL glass beaker with a sample volume of 500 mL. The maximum allowable addition of ZOPAT was 10 mL from a stock solution of 20,000 mg/L. The pH adjustment was made using NaOH or $H_2SO_4$, with a maximum addition of 30 mL for each beaker, which was less than 10% of the total 500 mL of textile wastewater. The preliminary test was used to determine the optimal range for pH, dosage, speed of rapid mixing, duration of rapid mixing, speed of slow mixing, duration of slow mixing, and sedimentation time.

Following the previous method [15], the impact of storage conditions was evaluated for a 60-day period. ZOPAT samples were subjected to two different conditions: room temperature (30 °C) and cold storage (4–6 °C). The percentage reduction of color and COD was monitored and graphed over the course of the experiment to observe any differences between the two storage conditions.

## 3 Results and Discussion

### 3.1 A Comparative Analysis of Coagulation Studies Utilizing Different Polymers

Various polymers, including ZnO, ZnO + PAM, PAM, ZOPAT, and Tannin, were employed to treat wastewater to reduce turbidity, color, COD, and SS. Table 1 presents the parameters used for each polymer in the coagulation treatment based on the results obtained in the preliminary study. The residual values, measured in mg/L (except for turbidity and color, which were measured in NTU and Pt/Co, respectively), were used to report the results. As shown in Fig. 1, the hybrid polymer ZOPAT demonstrated strong performance in reducing turbidity, color, and suspended solids in textile wastewater. The study also showed that the hybrid polymer is effective over a wide range of pH [7]. Previous studies have reported that hybrid polymers can lengthen polymer chains and provide additional binding sites with various functional groups, which may contribute to their effectiveness [8].

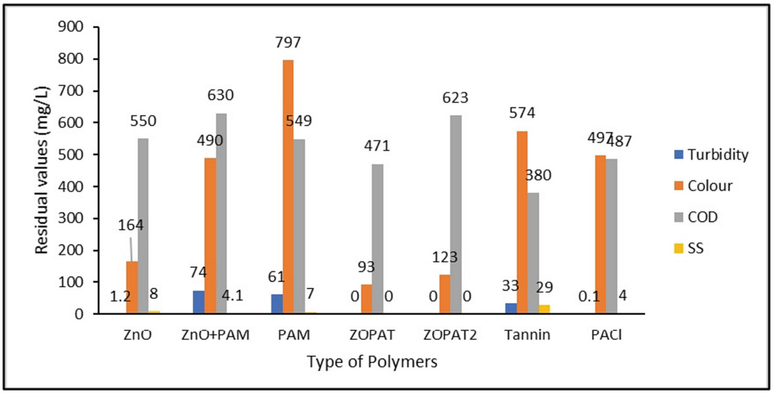


**Fig. 1.** The residual value of turbidity, colour, COD and SS for different type polymer.

ZOPAT demonstrated excellent performance in decolorizing wastewater, with residual color of less than 100 Pt/Co observed across a wide pH range (from pH 4 to pH 10). The broad pH range treatment provides significant benefits for treating various types of wastewater, and the low cost of pH adjustment prior to treatment is advantageous [16]. The reduction of color was consistently higher than the reduction of COD due to the formation of complex coagulants. Even if the wastewater is colorless after treatment, the combined complex with the surface of the dye molecule may reduce the color point but not the COD. Previous studies have reported that the reduction of color is faster than the oxidation of organic compounds (COD) [17]. At pH 8 and 800 mg/L of ZOPAT, the reduction rate of color was 94%, while the oxidation of COD was only 79%. Thus, it can be concluded that the rate of COD reduction is lower than that of color, even under the same treatment conditions.

In contrast, tannin at a dose of 400 mg/L resulted in the best residual COD concentration, achieving a value of 380 mg/L, although it did not show the best performance in reducing turbidity, colour, and suspended solids. However, a previous study [18] reported achieving a water quality of less than 10 NTU using 3000 mg/L tannin obtained from Acacia catechu. In this study, the reduction of colour was observed up to 574 Pt/Co at a minimal concentration of less than 400 mg/L. However, exceeding the limit of tannin concentration can lead to re-stabilisation, resulting in high colour content in the wastewater. It is generally observed that increasing the amount of coagulant improves efficiency before reaching a point of overdosing [19]. Furthermore, the bridging site must not be limited by the adsorbed amount.

