REMOVAL OF RESIDUAL CARCINOGENIC DYESTUFFS FROM INDUSTRIAL WASTEWATER USING FLOCCULATION TECHNIQUE

Abstract

Due to inefficient dyeing procedures in a typical dye industry, a large quantity of dye spills out into the wastewater, polluting it and causing serious harm to the environment. Consequently, special attention was focused on the use of a novel combination of a coagulant and a flocculant. As potato starch has already proved its strength as a bioflocculant, a combination of potato starch with iron(III) chloride as a coagulant was tested in order to achieve favorable results of dye reduction in simulated wastewater. The effect of various parameters on dye removal was investigated, like dosage of flocculant, temperature of treatment and flocculation time. Batch experimentation mode was adopted for the flocculation process, using a jar test apparatus. A mixed level parametric design (L_{16}) was employed for experimentation. The orthogonal tests revealed that the best operating parameters were: 2% of potato starch, 60 °C and 20 min of flocculation time. Furthermore, the significant factor test was performed using Minitab-17 from where the dosage of potato starch was proven to be the most significant factor. The study successfully raised dye removal efficiency up to 85% using a novel coagulant-flocculant combination. Finally, the results were compared with existing literature.

Keywords: ANOVA, iron chloride, potato starch, residual reactive dye, significance factor.
It is also observed that azo- and nitro- based dyes reduce to toxic amines. Subsequently, the handling and treatment of dye effluents becomes more complicated and leads to serious environmental concern. Furthermore, it is hard to decompose dyes due to their complex aromatic and molecular structure that provide stability to dyes. In addition, dyes are synthesized to resist fading by exposure to soaps, detergents, sunlight or oxidizing agents [3]. Consequently, eradication of residual dyes from textile runoffs has become vital and has gained more consideration than that of soluble colorless organic substances. In past, researchers focused on dye removal through ozonation, advanced oxidation, chemical precipitation and immersion that can be both expensive and cause further secondary pollution. Catalytic degradation and photochemical oxidation have also been utilized [1,4,5] but such oxidation processes can originate hazardous products, so that the treated wastewater becomes more hazardous than it originally was [6]. Biological treatments are also considered in combination with sorption processes for dye eradication from effluent streams [7,8]. However, various researchers have the opinion that the coagulation process proved to be the most efficient in comparison to other processes like anaerobic reduction, oxidation and adsorption [9].

A coagulant comparison study has been reported by Bidhendi and coworkers. They used lime, alum, FeCl₃, FeSO₄, and MgCl₂ in dye removal. The results revealed that only lime eliminates color and COD successfully but FeSO₄ was found to be optimal in dye removal owing to its lowest dosage, minimum sludge volume and maximum decoloration [10]. Recently, Guendy et al. performed a coagulation process in combination with adsorption for dye eradication and reported promising results. They further report that the dye removal was 71% at 6-8 pH and 53.7% at 4-6 pH when alum and FeCl₃ were utilized, respectively [11]. In contrary, Mitrovic et al. suggested the use of natural coagulants obtained from seeds of Moringa oleifera, Strychnos potatorum, extracts of cacti (Opuntia ficus-indica and Cactus latifaria) and different leguminous species such as Cassia angustifolia and Phaseolus vulgaris instead of chemical coagulants because of their biodegradability and environmentally friendly nature [12]. Subsequently, plant-based coagulants were also used for dye removal owing to their cost-effectiveness and environmental benefits [13]. For instance, the coagulation studies carried out by the use of coagulant extracted from the seeds of Moringa oleifera, Strychnos potatorum and other leguminous species provided a relatively low-cost solution to the problem [12]. Furthermore, the studies conducted on the usage of guar, locust bean [14].

Regarding the use of plant-based bioflocculants, it has been investigated that potato starch can be effectively utilized to reduce the concentration of dye from its solution. The results of the experimental investigations revealed that the dye removal was 37% in an acidic environment, i.e., at pH 3 [15]. Victor and coworkers investigated the usage of Moringa oleifera seed oil in combination with metallic salts, i.e., NaCl and FeCl₃ for reactive dye removal. They reported that dye removal with NaCl (as a coagulant) is better than that of FeCl₃. Further, the coagulation process is independent of pH but depends upon the chemical structure and the number of sulfonic groups present on the dye molecule [16]. Hence, contemporary studies focus on the use of FeCl₃ as a coagulant and potato starch as a bioflocculant. During the experiments, the pH of the solution was maintained at 3 by using FeCl₃, which also served as coagulant. A robust statistical experimental design (L₁₀) was used to vary the process parameters, i.e., flocculant dosage, temperature and flocculation time.

