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# Investigation of the treatability of paint industry wastewater using hybrid coagulant poly-aluminum-chloride-sulfate

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## ABSTRACT

In this study, coagulation–flocculation method with poly-aluminum-chloride-sulfate (PACS) was used to pre-treat paint industry wastewater (PIWW). The pH, centrifugation time, revolutions per minute and PACS dose were selected as independent parameters for an experimental design employing Taguchi orthogonal arrays. These independent parameters were varied at four different levels (pH: 5, 6, 7 and 8; centrifugation time: 1, 2, 3 and 4 min; revolutions per minute: 1,000; 2,000; 3,000 and 4,000 rpm; and PACS doses: 1, 2, 3, and 4 mg/L) to determine their effects on the removal efficiencies of selected dependent parameters. Chemical oxygen demand (COD) and color were selected as the dependent parameters and analyzed at the beginning and end of each batch experiment. The maximum removal efficiencies of COD and color were found to be 37% (for 3-3-1-2 levels) and 89% (for 4-1-4-2 levels), respectively. According to the Taguchi method, the contributions to COD removal performance of PACS dose, pH, revolution per minute and centrifugation time to be 33.09%, 37.39%, 3.76% and 13.42%, respectively. On the other hand, the contributions to color removal performance of PACS dose, pH, revolution per minute and centrifugation time to be 3.75%, 86.97%, 3.75% and 4.25%, respectively. According to obtaining results, PACS can be used as a pre-treatment process for PIWW treatment.

*Keywords:* Chemical oxygen demand removal; Color removal; Paint industry wastewater; Poly-aluminum-chloride-sulfate; Taguchi method

## 1. Introduction

Paint industry wastewater (PIWW) contains many organic and inorganic pollutants and it is difficult to provide a treatment that will meet the discharge standards. PIWW may contain excessive concentrations of many organic or inorganic pollutants such as chemical oxygen demand (COD), BOD, suspended and dissolved solids, oil and grease, and heavy metals. Today, many methods [1] such as physical–chemical [2], chemical–biological [3–5], coagulation–flocculation [6–8], coagulation–electrochemical [9–12], advanced oxidation processes (AOPs) [13–15], and membrane processes [16] are applied for the treatment of PIWW. Coagulation–flocculation is an important unit operation in wastewater treatment for solid/liquid separation [17]. Inorganic coagulant such as aluminum and iron-based substances plays a major role in neutralizing the surface charge of suspended particles or colloidal systems and facilitating particle aggregation and settling under gravity as a result of electrical double-layer compression [18]. The flocculation process involves the addition of flock-forming chemical reagent usually after coagulation to agglomerate non-settable and slow-settling colloidal solids and it plays a major role in the fate and transport of contaminants in aquatic environments by bridging the aggregated flocks to form larger agglomerates in the presence of polymeric materials

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[19]. Various materials have been developed in recent years for coagulation and flocculation purposes. Among them are inorganic-based coagulants, organic-based flocculants as well as hybrid materials [20]. Although many materials have been developed for wastewater treatment, it can be said that there is still much to be done to increase treatment efficiency. Increasing market demand in wastewater treatment has made it necessary to develop hybrid materials to increase treatment efficiency. Hybrid materials come to the fore in wastewater treatment due to their high treatment efficiency and lower cost compared to conventional coagulants and flocculants. [21]. Hybrid materials used in the coagulation/flocculation of wastewater are materials obtained from the addition of effective components into the original material to enhance the aggregating power. It is logical to introduce functional chemical groups or components into the initial chemical which can strengthen the aggregating power [22]. Due to the synergetic effect of hybrid components in one material, hybrid materials hence pose a superior performance than that of individual components [23]. Hybrid materials retain functional components in a single structure. For this reason, the whole process can be performed in a single tank without the need for separate coagulation and flocculation tanks traditionally used in treatment plants. The shortening of the waiting time as a result of the application of these hybrid materials in a single tank is advantageous for industries that discharge large volumes of wastewater. Therefore, it is clear that they are seen as an alternative material for plants when compared to traditional coagulants and flocculants [24]. The superior performance of pre-polymerized coagulants is manifested in their wider working pH range, lower sensitivity to low water temperatures, lower dose required to achieve equivalent treatment efficiency, and lower residual metal-ion concentrations. This has been attributed to the presence of a range of polymeric species with high molecular weights and high cationic charge, which enhance the rate of colloid charge neutralization and flock development and settlement [25]. Hybrid material preparation methods can be given as hydroxylation-pre-polymerization, physical blending, high-temperature blending, copolymerization, and chemical grafting/crosslinking, depending on the type of hybrid materials. The hydroxylation-pre-polymerization method is widely used to prepare chemically bonded hybridized materials in which a new chemical group is incorporated into the composition of materials, and poly-aluminum-chloride-sulfate (PACS) is also produced by this method. Hybrid materials which have been developed are indicated with black line, for example, inorganic–inorganic hybrid, inorganic–organic hybrid, inorganic–natural polymer hybrid, inorganic–biopolymer hybrid, organic–organic hybrid, organic–natural polymer hybrid and natural polymer–natural polymer hybrid [24]. PACS used in this study is one of the inorganic–inorganic hybrid materials. PACS is prepared using $AlCl_3$, $Al_2\,(SO_4)_3$ and $Na_2CO_3$ as raw materials. The total aluminum concentration and specific gravity of PACS products are 3.64–3.71% as Al and 1.182–1.184 g/L, respectively. Previous study about PACS was showed that the particle size distribution of coagulant PACS was found to be highly dependent on $SO^{2-}{}_4/Al^{3+}$ molar ratio and $OH^-/Al^{3+}$ molar ratio. Moreover, at a fixed $OH^-/Al^{3+}$ molar ratio value of 2.0, the average size of PACS increased with the increase of $SO^{2-}{}_4/Al^{3+}$ molar ratio [25]. The removal efficiency of the pollutants is vital parameters of PIWW treatment systems and, in turn, depends on operational independent factors such as pH, centrifugation time, revolutions per minute and PACS dosages. Hence, independent factors need to be optimized to increase the treatment efficiency. In addition, in classical optimization, all factors are optimized one by one while changing the level of one factor, keeping the other factor levels constant. For this reason, the number of experimental studies and workload required in the classical optimization method can cause time losses [26]. There are many statistical experimental design techniques the widely used, such as response surface methodology and full or partial factorial designs. One of these techniques is the Taguchi method [27–34] and involves the design of an experimental process using orthogonal arrays (OA) to allow independent evaluation of factors in the least number of trials. This technique involves data conversion to a signal-to-noise (S/N) ratio, which is a measure of the changes presented [35]. The Taguchi method has the feature of being able to examine the parameters affecting an experiment in a controlled and uncontrolled manner and can be applied to an experimental design that includes a large number of design factors [36].