A complete removal of suspended solids was achieved at a concentration of 200 mg/L and 800 mg/L of PAM and ZOPAT, respectively, while ZnO required a concentration of 1200 mg/L to achieve a concentration of 1 mg/L of suspended solids. However, ZnO showed better removal of colour, achieving a reduction of up to 90%, but requiring a dosage of more than 1000 mg/L. When PAM was added alone, a worse reduction of colour was observed. However, when added in combination with ZnO as the primary coagulant, the colour degradation showed better performance. This indicates that PAM requires a metal coagulant to achieve an efficient coagulation-flocculation process. Regarding turbidity reduction, ZOPAT, PACl, and ZnO achieved almost 100% efficiency, while PAM, ZnO + PAM, and Tannin showed the worst reduction. Tannin required pH 2 to perform at its best. Generally, natural organic polymers have optimum pH conditions in the acidic range [20]. If strong alkaline is applied, it may cause another problem such as high colour content in the water, which is not favourable for textile wastewater, as it usually releases raw effluent at alkaline pH [5].

The effectiveness of PACl in reducing colour in textile wastewater was found to be less favourable compared to COD reduction. Even with the application of 200 mg/L PACl, the residual colour in the wastewater was still high at 900 Pt/Co, and up to 4000 mg/L PACl was required to achieve a reduction to 300 Pt/Co. However, a study involving the use of 300 mg/L of PACl under the influence of temperature reported positive results [21]. This indicates that PACl alone may not be suitable for treating textile wastewater due to the high colour residue. In contrast, the COD reduction achieved with 200 mg/L of PACl was near 500 mg/L. Nonetheless, a previous study reported that 100 mg/L of PACl as a flocculant could reduce COD to 700 mg/L [22]. Therefore,

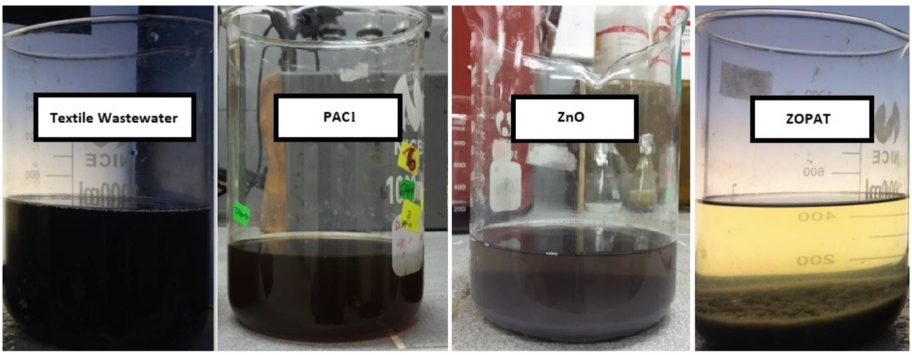


**Fig. 2.** The coagulation process after the treatment using ZOPAT, PACl and ZnO at optimum condition.

PACl needs to be used in combination with other polymers to achieve better coagulation results. Figure 2 provides a comparison of the sedimentation phase between ZOPAT, PACl, ZnO, and raw textile wastewater.

### 3.2 Optimization of Using RSM-CCD

In this section, a study on optimization using RSM-CCD was conducted with a rotatable design to reduce prediction errors and provide constant prediction variance at all points. The pH and dose ranges were selected based on the highest reduction observed in the preliminary jar test condition. The pH range was narrowed down to pH 8 for the lower limit and pH 10 for the upper limit, while the ZOPAT dosage range was set at 600 mg/L for the lower limit and 1000 mg/L for the upper limit. The speed and duration of rapid mixing, slow mixing, and sedimentation time were kept constant at the best reduction as observed in Table 1. The results showed almost 100% removal of turbidity and suspended solids, but only 93% and 78% reduction in colour and COD, respectively. ANOVA was then used to calculate the results obtained from the CCD experimental design, which are tabulated in Table 2. Further analysis, such as ANOVA, 3D plot surface, and validation for optimization, will be discussed in detail.