The design of experiments (DOE) was utilized as it proved to be a sturdy experimental design system that can analyse the significant factorial effects and conditions in the current manufacturing industry. The orthogonal arrays were utilized to arrange the factors that affect the process and the extent of their fluctuations [17,18]. Finally, the significant extent of the variables for the dye removal was deduced using nearly the 95% confidence level of the ANOVA. The variance analysis (ANOVA) has been extensively used in the interpretation of experimental data [19]. For this purpose, the latest version of available Mini-tab Software was utilized, as this software ensured the accuracy of numerous statistical calculations and provided improved quality calculation in the fields of engineering, statistics & mathematics.

**EXPERIMENTAL**

**Materials**

Analytical grade iron(III) chloride was purchased from Merck, Germany, to coagulate reactive dye. Reagent grade flocculant, i.e., potato starch was purchased from DaeJung, Korea. A yellow reactive dye with color index Y-145A was provided by Sandal Dye and Dyestuff Industries Limited, Faisalabad, Pakistan. It is worth noting that the aforementioned yellow dye is a single azo bi-functional dye that contains two functional groups, i.e., monochlorotriazine (MCT) and
vinyl sulfone (VS). The chemical structure of the dye is shown in Figure 1. In order to minimize disturbances and to compare the results with existing published literature, a synthetic stock solution of dye was prepared using reverse osmosis (RO) water available at University of Engineering & Technology, Faisalabad Campus, Pakistan.

![Figure 1. Structure of Y-145A yellow dye SDC.](image)

Preparation of the stock solution and characterization

The synthetic solution of reactive yellow dye was prepared by dissolving 150 mg of dye in 1000 ml RO water. The solution was heated to 60 °C after adding 10 g of sodium carbonate. The pH of the solution was adjusted to 10 by adding 1 M sodium hydroxide solution. The solution was stirred at a high temperature of 60 °C for 60 min. The solution was then cooled to room temperature and stored in an airtight container in order to avoid any nucleophilic reactions. The procedure of preparing the stock solution was described in Blackburn’s study [20]. The synthetic solution of dye was used during experimental runs to minimize the external disturbances produced by a typical dye house. Further, 150 ppm of reactive dye concentration was considered the highest in the wastewater [15].

The initial and final dye concentration was determined by estimating the true color of the solution, before and after treatment. Filtration was carried out using Whatman filter paper no. 42 and the filtrate was examined using a ZAR/HEC-1830/UV-2800 spectrophotometer at maximum absorption wavelength (λ_max) of 436 nm, as a reference. The calibration curve of absorbance vs. dye concentration was formulated (Figure 2) and the linear equation (Eq. (1)) of the calibration plot, \[ y = mx + c \] (\( y \) = absorbance; \( m \) = gradient; \( x \) = concentration; \( c = 0 \)), was used to calculate the concentration of the residual solution from the absorbency tests.

\[ y = 0.0019x + 0.175 \]  

Figure 2. Calibration curve of absorbance vs. dye concentration.

Experimentation

The coagulation-flocculation experimental trial was carried out in a jar test apparatus. 250 ml of stock solution was placed in a beaker and 3.2 g of iron(III) chloride was added to the solution, which not only reduced the pH from 10 to 3 but also served as coagulant. The solution was stirred at the rate of 100 rpm for 5 min to speed up the coagulation process. Then stirring was reduced to 40 rpm and potato starch (bioflocculant) was added. Further, the stirring was carried out for 20 min and the flocculation time was up to 50 min to study the effect of flocculation time. Afterwards, the stirring was stopped and sediments were allowed to settle down for 1 h. In addition, the experimental procedure was repeated by altering the flocculant dosage, solution temperature and flocculation time according to Table 1, to determine the parametric effects. It is also worth noting that the dye concentration, pH, coagulant dosage, coagulation time, flocculation speed and coagulation stirring was kept constant at 150 ppm, 3, 3.2 g per 250 ml, 5 min, 40 and 100 rpm, respectively. All experiments were carried out as shown in Table 2. The supernatant was filtered after sedimentation and the residual dye concentration of filtrate was determined by a UV-visible spectrophotometer. The removal efficiency of the reactive dye was calculated according to Eq. (2):