In this study, raw PIWW was taken from the equalization basin of the dye production factory located on the European side of Marmara Region of Turkey, was subjected to coagulation/flocculation process with poly-aluminum-chloride-sulfate (PACS) for batch studies in the laboratory. The PACS used in the study was purchased, not produced in this study. The main objective of the study was to evaluate the treatability of PIWW and optimize pollutant removal efficiencies by using the Taguchi method. Hence, a batch studies matrix was planned using Minitab 21.0 software for optimized the studies using the Taguchi method. During batch studies, removal efficiencies of selected dependent variables (COD and color) were analyzed both at the beginning and at the end of each batch study based on independent variables (pH, PACS dose, centrifugation time and revolution per minute). This study is important because it is the first study using the Taguchi optimization method and the $L_{16}$ orthogonal arrays in investigating PIWW treatment.

## 2. Materials and method

### *2.1. Experimental set-up*

In the study, PIWW was used taken from the dye production factory at located on the European side of Marmara Region of Turkey. 0.5 L plexiglas reactors were used for each batch experiment in the laboratory. Batch tests were conducted using 0.05 L of raw PIWW for each experimental set. For pH adjustment, 6 M of NaOH and/or $H_2SO_4$ of analytical grade were used. The pH and conductivity were measured by a WTW pH/Cond 340i SET 2. COD were measured by a closed reflux method and color was measured by the platinum–cobalt (Pt-Co) scale [37]. All analyses were carried out in triplicate (deviations were lower than 5% in all cases).

PIWW was kept in the refrigerator at 4 degrees centigrade in the Environmental Engineering laboratory of Yildiz Technical University. Before each experimental study, PIWW was removed from the refrigerator and the test was not started until its temperature had reached the ambient temperature in the laboratory. The characteristics of PIWW are given in Table 1. After each batch work, all wastewater analyses were performed in accordance with The Standard Methods for Examination of Water and Wastewater [37].

### *2.2. Experimental design based on the Taguchi method*

The Taguchi method was used to create a set of experiments designed using Minitab software (Minitab 21.0 trial version). The Taguchi method includes the design of an experimental process that uses orthogonal arrays (OAs) to reduce the number of experiments required. OA refers to an experimental matrix designed with $L_i$ stages, where i is the number of trials in the experimental matrix or the total degrees of freedom and includes a set of experiments where the settings of process parameters are varied. OAs allows evaluation of the effects of several process parameters to be determined efficiently. The selection of a suitable OA depends on the number of control factors and their levels [31,38]. In the study, the Taguchi method was used to decide the ideal conditions for the process. For this purpose; pH, PACS dose, revolution per minute and centrifugation time were selected as independent variables during this Taguchi experimental design. Each factor, which consisted of four levels and $L_{16}$ orthogonal arrays, was taken to establish the ideal conditions for PIWW treatment with the least number of trials. The factors and their levels in the batch studies are presented in Table 2.

## 3. Results and discussion

In the study, Minitab software was used to analyze the collected data and to determine the effect of each parameter on the optimization criteria. The Taguchi design experiment ($L_{16}$) was carried out to optimize the effective parameters to efficiently remove PIWW pollutants using PACS. The larger-the-better S/N ratio was used to analyze the results of the batch experimental studies. Analysis of variance (ANOVA) was performed to examine the effective parameters and their confidence levels on the COD and color removal efficiencies. ANOVA is used to explore which process parameters significantly affect the process responses. Moreover, all levels of variables in Table 1 were used. During this work, COD and color results were expressed by percentage of removal through Eq. (1):

$$\text{Pollutant removal efficiency}\left(\%\right)=\left[\frac{C_i-C_e}{C_i}\right]\times 100 \qquad (1)$$

where $C_i$ is the initial concentration and $C_e$ is the final concentration of the pollutant (mg/L). The numerical value of the maximum point in each graph make clear the best value of that particular parameter, shown in Table 3, and indicates the optimum conditions within the range of experimental conditions. Results related to the removal efficiency of COD and color for 16 experimental batch studies are given in Table 3.

The results of the experimental studies obtained by using the most significant independent variables performed in the study are summarized in the following sub sections for independent factors based on Figs. 1 & 2 and Tables 3–6.