**Table 1.** Set of optimum parameters for each polymer applied in the jar testing.

| Parameters | ZnO | ZnO + PAM | PAM | Tannin | PACl | ZOPAT |
|---|---|---|---|---|---|---|
| pH | 12.0 | 12.0 | 2.0 | 12.0 | 8.0 | 7.2 |
| Dose (mg/L) | 1000 | 1000 | 400 | 400 | 800 | 800 |
| Speed of rapid mixing | 280 | 280 | 200 | 200 | 200 | 280 |
| Time of rapid mixing | 2.5 | 2.5 | 2 | 2 | 3 | 2.5 |
| Speed of slow mixing | 50 | 50 | 75 | 75 | 50 | 50 |
| Time of slow mixing | 5 | 5 | 15 | 15 | 15 | 5 |
| Sedimentation time | 30 | 30 | 30 | 30 | 30 | 10 |

### 3.3 Analysis of Variance (ANOVA)

The results in Table 2 present the P-values for four different responses, namely (a) turbidity, (b) colour, (c) COD, and (d) suspended solids, with two variables, pH and ZOPAT dose. The quadratic model was found to be statistically significant based on the P-value of less than 0.05 and the coefficient of determination (r2) of 0.95. The significance of the model equation was confirmed by the 95% confidence interval ($P < 0.05$), indicating the effects of quadratic and interaction terms on the predicted responses. The r2 value represents the proportion of variability in the response data that is explained by the fitted regression line, with values close to 1 indicating a good fit. The r2 values for the reduction percentages of turbidity, colour, COD, and suspended solids using

**Table 2.** The P-value of factors and responses included in RSM-CCD. *A: pH, B: ZOPAT dose.

| | Source | Sum of Squares | Mean Square | F Value | Prob > F | R- squared |
|---|---|---|---|---|---|---|
| Colour | Model | 258.73 | 51.75 | 26.68 | 0.00 | 0.95 |
| | A | 10.12 | 10.12 | 5.22 | 0.05 | |
| | B | 41.92 | 41.92 | 21.62 | 0.00 | |
| | A2 | 11.98 | 11.98 | 6.18 | 0.04 | |
| | B2 | 161.11 | 161.11 | 83.07 | 0.00 | |
| | AB | 42.25 | 42.25 | 21.78 | 0.00 | |
| COD | Model | 66.25 | 13.25 | 22.88 | 0.00 | 0.94 |
| | A | 4.25 | 4.25 | 7.33 | 0.03 | |
| | B | 1.12 | 1.12 | 1.94 | 0.21 | |
| | A2 | 23.49 | 23.49 | 40.56 | 0.00 | |
| | B2 | 38.01 | 38.01 | 65.64 | 0.00 | |
| | AB | 6.25 | 6.25 | 10.79 | 0.13 | |
| Turbidity | Model | 211.70 | 42.34 | 22.42 | 0.00 | 0.94 |
| | A | 8.00 | 8.00 | 4.24 | 0.08 | |
| | B | 115.40 | 115.40 | 61.10 | 0.00 | |
| | A2 | 0.03 | 0.03 | 0.01 | 0.91 | |
| | B2 | 70.68 | 70.68 | 37.42 | 0.00 | |
| | AB | 16.00 | 16.00 | 8.47 | 0.02 | |
| SS | Model | 230.40 | 46.08 | 13.49 | 0.00 | 0.96 |
| | A | 21.92 | 21.92 | 6.42 | 0.04 | |
| | B | 134.47 | 134.47 | 39.37 | 0.00 | |
| | A2 | 0.35 | 0.35 | 0.10 | 0.76 | |
| | B2 | 61.57 | 61.57 | 18.03 | 0.00 | |
| | AB | 12.25 | 12.25 | 3.59 | 0.10 | |

ZOPAT were 0.94, 0.95, 0.94, and 0.91, respectively, suggesting that more than 90% of the total variation was explained by the empirical models, with less than 10% remaining unexplained. Overall, the coefficient of determination values was satisfactory, as r2 values close to 1 were obtained.

The significance of the factors on the response was determined by P-values, where lower values indicated a greater impact of the factors [23]. In this study, all responses showed a fitted model with $P < 0.05$, except for the ZOPAT dose, which was insignificant only in relation to COD, indicating that COD was not affected by varying amounts of ZOPAT. Similarly, the effects of pH on turbidity and colour were not significant with P-values greater than 0.05, indicating that these responses were not influenced by changes in pH. However, the interaction between pH and ZOPAT dose was found to be significant for all responses except suspended solids, with $P < 0.05$.

