Statistical Modelling of a Comparative Phytotoxicity Study of Treated Yellow 10Gw Dye Solution With Copper and Aluminum in Electrocoagulation Process

Kalivel Parameswari*, M. Vijila**† and P. Jegathambal***
*Department of Chemistry, Karunya Institute of Technology and Sciences, Coimbatore-641114, Tamil Nadu, India
**Department of Mathematics, Karunya Institute of Technology and Sciences, Coimbatore-641114, Tamil Nadu, India
***Department of Water Institute, Karunya Institute of Technology and Sciences, Coimbatore-641114, Tamil Nadu, India
†Corresponding author: M. Vijila; vijilamoses@karunya.edu

ABSTRACT

This work was carried to compare the efficiency of Cu and Al electrodes in the elimination of Yellow 10 gw dye solution with the optimization of operative factors such as pH, NaCl, contact time, and current density in the electrocoagulation method. Analysis of variance (ANOVA) was used to assess the impact of these variables, with significance set at P<0.05. The data was statistically examined with Origin2021 and SPSS software, and significant differences between mean values were determined using analysis of variance (ANOVA). For each experiment, duplicates were kept, and the efficiency of Yellow 10 gw dye solution for those parameters was derived using analysis at a 5% level of significance. The utility of treated dye solutions using both the electrodes was tested on V.radiata in terms of germination percentage, root, and shoot length with distilled water as control. For all of the qualities examined, significant disparities were found among entries. The dye solution used with Al resulted in much higher germination (100%), root length (9.72 cm), and shoot length (24.5 cm).

INTRODUCTION

Textile industry processes use a lot of water, particularly for wet processes like dying, and as a result, the wastewater generated contains synthetic dyestuffs. It has also been documented that nearly 10% of the dye is lost during the dyeing process due to a lack of fabric adherence (Garg & Kaushik 2018). These synthetic dyes in water pollute and affect all water sources, including groundwater and surface water. They can have a negative impact on marine life, agricultural practices, and human health. Furthermore, the majority of the synthetic dyes used in these units have not been tested for their environmental and health effects. Chemical oxygen demand (COD), color, and salt levels in effluent from various units in a textile hub are all high, and the volume of water produced and discharged as waste by these sectors is rapidly expanding, and it contains a variety of contaminants (Rasalingam et al. 2014).

To treat the wastewater produced by the textile industries, methods like chemical, physical, biological, electrochemical are employed. Among which chemical treatments include coagulation, ozonation, advanced photochemical oxidation, (Glaze & Chapin 1987, Marcucci et al. 2002, Molkenthin et al. 2013), filtration techniques such as reverse osmosis, nanofiltration (Merayo et al. 2013), ultrafiltration, and microfiltration using suitable membranes (Chakraborty et al. 2003, Wang et al. 2016). Each of these approaches has its own advantages, but they are all costly and time-consuming. Physical treatment, on the other hand, necessitates the use of extra chemicals and produces a significant volume of sludge.

Disperse dyes are one of the many forms of synthetic dyes available, and are non-ionic, sparingly soluble in water, and applied to hydrophobic fibers from an aqueous phase (Clark 2011). They are mostly used on polyester, but they have also been used on nylon, cellulose acetate, and acrylic fibers, however, some of the dyes’ wet-fastness capabilities on these substrates are not great (Saquib & Muneer 2003, Hassan et al. 2009). Diverse chromophores for instance azo, anthraquinone, and triphenylmethane, contribute to the structural diversity of synthetic disperse dyes. Azo dyes are the most common disperse type, accounting for more than half of all disperse dyes (Qiu et al. 2020). Due to their resistive character and non-biodegradable activity, these dyes are classified as persistent (Jamil et al. 2020, Shamey 2009). Anthraquinone dyes are the second most often used dyes after azo dyes because of their inexpensive cost, quick accessibility, and high dyeing effectiveness. Anthraquinone dyes are more harmful to microorganisms and human cells because they have a more complicated and stable structure than azo dyes (Novotnyet al. 2006). In contrast to azo dyes,
the carbonyl group in the anthraquinone structure acts as an electron acceptor, requiring an electron donor to react and serve the structure; however, research reveals that anthraquinone dyes are difficult to degrade when compared to azo dyes (Mishra & Maiti 2018). The combined effects of resonance in the anthracene structure make it more difficult to decolorize AQ colors than azo dyes (Lizama et al. 2001, Sekuljica et al. 2016), raising questions about the possibility of a successful decolorization operation (Khataee et al. 2016).