The effects of performance criteria based on Taguchi method on COD removal efficiency for PIWW pre-treatment are illustrated in Fig. 1. It is seen from Fig. 1 that the pH values at which the highest and lowest COD removal efficiency occur are 7 and 6, respectively. It is seen that the PACS doses with the highest and lowest COD removal efficiency are 3

Table 1
PIWW characteristics

| PIWW characteristics | Values |
|---|---|
| pH (20°C) | 5.5–5.9 |
| Conductivity, mS/cm (20°C) | 13.5–13.8 |
| COD, mg/L | 5,200–5,300 |
| Color, Pt-Co, units | 27,000–28,000 |

Table 2
Factors and their values corresponding to the levels to be carried out in the study

| Independent factors | Levels of independent factors | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| *A*: pH | 5 | 6 | 7 | 8 |
| *B*: PACS, mg/L | 1 | 2 | 3 | 4 |
| *C*: Revolution per minute | 1,000 | 2,000 | 3,000 | 4,000 |
| *D*: Centrifugation time, min | 1 | 2 | 3 | 4 |

Table 3
Experimental variables, their levels, and results of conducted experiments corresponding to the $L_{16}$ experimental plan

| Batch experiment no (or Runs) | Independent variables and their levels | | | | Removals of pollutants | |
|---|---|---|---|---|---|---|
| | *A* | *B* | *C* | *D* | % COD | %Color |
| 1 | 1 | 1 | 1 | 1 | 27 | 76 |
| 2 | 1 | 2 | 2 | 2 | 33 | 80 |
| 3 | 1 | 3 | 3 | 3 | 33 | 81 |
| 4 | 1 | 4 | 4 | 4 | 31 | 82 |
| 5 | 2 | 1 | 2 | 3 | 25 | 77 |
| 6 | 2 | 2 | 1 | 4 | 31 | 80 |
| 7 | 2 | 3 | 4 | 1 | 31 | 79 |
| 8 | 2 | 4 | 3 | 2 | 32 | 82 |
| 9 | 3 | 1 | 3 | 4 | 33 | 87 |
| 10 | 3 | 2 | 4 | 3 | 30 | 87 |
| 11 | 3 | 3 | 1 | 2 | 37 | 88 |
| 12 | 3 | 4 | 2 | 1 | 36 | 87 |
| 13 | 4 | 1 | 4 | 2 | 33 | 89 |
| 14 | 4 | 2 | 3 | 1 | 33 | 88 |
| 15 | 4 | 3 | 2 | 4 | 34 | 87 |
| 16 | 4 | 4 | 1 | 3 | 35 | 87 |

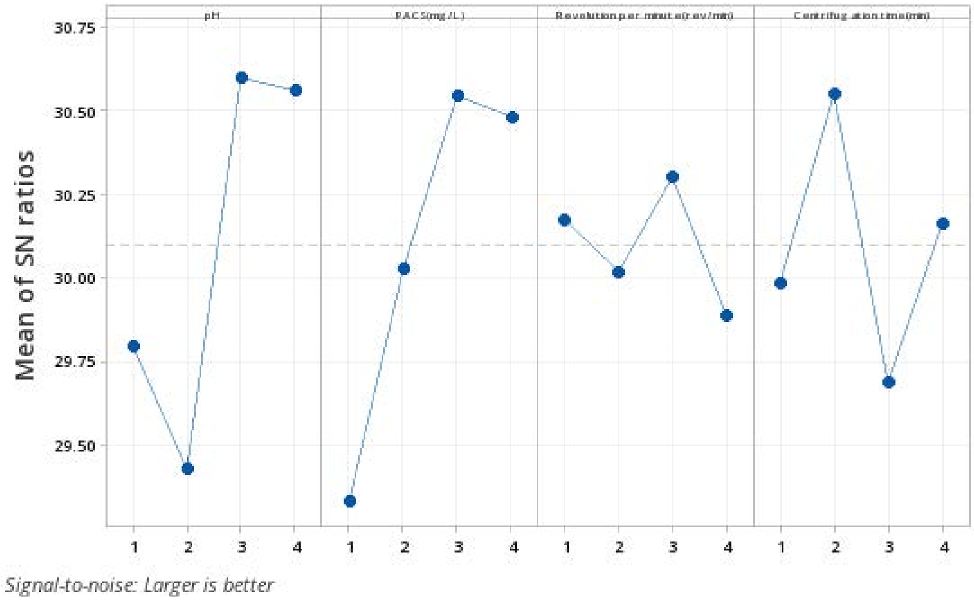

Fig. 1. Effect of the parameters on COD removal efficiency. On the left-hand side, it shows different initial pH (5, 6, 7 and 8) based on levels (1 to 4). Second on the left-hand side, it shows PACS doses (1, 2, 3 and to 4 mg/L) based on levels (1 to 4). Third on the left-hand side, it shows revolutions per minute (1,000; 2,000; 3,000 and 4,000 rev/min) based on levels (1 to 4). On the right-hand side, it shows reaction time (1, 2, 3 and 4 h).

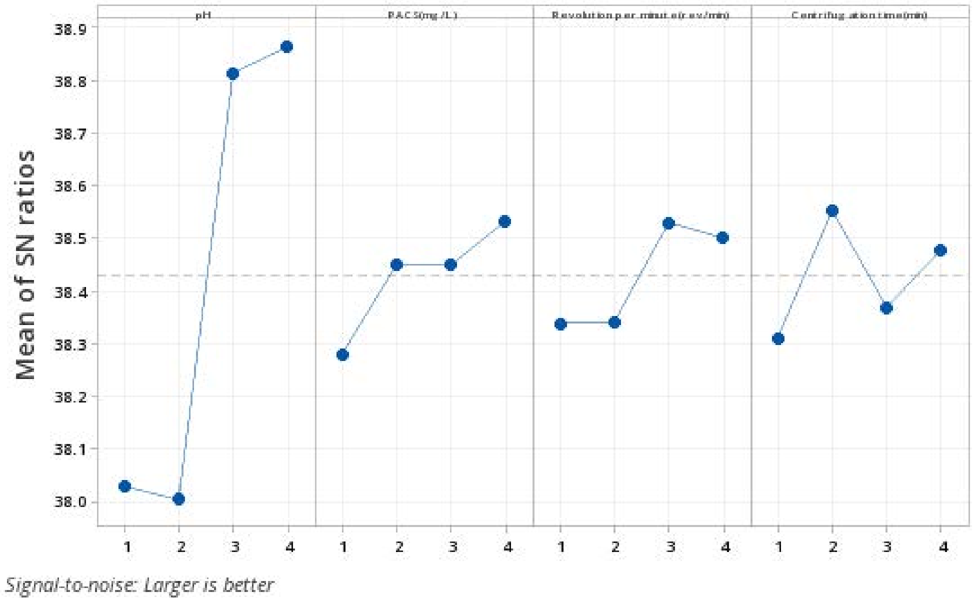

Fig. 2. Effect of each parameter on color removal efficiency. On the left-hand side, it shows different initial pH (5, 6, 7 and 8) based on levels (1 to 4). Second on the left-hand side, it shows PACS doses (1, 2, 3 and to 4 mg/L) based on levels (1 to 4). Third on the left-hand side, it shows revolutions per minute (1,000; 2,000; 3,000 and 4,000 rev/min) based on levels (1 to 4). On the right-hand side, it shows reaction time (1, 2, 3 and 4 h).