The purpose of plotting Fig. 3 was to examine the impact of different conditions on the percentage reduction. It was observed that sets 4 and 9 performed poorly due to a higher dosage of ZOPAT, which caused an overdose reaction resulting in re-dispersion of particles and a positive charge. This is supported by a significant P value of coagulant dose in Table 2. On the other hand, set 2 with a pH of 9 and 800 mg/L of ZOPAT showed excellent performance, achieving the highest reduction for all associated responses. Although COD had the lowest removal rate of approximately 80%, turbidity and suspended solids were effectively removed from the wastewater.

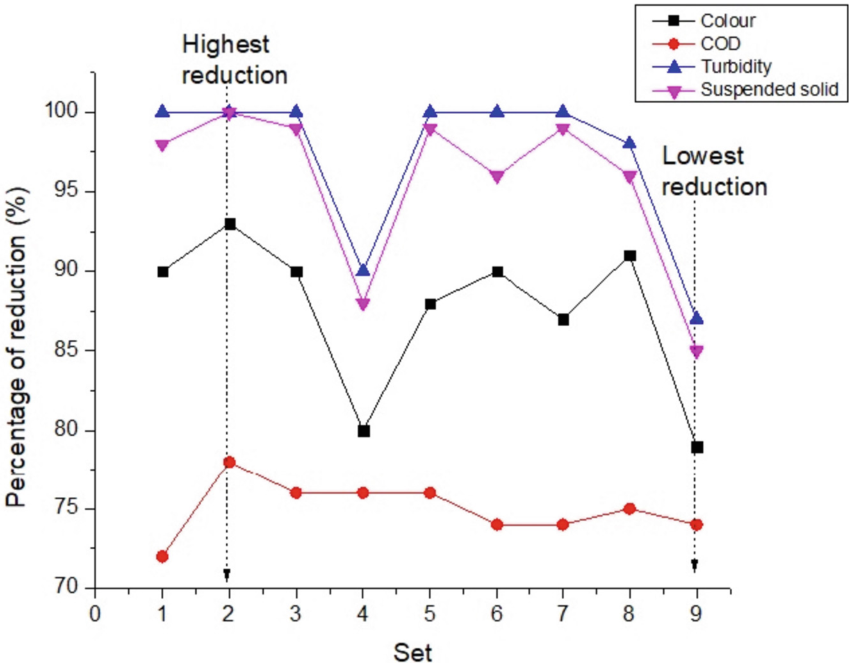


**Fig. 3.** Nine sets of different pH and polymer dose of ZOPAT were plotted to see the percentage of reduction for turbidity, colour, COD and suspended solids.

Previous research has demonstrated that the removal of suspended solids is influenced by gravity. The addition of chemicals can attract charges on the surface of colloidal particles, causing them to clump together and settle due to the effects of gravity [24]. Set 2 managed to achieve a color reduction of up to 94%. This is because the blended ZnO, PAM, and tannin generated reactive functional groups such as carboxyl, hydroxyl, and amide groups that can attack dye compounds. For instance, the reaction between the hydroxyl group (OH-) and sodium (Na +) forms sodium hydroxide compound. When a negatively charged ion forms a bond with a positively charged ion, and one atom transfers electrons to another, an ionic bond is formed. This destabilizes the colloidal particles, neutralizes the electrostatic charges on the dye particles, facilitates agglomeration, and results in separation from the aqueous phase.

The best result obtained was an 80% reduction in COD, which could be due to the strong oxidizing behavior of the process, which causes a reduction in pH, resulting in a more transparent solution and compact sludge. On the other hand, the worst conditions were observed in sets 4 and 9, where a higher dose of ZOPAT ($>$1000 mg/L) resulted in lower efficiency for all responses. The increase in COD is mainly attributed to the redispersion of solids containing inorganic material [25]. This can occur because the amount of metal ions used can destabilize negatively charged colloids, leading to their adsorption onto the solid. Additionally, the use of Ethylenediaminetetraacetic acid (EDTA) or Diethylenetriamine pentaacetic acid (DTPA) in the bleaching process can also disrupt the metallic ions, resulting in lower COD reduction [26]. Moreover, the presence of substantial chemicals and auxiliaries in textile wastewater can make it challenging to remove [27].