\[ \eta = 100 \left( 1 - \frac{C_e}{C_0} \right) \]  

where \( \eta \) is the percentage removal efficiency, \( C_0 \) is the initial concentration of dye at the start of experimentation and \( C_e \) is the final concentration of dye after experimentation at flocculation time \( t \). The experimental data used in the study was the average of threefold determination. The relative standard error of the data was less than 5%.
Table 1. Parameters and their values corresponding to their levels

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
<th>Parameter level</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>Flocculant dosage, %</td>
<td>0.25 0.5 1 2</td>
</tr>
<tr>
<td>B</td>
<td>Temperature of wastewater, °C</td>
<td>25 40 50 60</td>
</tr>
<tr>
<td>C</td>
<td>Flocculation time, min</td>
<td>20 30 40 50</td>
</tr>
</tbody>
</table>

Table 2. Experimental design and results of conducted experiments corresponding to L16 OA experimental plan

<table>
<thead>
<tr>
<th>Exp. #</th>
<th>Parametric level</th>
<th>Absorbance/percentage absorbance reduction</th>
<th>Concentration (ppm)/percentage reduction in concentration</th>
<th>Conc. reduction, mean (%)</th>
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<tr>
<td>A B C</td>
<td>I II III</td>
<td>I II III</td>
<td>I II III</td>
<td></td>
</tr>
<tr>
<td>1 1 1</td>
<td>0.65/56</td>
<td>0.639/57</td>
<td>0.645/57</td>
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<td>2 3 1</td>
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<td>0.799/46</td>
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<td>329/52.3</td>
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<tr>
<td>3 2 2</td>
<td>0.542/64</td>
<td>0.544/63</td>
<td>0.539/64</td>
<td>193/72</td>
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<tr>
<td>4 3 1</td>
<td>0.53/64</td>
<td>0.529/64</td>
<td>0.563/64</td>
<td>187/72.9</td>
</tr>
<tr>
<td>5 3 2</td>
<td>0.42/72</td>
<td>0.418/72</td>
<td>0.411/72</td>
<td>129/81.3</td>
</tr>
<tr>
<td>6 3 4</td>
<td>0.44/70</td>
<td>0.438/71</td>
<td>0.433/71</td>
<td>139/79.8</td>
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<tr>
<td>7 4 4</td>
<td>0.391/74</td>
<td>0.389/74</td>
<td>0.355/76</td>
<td>114/83.5</td>
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<td>1.974/-44.6</td>
<td>1.958/-43.4</td>
<td>937/-49.7</td>
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</table>

RESULTS AND DISCUSSION

In this study, a novel combination of iron(III) chloride as a coagulant and potato starch as a flocculant, was tested to remove reactive yellow dye from its solution. The effects of the flocculant dose (%), temperature (°C) and flocculation time (min) on dye removal was examined in accordance to the L16 robust design. The results are described, statistically supported and graphically explained in the subsequent section.

Effect of flocculant dosage on dye removal

It has already been reported that flocculant dosage is a crucial parameter in the removal efficiency of dye from wastewater, as inadequate dosage may result in performance reduction [21]. Therefore, the impact of flocculant dosage was analyzed in the range 0.25 to 2 wt.%. It is evident, from Figure 3, that the dye removal percentage increased drastically with an increase in the flocculant dose up to the concentration of 1 wt.%. The behavior was the same as observed during the performance evaluation of other plant-based biopolymers. This sudden increase in performance is due to the increase in charge density when increasing dosage, resulting in the availability of extended surface area [22]. According to coagulation theory, the charge on the dye molecule is neutralized by the polymer and it bounds to the polymer surface by weak forces like van der Waals forces. This floc combines with other flocs to form a high-density floc. The phenomena are modelled in Figure 4a. In contrast, the dye removal percentage decreases sharply to the negative values with further increase in the amount of the flocculant and the reason can be best explained on the basis of the phenomenon of producing restabilized colloids on excessive polymer dosage [22]. The potato starch ionizes in water, producing polymer ions which are bonded to one another with van der Waals forces, so the excess dosage always results in an agglomeration of particles, producing restabilized colloids. This phenomenon is modelled in Figure 4b, where excess polymer dosage resulted in the formation of restabilized colloids. As a result, the high concentration of potato starch causes damping the active sites which results in the decrease
of dye removal percentage. As a matter of fact, the coagulant neutralizes the charge on dye molecules in water so that the flocculant may work effectively. Hence, very low and very high flocculant dosages will fail to produce restabilized colloids, which would result in the increase in the haziness of the solution.