and 1 mg/L, respectively. It is seen that the revolution per minute values, where the highest and lowest COD removal efficiency occur, are 3,000 and 4,000 rpm, respectively. It is seen that the centrifugation time values at which the highest and lowest COD removal efficiency occur are 2 and 3 min, respectively.

The effects of performance criteria based on Taguchi method on color removal efficiency for PIWW pre-treatment are illustrated in Fig. 2. It is seen from Fig. 2 that the pH values at which the highest and lowest color removal efficiency occur are 8 and 6, respectively. It is seen that the PACS doses with the highest and lowest color removal

Table 4
ANOVA values for COD removal efficiency

| Source | DF | Seq. SS | %*C* | Adj. SS | Adj. MS | *F*-value | *p*-value |
|---|---|---|---|---|---|---|---|
| pH | 3 | 52.25 | 37.39 | 52.25 | 17.417 | 3.03 | 0.194 |
| PACS (mg/L) | 3 | 46.25 | 33.09 | 46.25 | 15.417 | 2.68 | 0.22 |
| Revolution per minute | 3 | 5.25 | 3.76 | 5.25 | 1.75 | 0.3 | 0.823 |
| Centrifugation time (min) | 3 | 18.75 | 13.42 | 18.75 | 6.25 | 1.09 | 0.473 |
| Residual error | 3 | 17.25 | 12.34 | 17.25 | 5.75 | | |
| Total | 15 | 139.75 | 100 | | | | |

Table 5
ANOVA values for color removal efficiency

| Source | DF | Seq. SS | %*C* | Adj. SS | Adj. MS | *F*-value | *p*-value |
|---|---|---|---|---|---|---|---|
| pH | 3 | 248.688 | 86.97 | 248.688 | 82.896 | 67.44 | 0.003 |
| PACS (mg/L) | 3 | 10.687 | 3.75 | 10.687 | 3.562 | 2.9 | 0.203 |
| Revolution per minute | 3 | 10.687 | 3.74 | 10.687 | 3.562 | 2.9 | 0.203 |
| Centrifugation time (min) | 3 | 12.187 | 4.25 | 12.187 | 4.062 | 3.31 | 0.176 |
| Residual error | 3 | 3.688 | 1.29 | 3.688 | 1.229 | | |
| Total | 15 | 285.938 | 100 | | | | |

Table 6
Predicted pollutant removal efficiency values for optimum experimental conditions

| Sources | pH | PACS | Revolution per minute | Centrifugation time | Predicted, % | 95% CI |
|---|---|---|---|---|---|---|
| COD | 3 | 3 | 1 | 2 | 36.75 | (30.75–44.50) |
| Color | 4 | 1 | 4 | 2 | 85.13 | (83.56–91.49) |

efficiency are 4 and 1 mg/L, respectively. It is seen that the revolution per minute values, where the highest and lowest color removal efficiency occur, are 3,000 and 1,000 rpm, respectively. It is seen that the centrifugation time values at which the highest and lowest color removal efficiency occur are 2 and 1 min, respectively.

The resulting ANOVA values for COD and color removal performance for the independent factors are given in Tables 4 and 5, respectively.

Table 4 shows the result of the ANOVA test for COD removal performance. According to the ANOVA analysis, the factors in the tables are in accordance with their significance. According to Table 4, the first important independent parameter for efficient removal of COD was pH with a contribution value of 37.39%. The second important independent parameter for COD was the PACS with a contribution value of 33.09%. The third important independent parameter for COD was revolution per minute with a contribution value of 13.19%. The fourth important independent parameter for COD was centrifugation time with a contribution value of 3.76%. The sequence related to the importance of color removal efficiency was found to be pH > PACS dose > centrifugation time > revolution per minute.

Table 5 shows the result of the ANOVA test for color removal performance. According to the ANOVA analysis, the factors in the tables are in accordance with their significance. According to Table 5, the first important independent parameter for efficient removal of color was the pH with a contribution value of 86.97%. The second important independent parameter for color was centrifugation time with a contribution value of 4.25%. The third important independent parameter for color was PACS dose with a contribution value of 3.75%. The fourth important independent parameter for color was revolution per minute with a contribution value of 3.74. The sequence related to the importance of color removal efficiency was found to be pH > centrifugation time > PACS dose > revolution per minute. Moreover, predicted pollutant removal efficiency values for optimum experimental conditions are given Table 6.

Table 6 shows the optimum operating conditions and estimates the response under these conditions. The best COD removal conditions for the process were estimated to be 7.0, 3.0 mg/L, 1,000 rpm and 2 min for pH, PACS dose, and revolution per minute and centrifugation time, respectively. Under these conditions, the estimated COD removal efficiency was 36.75%. According to Table 6, the best color removal conditions were estimated to be 8.0, 1.0 mg/L, 4,000 rpm and 2 min for pH, PACS dose, revolution per minute and centrifugation time, respectively. Under these conditions, the estimated color removal efficiency was 85.13%. Moreover, the comparison of predicted and experimental pollutant removal efficiency based on 2 different levels of the independent factors are given in Table 7.