### 3.4 Perturbation Plot of pH and Dose of ZOPAT

Figure 4, which is a perturbation plot, shows the effect of A (pH2) and B (the dose of ZOPAT2) on the reduction percentage of turbidity, color, COD, and SS. The sharp curvature observed in the plot indicates that the pH and the dose of ZOPAT are highly sensitive towards the reduction of color and COD. It can be observed from the plot that increasing the dose of coagulant leads to an increase in the percentage reduction for all parameters. However, overdosing with more than 1000 mg/L causes a certain degree of charge reversal of the particles, which reduces the effectiveness of the treatment [8]. The effect of overdosing results in the re-stabilization of dye particles and increased sludge formation due to the high amount of added chemicals [28].

In addition, Fig. 4 shows a straight line for A, which represents pH2, in relation to (c) turbidity and (d) suspended solid. This suggests that both lines are less sensitive when compared to the others. The perturbation plot also reveals that the p-value for pH2 for turbidity and suspended solid was 0.91 and 0.76, respectively. These values indicate that both variables have insignificant p-values $> 0.05$. The flat surface of pH on the plot indicates less sensitivity towards the pH environment between pH 8 and pH 10. This finding is consistent with a previous study that rejected the correlation between pH and turbidity of wastewater samples in India, as the correlation coefficient was only 0.11 [29]. This supports the idea that both studies involved real wastewater from the textile industry, which can influence the correlation between pH and turbidity.

The purpose of Fig. 5 is desirability ramp is to optimize multiple responses concurrently. The desirability range for a given response ranges from zero to one, indicating how close the response is to its ideal value.

As shown in Fig. 6, the desirability ramp resulted in a desirability value of 0.592. A value of one indicates a significant P-value for all parameters, whereas a value near zero indicates that one or more responses fall outside the desirability range. The low desirability value suggests that suspended solids were responsible for the reduced performance. According to the p-value, suspended solids were not significant for the interaction between pH and ZOPAT dose. Therefore, higher suspended solid removal can be

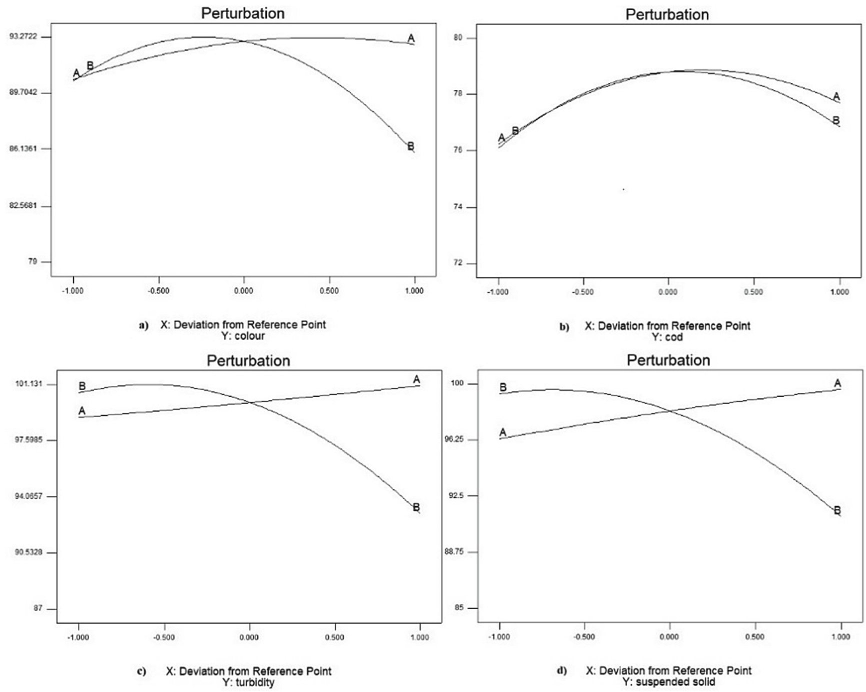


**Fig. 4.** Perturbation plot for each reduction such as a) colour, b) COD, c) turbidity and d) suspended solid at different pH2(A) and dose2(B).