Effect of flocculation time on dye removal

The effect of flocculation time on dye removal was investigated and is presented in Figure 3. It is evident that there is a sharp decrease in dye removal when prolonging the experiment and the trend is leveled off after 40 min of flocculation time. In a flocculation process, the flocculant adsorbs on the particle surface, making inter-particle bridging and development of flocs possible, which helps in the agglomeration of particles (Figure 5a). Hence, the density is increased and the colloids settled down in the form of sludge. If the flocculation is given more time the molecular chains tend to disintegrate resulting in small size flocs which are not dense enough to settle in the wastewater causing the sample to be turbid again [23]. This phenomenon was observed in Figure 3 which showed rather negative values for the dye removal at longer flocculation time. Hence, it can be concluded that longer flocculation time will lead to an increase in floc disintegration due to prolonged interaction, therefore decreasing the flocculation rate.

Effect of temperature on dye removal

The effect of temperature on dye removal was investigated in the range of 25-60 °C and the results are presented in Figure 3. It can be deduced that adequate levels of dye removal were observed at high and low temperatures, i.e., 20 and 60 °C. The
elevated temperature favors dye removal as it helps to break the inter- and intra-molecular hydrogen bonds between the polymer molecules. As a matter of fact, potato starch, similar in its structure with cellulose, requires high energy to break the hydrogen bonds between polymer chains, in order to allow formation of hydrogen bonds with the dye molecule for its removal. When the polymer is subjected to elevated temperatures, all the polymer chains (11 hydrogen bond collectors) will be unlocked, enriching the surface with negative charge. This allows hydrogen bonding and van der Waals interactions during its contact with positively charged functional groups of the reactive yellow dye [20]. On the other hand, adequate levels of dye removal were observed at a low temperature, and this increase in dye removal may be due to electrostatic forces. At low temperatures, active sites are not fully available, with the positive charge dominating on the surface of potato starch due to the low pH and hydrogen bond donors. This results in a sensible elimination of dye with the interaction of potato starch with hydrophobic sites of the dye, stabilizing the negative charge by electrostatic forces. In conclusion, low temperature is also successful in giving reasonable dye removal rates, but in combination with low pH as electrostatic forces prove to be significant only at low pH [6].

ANOVA results

To determine the effect of each factor on percentage reduction in dye concentration, variance analysis was applied. Statistical significance of the model equation and model terms was evaluated by the significant factor (f) test and ANOVA. To simplify and standardize experimental design and to minimize the number of factor combinations required to test the factor effects, a special design of orthogonal arrays (L16) was employed. In this study, Minitab-17 computer software package was used to establish the experimental matrix according to parameters and their levels, and for the evaluation by analysis of variance (ANOVA) analysis of the obtained results. The results of ANOVA are illustrated in Table 3 and the resulting regression equation is Eq. (3). It can be inferred that the most critical and sensitive parameter for the coagulation process is the dosage percentage, whose maximum f value is 5.78. The removal of reactive dyes with potato starch is less sensitive to the effects of temperature. The p-value was also calculated from ANOVA, concluding that the null hypothesis is true as p-value is less than the significance level. To verify to what extent the given model fits the data, goodness of fit statistics were examined for the presented model and are presented in Table 3. The standard deviation ‘S’ was evaluated in the units of the response variable which represents the deviation to the extent at which the data values fall from the fixed values. For the model, 62% of data lies within the standard deviation from the mean. Further, $R^2$ was estimated as it is the percentage of variation in the response that is clarified by the model. The model shows a good $R^2$ value of 85.6%.