According to Table 7, the experimental results obtained in the study using the second levels of independent variables are seen. According to the results of two repetitive studies made considering the second levels of the independent variables; It is seen that there is a difference of 2.8% and 1.7% between the experimental and estimated COD and color removal results, respectively. According to the results of two repetitive studies made considering the third level of the independent variables; it is seen that there is 1.2% and 1.1% difference between experimental and predicted COD and color removal results, respectively.

### 3.1. Effect of operating parameters on the process

To initiate coagulation/flocculation process of wastewater, through coagulation or flocculation process, several operating factors, such as pH, dosage, stirring speed, stirring time as well as temperature are taken into account to optimize the wastewater treatment performance [39]. In the study, pH and PACS dose were optimized with the other independent factors planned this study concept (revolution per minute and centrifugation time). Moreover, stirring speed and stirring time were applied all batch experiments the same in this study. The coagulation or coagulation process is usually carried out sequentially in the same reactor with fast and slow mixing processes. Firstly, rapid mixing is applied at 75 to 700 rpm for 0.5–3 min; and then, slow mixing is applied at ranges from 30 to 150 rpm for 5–30 min. The purpose of rapid mixing is to provide a good dispersion of the coagulant or flocculent to destabilize colloidal systems and particulate matter, whereas slow mixing is to limit the disintegration of aggregates, thereby promoting the growth of agglomerates [39]. In the study, in all batch experimental sets, rapid mixing is applied at 200 rpm for 1 min; slow mixing is applied at 30 rpm for 30 min. In the study, in all batch experimental sets, firstly PACS added to rapid mixing was applied at 200 rpm for 1 min; afterword, slow mixing was applied at 30 rpm for 30 min. In previous some physico-chemical treatability studies of PIWW, COD removal efficiencies of 88% [40], 40% [41] and 85% [42] were obtained. In this study, in which PACS hybrid material was used as coagulant/flocculent, the COD removal efficiency was 37% and the color removal efficiency was 89%. The COD removal efficiency is very low compared to the receiving environment standards. This is due to the fact that the PIWW sample, whose treatability study was carried out, was heavily polluted. So, PIWW, whose treatability study was conducted in this study, includes wastewater from all production processes such as water-based paint production, oil-based paint production. The aim of this study is to provide a pre-treatment with PACS and to determine the process independent variable levels that can help reduce the load of the biological treatment plant in the facility.

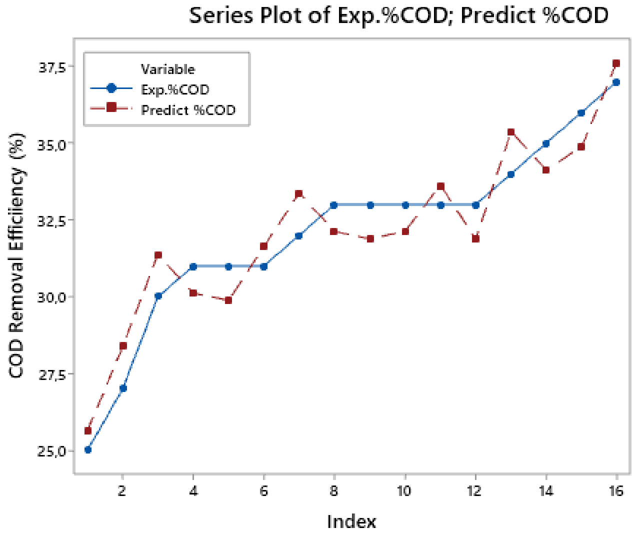

Fig. 3. Comparisons of experimental and model predicted results for COD removal efficiency.

#### 3.1.1. Effect of pH on the process

The pH is one of the most important parameter for efficient removal of pollutants in the coagulation/flocculation process. With the support of OH– group, a variety of hydrolysis reactions take place rapidly with the dissolution of any aluminum salt in aqueous solution. The coagulation efficiency depends primarily on the formation of $Al(OH)_3$ precipitates rather than on the charge neutralization mechanism favored at pH value in the range of 6.5–7.0. In the case of low degree of aluminum polymerization, once pH rises, the formation of $Al(OH)^-_4$ species becomes prominent in solution and take in radical fall of coagulation efficiency [43]. Sufficient amount of effective species (e.g., $Al_{13}$) at the optimal pH is required to supply a maximum coagulation performance. During the coagulation process, this effective species can efficiently destabilize suspended particles and colloids [44]. Hybrid materials can improve the pH resistance (e.g., polyaluminum silicate chloride). This material has been proven

Table 7
Comparison of predicted and experimental pollutant removal efficiency based on 2 different independent factor levels

| pH (levels) | PACS, mg/L (levels) | Revolution per minute (levels) | Centrifugation time (levels) | COD experimental (%) | COD predicted (%) | Color experimental (%) | Color predicted (%) |
|---|---|---|---|---|---|---|---|
| 6 (2) | 2 (2) | 2,000 (2) | 2 (2) | 30.5 | 30.875 | 82 | 80.06 |
| 6 (2) | 2 (2) | 2,000 (2) | 2 (2) | 31.4 | | 80 | |
| 7 (3) | 3 (3) | 3,000(3) | 3 (3) | 34.5 | 34.875 | 88 | 87.81 |
| 7 (3) | 3 (3) | 3,000(3) | 3 (3) | 35.1 | | 86 | |