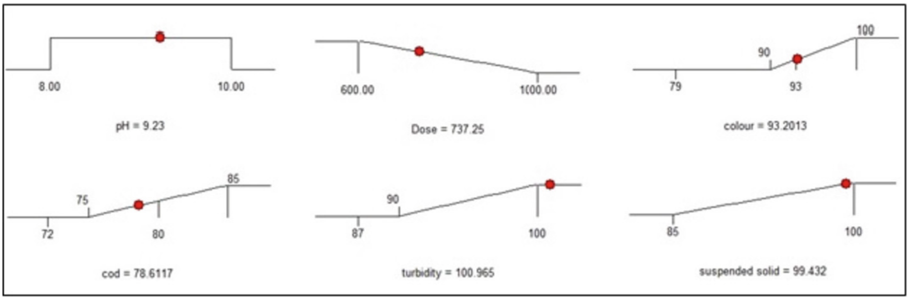


**Fig. 5.** The desirability ramp based on the outcome solution.

achieved with any pH and dose within the specified range. The gravitational effect and floc size make it easier to remove suspended solids during the sedimentation phase [30].

The optimization process was validated three times, as outlined in Table 3, using the outcome solution obtained from the desirability ramp.

The results of the chosen pH and ZOPAT dosage were evaluated based on their percentage reduction of turbidity, colour, COD, and suspended solids. The desirability ramp suggested the conditions that achieved the highest percentage reduction. The validation

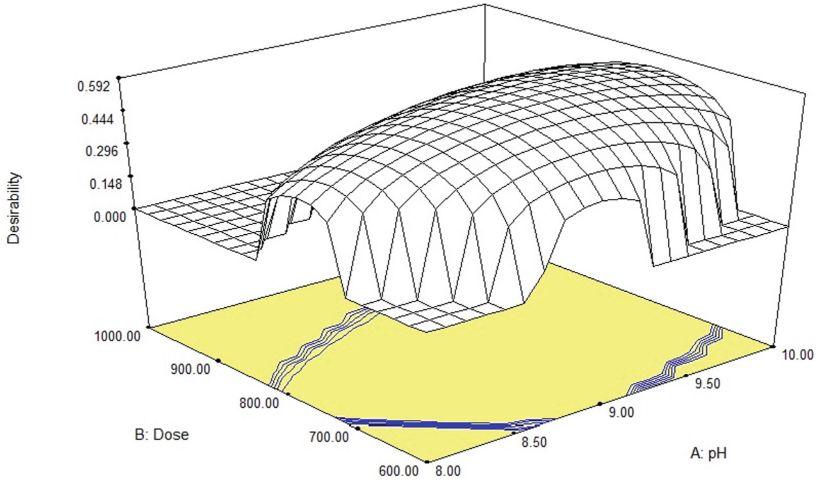


**Fig. 6.** The desirability plot at varied pH and doze ZOPAT.

**Table 3.** Validation of experimental results based on desirable ramp.

| Experimental of percentage reduction (%) | | | | | | |
|---|---|---|---|---|---|---|
| Set of Exp | pH | ZOPAT dosage (mg/L) | Turbidity (%) | Colour (%) | COD (%) | Suspended Solid (%) |
| 1 | 9.22 | 737 | 100 | 93 | 79 | 99 |
| 2 | 9.20 | 737 | 100 | 92 | 78 | 99 |
| 3 | 9.22 | 737 | 100 | 93 | 80 | 100 |

* The initial concentration of the raw textile wastewater: Turbidity: 151 NTU, Colour: 1724 Pt/Co; COD: 2250 mg/L, Suspended Solid: 173 mg/L.

tests demonstrated that the reduction of colour, COD, turbidity, and suspended solids differed by less than 1%. The model's accuracy in estimating the reduction percentage for all parameters was acceptable. Therefore, the final optimal condition, which involved applying 737 mg/L of ZOPAT at pH 9.22, successfully achieved a high reduction of colour, COD, turbidity, and suspended solids.

### 3.5 Influence on pH After the Treatment with ZOPAT

Table 4 shows that there was a slight pH difference before and after the coagulation treatment, which was attributed to the addition of ZOPAT to the suspension. The data in Table 4 reveals that the initial pH values for pH 4, pH 6, pH 8, and pH 12 were lowered as a result of the influence of ZOPAT.