\[
\eta = -3.41D_1 - 22.9D_2 + 68.3D_3 - 19.5D_4 + 5.6T_1 + \\
+ 9.8T_2 - 27.6T_3 + 12.2F_4 + 64.8F_1 - \\
-21F_2 - 22.5F_3 - 21.4F_4
\]  

(3)

where $D_i$ is dosage of 0.25%; $D_i$ is dosage of 0.50%; $D_i$ is dosage of 1%; $D_i$ is dosage of 2%; $T_1$ is temperature of 25 °C; $T_2$ is temperature of 40 °C; $T_3$ is temperature of 50 °C; $T_4$ is temperature of 60 °C; $F_1$ is flocculation time of 20 min; $F_2$ is flocculation time of 30 min; $F_3$ is flocculation time of 40 min; $F_4$ is flocculation time of 50 min, while $\eta$ is the percentage removal efficiency.

Comparison of results

The results were compared with existing literature regarding the removal of carcinogenic dye from aqueous waste. Kim and co-workers studied the coagulation process for the removal of Reactive Blue 49 and Reactive Yellow 84 dyes and reported that the concentration of the dyestuff was reduced to an acceptable percentage of 60.9 and 70.3% respect-
The rates were obtained at the optimum coagulation conditions of pH 7 and 1.85 mmol/L of FeCl₃ for Reactive blue 49 and pH 6 and 2.78 mmol/L of FeCl₃ for Reactive blue 49. Iron(III) chloride successfully neutralized the charge on dye molecules which resulted in the form of dye eradication via sludge formation [24]. Most recently, the same class of dye (reactive) was eradicated from its synthetic solution via a plant-based biopolymer, i.e., potato starch. The studies tested this novel polysaccharide on the removal of Reactive Yellow 145 and reported that the potato starch behaves both as a coagulant and a flocculant when varying the mixing rate. However, the removal of dye concentration was only 41.3%, but the sludge formation was minimized to the lowest level of 0.06%, which was the main novelty of the process. Moreover, it was reported that the 41.3% reduction was observed at pH 3 [15].

This study successfully raised dye removal efficiency using a novel coagulant-flocculant combination. The process utilized potato starch as the bioflocculant, while fixing the pH of the synthetic solution at 3. Iron(III) chloride was used as a pH depressant as well as the coagulant. As a result, 85% reduction in dye concentration was observed at flocculant dosage of 2%, temperature of 60 °C and 20 min flocculation time. The comparison of studies is well illustrated in Figure 6, along with the literature cited. In addition, Figure 6 also shows the comparison in terms of percentage reduction in absorbance. In conclusion, the study successfully uplifted the study of dye removal using a novel coagulant-flocculant combination.

CONCLUSIONS

The study focused on the coagulation-flocculation process for the elimination of Reactive Yellow 145 dye from its synthetic solution. The process successfully eradicated the dye using a novel coagulant-flocculant combination. Based on the results of the current investigation on the use of FeCl₃ as a coagulant and potato starch as a bioflocculant, it was observed that the above combination provided promising results during the initial investigation and reduced the concentration of dye up to 85%. Hence, the combination proved its worth regarding the pre-treatment process of wastewater containing dye. Among the parameters investigated, the dosage of potato starch has proved to be the most significant parameter having the most weighted significance, i.e., 5.78. Further, the best operating conditions came to be: flocculant dosage: 2%, temperature: 60 °C and flocculation time: 20 min. Finally, the results were compared with the latest existing literature and the combination proves its novelty. The current combination of sorbents increased the eradication of dye by 50% as compared to the most recent published literature. In conclusion, the combination can be effectively utilized as a pre-treatment step for the treatment of textile effluents. The treated wastewater will not pose considerable harm to microorganisms and, if drained into open water channels, will pose less harm to the ecosystem.

Future scope. Very limited work has been carried out on the desorption of dyes to study the exact mechanism of dye removal. It would help to study the regeneration of exhausted adsorbents and dye in...
order to make the adsorption process more economical. Conducting more research into coagulant-flocculant combinations which are capable of eradicating the dyes even in the presence of various interfering agents of textile wastewaters is also needed. In addition, the effectiveness of a greater number of natural coagulants needs to be assessed at a wide variation of pH.

REFERENCES