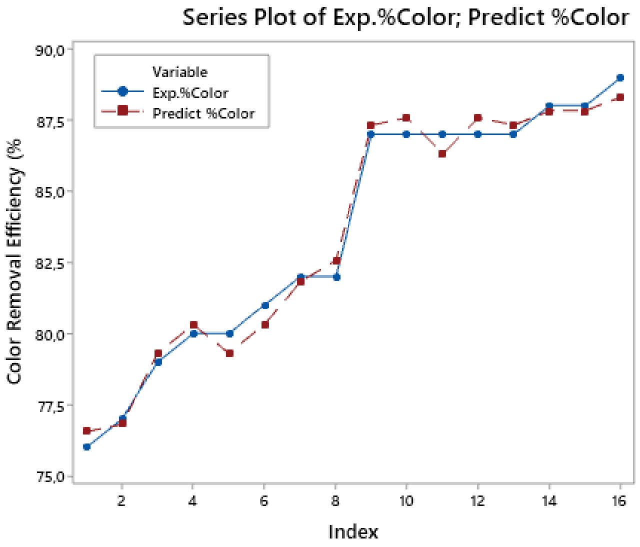

Fig. 4. Comparisons of experimental and model predicted results for color removal efficiency.

to have wider optimum coagulation pH range (6.0–8.5) compared to that of unmodified polyaluminum-chloride (6.0–8.0) in removing oil from oil refinery wastewater [45]. Consequently, it can be concluded that the hybridization of foreign species into the coagulant can increase the efficiency of treatment as well as decreases the effect of pH which in turn can treat different kinds of wastewater.

In this study, it is obtained that pH is the most important factor both COD and color removal efficiencies for PIWW treatment. As can be seen from Fig. 1, level 3 corresponds to the pH with the highest COD removal efficiency (pH = 7.0). Also, Table 4 shows that the highest contribution to COD removal is from the pH factor (%CI = 37.39). Moreover, from Fig. 2, level 4 corresponds to the pH with the highest COD removal efficiency (pH = 8.0). Also, Table 5 shows that the highest contribution to color removal is from the pH factor (%CI = 86.97). The removal efficiencies of COD and color based on the changes of pH are summarized in Table 3. The highest removal efficiency for COD was obtained at the third level (pH = 7) in the PIWW pretreatment batch experiments. On the other hand, the highest removal efficiency for color was obtained at the fourth level (pH = 8). According to Table 3, COD removal efficiency at pH = 6 was reduced by 8% compared with the value at pH = 7. The highest color removal efficiency was realized at pH = 8. The color removal at pH = 9 was reduced by 10% compared with the value at pH = 8.

### *3.1.2. Effect of PACS dosage on the process*

The dose of coagulant/coagulant to be used in the coagulation/flocculation process varies depending on the content of colloids or suspended solids in the liquid to be treated. It can be assumed that the treatment efficiency increases with increasing coagulant/flocculant content, however, under certain conditions, the treatment efficiency reaches its maximum and then decreases with increasing dosage [17]. The reason for this can be explained by the reversal of the particle surface charge due to the excess of inorganic coagulant, and consequently a reduction in treatment efficiency is expected. This disadvantage can be compensated for by the application of hybrid materials with a wider optimum dose range than conventional coagulant/flocculating chemicals. In a study [45], a comparison was made between polyaluminum-chloride (PAC) and polyaluminum-silicate-chloride (PASiC) in terms of turbidity reduction. It has been determined that PASiC coagulant provides a wider effective dosage range than PAC. That is, due to the synergistic effect of two different components in a single hybrid matrix, it has been demonstrated that maximum purification efficiency can be achieved by using less coagulant.

In this study, one of the most important independent factor for efficient removal of pollutants (COD and color) in the process is PACS and used as coagulation/flocculation hybrid material for PIWW treatment. It is obtained that PACS dose is one of the most important factors both COD and color removal efficiencies for PIWW treatment. As can be seen from Fig. 1, level 3 corresponds to the PACS dose (3 mg/L) with the highest COD removal efficiency. Also, Table 4 shows that the second highest contribution to COD removal is from PACS factor (%C = 33.09). Moreover, from Fig. 2, level 4 corresponds to PACS dose (4 mg/L) with the highest color removal efficiency. Also, Table 5 shows that the third important contribution to color removal is from PACS factor (%C = 3.75). The removal efficiencies of COD and color based on the changes of PACS dose are summarized in Table 3. The highest removal efficiency for COD was obtained at the third level (3 mg/L) in the PIWW pre-treatment batch experiments. On the other hand, the highest removal efficiency for color was obtained at the first level (1 mg/L).

### *3.1.3. Effect of revolutions per minute (rpm) on the process*

In this study, it is obtained that rpm is the least important factor both COD and color removal efficiencies for PIWW treatment. As can be seen from Fig. 1, level 3 corresponds to rpm factor with the highest COD removal efficiency (rpm = 3,000 rpm). Also, Table 4 shows that the least contribution to COD removal is from rpm factor (%C = 3.76). Moreover, from Fig. 2, level 3 corresponds to rpm with the highest COD removal efficiency (rpm = 3,000 rpm). Also, Table 5 shows that the least contribution to color removal is from rpm factor (%C = 3.74). The removal efficiencies of COD and color based on the changes of rpm factor are summarized in Table 3. The highest removal efficiency for COD was obtained at the first level (rpm = 1,000 rpm) in the PIWW pretreatment batch experiments. On the other hand, the highest removal efficiency for color was obtained at the fourth level (rpm = 4,000 rpm).

### *3.1.4. Effect of centrifugation time on the process*

In this study, it is obtained that centrifugation time (CT) is the second or third important factor both COD and color removal efficiencies for PIWW treatment. As can be seen from Fig. 1, level 2 corresponds to CT factor with the highest COD removal efficiency (CT = 2 min). Also, Table 4 shows that the third important contribution to COD removal is from CT factor (%$C$ = 13.42). Moreover, from Fig. 2, level 2 corresponds to CT with the highest COD removal efficiency (CT = 2 min). Also, Table 5 shows that the second important contribution to color removal is from CT factor (%$C$ = 4.25). The removal efficiencies of COD and color based on the changes of CT factor are summarized in Table 3. The highest removal efficiency for both COD and color obtained at the second level (CT = 2 min) in the PIWW pre-treatment batch experiments.