When metal coagulants are added during the treatment of wastewater, the pH value of the wastewater decreases [31]. Additionally, some hydrolytic reactions take place during

**Tabel 4.** Result of pH before and after treatment with ZOPAT.

| pH before treatment | pH after treatment with ZOPAT |
|---|---|
| 2 | 2.0 |
| 4 | 3.9 |
| 6 | 5.4 |
| 8 | 6.5 |
| 10 | 8.0 |
| 12 | 10.2 |

the coagulation process, producing numerous positively charged hydrolysis products that interact chemically with negatively charged dye colloids. This generates multivalent charged hydroxyl species [32], as shown in Eqs. 1, 2, 3, 4, 5, and 6. The formation of metal hydrolysis also contributes to the solubility constant in Eq. 6.

$$\text{ZOPAT} \Leftrightarrow \text{Zn}^{2+} + \text{O}^{2-} + \text{PAM} + \text{Tannin} \tag{1}$$

$$\text{H2O} \Leftrightarrow \text{H}^{+} + (\text{OH})^{-} \tag{2}$$

$$\text{Zn}^{2+} + \text{H2O} \Leftrightarrow \text{Zn(OH)}^{+} + \text{H}^{+} \tag{3}$$

$$\text{Zn(OH)}^{+} + \text{H2O} \Leftrightarrow \text{Zn(OH)}_2 + \text{H}^{+} \tag{4}$$

$$\text{Zn(OH)}_2 + \text{H2O} \Leftrightarrow \text{Zn(OH)}_3^{-} + \text{H}^{+} \tag{5}$$

$$\text{Zn(OH)}_2 \Leftrightarrow \text{Zn}^{2+} + 2\text{OH}^{-} \tag{6}$$

The ANOVA test indicated that both the pH and the dose of ZOPAT had a significant effect, as indicated by their P-values. This suggests that there is a strong correlation between the pH and the coagulant dose.

### 3.6 Zeta Potential at Optimum Condition

Table 5 presents the evaluation of the zeta potential of ZOPAT, as well as the zeta potential of the agglomerated dye particles during jar testing. Prior to treatment, the wastewater sample exhibited a zeta potential of −28 mV. However, with the introduction of ZOPAT into the textile wastewater, destabilization occurred among the particles.

The negatively charged particles on the colloids were neutralized by cations in the polymer. In this case, the cations may include Zn2 + and Zn(OH) +, which attract negative dye compounds such as Cl-, SO32-, OH-, and O2-, causing agglomeration among the flocs. This indicates that bond breakage occurs in the dye structure. During the rapid

**Table 5.** Different sample wsamplesken for wastewater (WW), during rapid mixing (RM), slow mixing (SM) and after sedimentation (AS) for zeta potential analysis.

| Coagulation phase | Zeta Potential (mV) |
|---|---|
| Initial wastewater | -28 |
| Rapid mixing (RM) | 3.0 |
| Slow mixing (SM) | 2.4 |
| After sedimentation (AS) | 0.9 |

mixing phase, the zeta potential was close to 5 mV, which is consistent with a previous study that reported agglomeration occurring between −5 mV to + 5 mV [33]. Charge neutralization and sweep flocculation occurred due to the reaction between the positively charged polymers and the sulfonic group of dye molecules [34]. The zeta potential of the flocs during the slow mixing time remained positive, and their size gradually increased through adsorption-bridging ability. As the flocs became larger, they settled and reduced the color in the wastewater. Surface adsorption was also activated, which removed the balance of free colloids by enmeshing them in the flocs [35]. After sedimentation, the treated wastewater had a zeta potential closer to + 1 mV. The maximum agglomeration can be between 0 charges and 3 mV [33].

**Effect of Temperature on Storage Conditions.** A previous study [15] conducted a storage test on ZOPAT, analyzing the effect of storage temperature in a cold room (4–6 °C) and at room temperature (30 °C) for a duration ranging from 0 to 60 days. The results were presented for color reduction and COD reduction in Fig. 7. Figure 7 illustrates that the reduction of color was notably affected after 28 days, but it deteriorated considerably after 60 days at room temperature. This suggests that storing ZOPAT in a cold environment can help stabilize it.

Additionally, Fig. 8 shows that the physical appearance of ZOPAT became foamy and darker after 60 days. Similar observations were made in another study involving the use of natural coagulant (M. oleifera) in the hybrid coagulant, which resulted in changes after 30 days [15].