### *3.1.5. Costs analysis*

In the process, cost is considered a vital parameter that affects the application of any method of wastewater treatment. Inorganic–organic hybrid materials can be considered as a more effective material in treating wastewater. They are more cost effective compared to inorganic–inorganic hybrid [39]. Hence, it can be said that the inorganic–inorganic hybrid chemical PACS used in this study is more costly than conventional coagulants.

## 4. Conclusions

PIWW, whose treatability study was carried out, was taken from the paint production factory equalization pool and includes wastewater from all production processes in the factory. For this reason, PIWW contain both water-based and oil-based paint production processes wastewater. It is clear that the PIWW, whose treatability study has been carried out here, can be treated at a level that can be given to the receiving environment by sequential use of physicochemical and biological treatment methods. So, the aim of this study is to determine the working conditions that will reduce the burden of subsequent treatment processes by performing a pre-treatment with PACS. According to the results obtained in the studies, the highest COD removal efficiency is obtained as 37% at pH = 7.0. Considering COD as the most important pollutant in the PIWW, the contribution of independent variables to the process can be shown pH > PACS dose > centrifugation time > revolution per minute. Moreover, according to the results obtained in the studies, the highest color removal efficiency is found to be 89% at a pH = 8. The contribution of independent variables to the process can be given pH > centrifugation time > PACS dose > revolution per minute.

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## References

[1] K. Surya Nair, M. Basavaraju, A. Adani, Sustainable treatment of paint industry wastewater: current techniques and challenges, J. Environ. Manage., 296 (2021) 113105, doi: 10.1016/j.jenvman.2021.113105.

[2] T.E. Aniyikaiye, T. Oluseyi, J.O. Odiyo, J.N. Edokpayi, Physicochemical analysis of wastewater discharge from selected paint industries in Lagos, Nigeria, Int. J. Environ. Res. Public Health, 16 (2019) 1235, doi: 10.3390/ijerph16071235.

[3] M.A. Aboulhassan, S. Souabi, A. Yaacoubi, M. Baudu, Treatment of paint manufacturing wastewater by the combination of chemical and biological process, Int. J. Sci. Environ. Technol., 3 (2014) 1747–1758.

[4] S. Popli, U.D. Patel, Destruction of azo dyes by anaerobic–aerobic sequential biological treatment: a review, Int. J. Environ. Sci. Technol., 12 (2015) 405–420.

[5] D. Krithika, L. Philip, Treatment of wastewater from water based paint industries using submerged attached growth reactor, Int. Biodeterior. Biodegrad., 107 (2016) 31–41.

[6] O. Dovletoglou, C. Philippopoulos, H. Grigoropoulou, Coagulation for treatment of paint industry wastewater, J. Environ. Sci. Health. Part A Toxic/Hazard. Subst. Environ. Eng., 37 (2002) 1361–1377.

[7] O.Y. Balik, S. Aydin, Coagulation/flocculation optimization and sludge production for pre-treatment of paint industry wastewater, Desal. Water Treat., 57 (2016) 12692–12699.

[8] I.G. Ezemagu, M.I. Ejimofor, M.C. Menkiti, Turbidimetric study for the decontamination of paint effluent (PE) using mucuna seed coagulant (MSC): statistical design and coag-flocculation modelling, Environ. Adv., 2 (2020) 100023, doi: 10.1016/j.envadv.2020.100023.

[9] B.K. Korbahti, N. Aktas, A. Tanyolaç, Optimization of electrochemical treatment of industrial paint wastewater with response surface methodology, J. Hazard. Mater., 148 (2007) 83–90.

[10] B.K. Korbahti, A. Tanyolaç, Electrochemical treatment of simulated industrial paint wastewater in a continuous tubular reactor, Chem. Eng. J., 148 (2009) 444–451.

[11] L.F. da Silva, A.D. Barbosa, H.M. de Paula, L.L. Romualdo, L.S. Andrade, Treatment of paint manufacturing wastewater by coagulation/electrochemical methods: proposals for disposal and/or reuse of treated water, Water Res., 101 (2016) 467–475.

[12] A.D. Barbosa, L.F. da Silva, H.M. de Paula, L.L. Romualdo, G. Sadoyama, L.S. Andrade, Combined use of coagulation (*M. oleifera*) and electrochemical techniques in the treatment of industrial paint wastewater for reuse and/or disposal, Water Res., 145 (2018) 153–161.

[13] I.S. de Oliveira, L. Viana, C. Verona, V.L.V. Fallavena, C.M.N. Azevedo, M. Pires, Alkydic resin wastewaters treatment by Fenton and photo-Fenton processes, J. Hazard. Mater., 146 (2007) 564–568.

[14] U. Kurt, Y. Avsar, M.T. Gonullu, Treatability of water-based paint wastewater with Fenton process in different reactor types, Chemosphere, 64 (2006) 1536–1540.

[15] A. Marco, R. Erick, A. Carlos, Advanced Oxidation Processes (AOPs) for Removal of Pesticides From Aqueous Media, M. Stoytcheva, Ed., Pesticides – Formulations, Effects, Fate, London, 2011. doi: 10.5772/13597.

[16] D.P. Zagklis, P.G. Koutsoukos, C.A. Paraskeva, A combined coagulation/flocculation and membrane filtration process for the treatment of paint industry wastewaters, Ind. Eng. Chem. Res., 51 (2012) 15456–15462.

[17] J. Zou, H. Zhu, F. Wang, H. Sui, J. Fan, Preparation of a new inorganic–organic composite flocculant used in solid–liquid separation for waste drilling fluid, Chem. Eng. J., 171 (2011) 350–356.

[18] J. Addai-Mensah, C.A. Prestidge, Structure Formation in Dispersed System, H. Techemesser, B. Dobias, Eds., Coagulation and Flocculation, 2nd ed., Taylor & Francis Group, Boca Raton, 2005.

[19] M. Natalia, D. Olli, Environmental implications of aggregations phenomena: current understanding, Curr. Opin. Colloid Interface Sci., 11 (2006) 246–266.

[20] P.A. Moussas, A.I. Zouboulis, A new inorganic–organic composite coagulant, consisting of polyferric sulphate (PFS) and polyacrylamide (PAA), Water Res., 43 (2009) 3511–3524.

[21] Y. Wang, B.Y. Gao, Q.Y. Yue, J.C. Wei, W.Z. Zhou, Novel composite flocculent polyferric chloride–polydimethyldiallylammonium chloride (PFC – PDADMAC): its characterization and flocculation efficiency, Water Pract. Technol., 1 (2006) 1–9.

[22] N.D. Tzoupanos, A.I. Zouboulis, Preparation, characterisation and application of novel composite coagulants for surface water treatment, Water Res., 45 (2011) 3614–3626.

[23] W.Y. Yang, J.W. Qian, Z.Q. Shen, A novel flocculant of Al(OH)$_3$ polyacrylamide ionic hybrid, J. Colloid Interface Sci., 273 (2004) 400–405.

[24] K.E. Lee, T.T. Teng, N. Morad, B.T. Poh, Y.F. Hong, Flocculation of kaolin in water using novel calcium chloride–polyacrylamide (CaCl2 PAM) hybrid polymer, Sep. Purif. Technol., 75 (2010) 346–351.

[25] B.Y. Gao, Q.Y. Yue, Effect of SO$^{2-}_4$/Al$^{3+}$ ratio and OH$^-$/Al$^{3+}$ value on the haracterization of coagulant poly-aluminum-chloride-sulfate (PACS) and its coagulation performance in water treatment, Chemosphere, 61 (2005) 579–584.

[26] K. Thirugnanasambandham, V. Sivakumar, J.P. Maran, Response surface modelling and optimization of treatment of meat industry wastewater using electrochemical treatment method, J. Taiwan Inst. Chem. Eng., 46 (2015) 160–167.

[27] N. Yusoff, M. Ramasamy, S. Yusup, Taguchi's parametric design approach for the selection of optimization variables in a refrigerated gas plant, Chem. Eng. Res. Des., 89 (2011) 665–675.

[28] J.M. Parks, On stochastic optimization: Taguchi methods™ demystified; its limitations and fallacy clarified, Probab. Eng. Mech., 16 (2001) 87–101.

[29] K. Yang, E.C. Teo, F.K. Fuss, Application of Taguchi method in optimization of cervical ring cage, J. Biomech., 40 (2007) 3251–3256.

[30] A. Deghles, U. Kurt, Treatment of raw tannery wastewater by electrocoagulation technique: optimization of effective parameters using Taguchi method, Desal. Water Treat., 57 (2016) 14798–14809.

[31] F. Özyonar, H. Muratcobanoglu, O. Gökkus, Taguchi approach for color removal using electrocoagulation with different electrode connection types, Fresenius Environ. Bull., 26 (2017) 7600–7607.

[32] H.Y. Yen, C.P. Lin, Adsorption of Cd(II) from wastewater using spent coffee grounds by Taguchi optimization, Desal. Water Treat., 57 (2016) 11154–11161.

[33] F. Özyonar, Optimization of operational parameters of electrocoagulation process for real textile wastewater treatment using Taguchi experimental design method, Desal. Water Treat., 57 (2016) 2389–2399.

[34] Ö. Apaydin, E. Özkan, Landfill leachate treatment with electrocoagulation: optimization by using Taguchi method, Desal. Water Treat., 173 (2020) 65–76.

[35] M.P. Elizalde-Gonzalez, L.E. Garcia-Diaz, Application of a Taguchi L$_{16}$ orthogonal array for optimizing the removal of Acid Orange 8 using carbon with a low specific surface area, Chem. Eng. J., 163 (2010) 55–61.

[36] S. Irdemez, Y.S. Yildiz, V. Tosunoglu, Optimization of phosphate removal from wastewater by electrocoagulation with aluminum plate electrodes, Sep. Purif. Technol., 52 (2006) 394–401.

[37] APHA, AWWA, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, Washington, D.C., 1998.

[38] O. Gökkus, Y.S. Yıldız, B. Yavuz, Optimization of chemical coagulation of real textile wastewater using Taguchi experimental design method, Desal. Water Treat., 49 (2012) 263–271.

[39] K.E. Lee, N. Morad, T.T. Teng, B.T. Poh, Development, characterization and the application of hybrid materials in coagulation/flocculation of wastewater: a review, Chem. Eng. J., 203 (2012) 370–386.

[40] G. Eremektar, S. Goksen, F. Babuna, S. Dogruel, Coagulation–flocculation of wastewaters from a water-based paint and allied products industry and its effect on inert COD, J. Environ. Sci. Health. Part A Toxic/Hazard. Subst. Environ. Eng., 41 (2006) 1843–1852.

[41] M.A. El-Shazly, E.A. Hasanin, M.M. Kamel, Appropriate technology for industrial wastewater treatment of paint industry, Am. J. Agric. Environ. Sci., 8 (2010) 597–601.

[42] A.I. Zouboulis, N.D. Tzoupanos, Polyaluminium silicate chloride—a systematic study for the preparation and application of an efficient coagulant for water or wastewater treatment, J. Hazard. Mater., 162 (2009) 1379–1389.

[43] P. Zhang, H.H. Hahn, E. Hoffmann, G. Zeng, Influence of some additives to aluminium species distribution in aluminium coagulants, Chemosphere, 57 (2004) 1489–1494.

[44] B.Y. Gao, Q.Y. Yue, Y. Wang, Coagulation performance of polyaluminum silicate chloride (PASiC) for water and wastewater treatment, Sep. Purif. Technol., 56 (2007) 225–230.

[45] W.P. Cheng, F.H. Chi, C.C. Li, R.F. Yu, A study on the removal of organic substances from low-turbidity and low-alkalinity water with metalpolysilicate coagulants, Colloids Surf., A, 312 (2008) 238–244.