This indicates that natural coagulants can also affect the storage stability of hybrid coagulants. The reduction of COD followed a similar pattern to that of color reduction, with no significant difference in the efficiency of the hybrid coagulant within a week. The COD percentage reduction began to decline significantly after 28 days, from 70% to 60%, and then decreased slowly until 60 days. According to [8], the aging of the hybrid coagulant may trigger some chemical reactions, such as an increase in temperature and duration of time. Based on these findings, it is recommended to store ZOPAT in a cold room for not more than 20 days to maintain its quality.

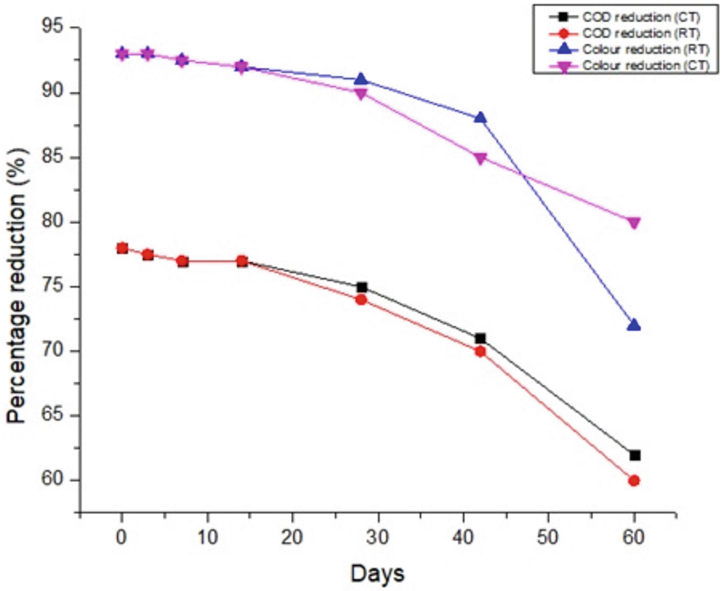


**Fig. 7.** The storage stability of ZOPAT in colour and COD reduction for 60 days *CT: Cold temperature and RT: Room temperature.

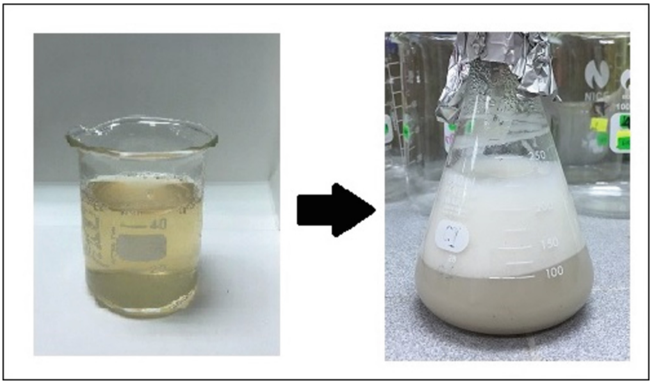

**Fig. 8.** ZOPAT appearance after 60 days in room temperature.

## 4 Conclusions

The study evaluated the effectiveness of different polymers in treating textile wastewater, including a hybrid polymer ZOPAT composed of zinc oxide, acrylamide, and tannin. ZOPAT demonstrated strong performance in reducing turbidity, color, and suspended solids in a wide range of pH levels. It was also more effective in reducing color than COD and consistent at low doses. Tannin showed the best residual COD concentration, but its performance in reducing other pollutants was not as good as ZOPAT. ZnO showed better removal of color but required a high dosage. PACl alone was found to be less effective in reducing color but could be used in combination with other polymers. According to the RSM-CCD, the model showed a strong relationship between the independent (pH and ZOPAT dose) and dependent variables, and the hybrid polymer had the highest efficiency in removing pollutants from wastewater. The plot indicated that the pH and the dose of ZOPAT had a significant effect on the reduction of color and COD. Increasing the dose of coagulant led to an increase in the percentage reduction for all parameters but overdosing with more than 1000 mg/L reduced the effectiveness of the treatment. The study recommended storing ZOPAT in a cold room for not more than 20 days to maintain its quality. Overall, the study provides valuable insights into the use of hybrid polymer ZOPAT in treating wastewater and sheds light on the optimal storage conditions for the hybrid polymer. It highlights the importance of using multiple polymers in treating wastewater to achieve better coagulation results. The study's findings can aid in developing efficient and cost-effective wastewater treatment methods.

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