Photocatalytic oxidation (Samanta et al. 2018), Fenton oxidation (Lovato et al. 2017), ultrasonic catalytic oxidation (Santos et al. 2005) are some of the treatment methods for anthraquinone dye degradation. AOP is notable for its extremely fewer reaction times, typically a few minutes, high efficacy, and dye sedimentation on decolorization of AQ dyes, but it is also notable for its high cost, which makes scaling up difficult (Castro et al. 2014, Khataee & Kasiri 2010).

Recent research has looked at biological strategies for AQ dye degradation in aerobic and anaerobic cultures (Cesaro & Belgiorno 2013, Padmanaban et al. 2013). The challenge is to develop reliable, cost-effective, and environmentally sustainable bioremediation methods that overcome the limitations of traditional methods (Husain & Ulber 2011, Li et al. 2019). There are also no data on the toxic, mutagenic, or carcinogenic intermediate products produced during the degradation of certain AQ colors, making it difficult to choose the correct type of treatment procedure.

Amongst the electrochemical methods, electrocoagulation does not involve any additional chemicals and is a relatively simple procedure that creates a small amount of sludge (Zhou et al. 2019) and it has become the focus of wastewater treatment research in recent years since it is easy to operate and produces less sludge. In this sense, electrocoagulation appears to be a viable alternative to physical and chemical methods since the procedure is simple to implement. EC appears to be a promising option for removing dissolved solids and colloidal particles from textile dyeing wastewater in the tertiary treatment stage. The efficacy in the dye abatement depends on the anodization, hydroxides production, size, and the colloidal properties of the particles. Reactive Blue 19 (Khoshhesab & Ahmadi 2016) and basic Yellow 28 dye effluent were successfully eliminated using the EC technique (Gaber et al. 2013, Sangeetha et al. 2009), Red disperse, Blue reactive, and mixed dyes (Phalakornkule et al. 2010, Polgumhang et al. 201). Abatement of Yellow 10gw dye (a type of anthraquinone disperse dye) aqueous solution was studied in this work focusing on optimizing the operative parameters such as pH, electrolyte, current density, and contact time for maximum abatement of the dye using two different electrodes, one with Al electrodes and the other with Cu electrodes and the findings were compared to the efficacy of the electrodes used.

An analytical technique like X-ray Photoelectron Spectroscopy (XPS) analysis was employed to investigate the efficiency of the EC process in the sludge separated. To examine the possibility of reusing the treated dye solution, phytotoxicity tests with V. radiata seeds were performed, and the results were compared to the control (distilled water) in terms of percent-age of germination, length of root, and shoot. We previously analyzed the performance of Zn/TiO₂ electrodes prepared by spray pyrolysis in treating Coralene Red 3G dye for color removal in electrocoagulation technique with optimization of operating parameters. The efficiency of color removal for parameters such as pH, dye concentration, electrolyte, applied current, and time was estimated using design experts software and an ANOVA design model (Nayak & Pal 2020, Praveen et al. 2011).

In another study, we had discussed and compared the efficiency of Al-Al and Cu-Cu electrodes in the elimination of Blue SI dye aqueous solution in the electrocoagulation process with the optimization of operational parameters such as pH, the concentration of electrolyte, current density, and electrolysis time using design experts’ software and the experimental data were analyzed by variance analysis (ANOVA) (Kalivel et al. 2019).

**MATERIALS AND METHODS**

Two sets of experiments were conducted with Cu and Al electrodes for optimization of operative factors such as contact time, pH, current density, and electrolyte concentration for the abatement of Yellow 10 gw dye solution.

For each process, 250 mL of the Yellow 10 gw dye (150 mg), solution as test solution was taken in a 500 mL beaker with DC connection and stirrer. In the first set, we used Al as anode and cathode, in the next set of experiments Cu was used as anode and cathode, and the results were compared for each operational parameter used. The experiments were conducted at 25°C. The consequence of initial pH (5, 6, 7, 8, 9), contact time (5, 10, 15, 20, 25 mins), current density (20, 40, 60, 80, and 100 Am⁻²) and electrolyte concentration (NaCl: 1 to 5 gm.L⁻¹) were studied on the dye abatement. The dye absorbance was determined before and after the process with the Jasco V-670 spectrophotometer, and the dye concentration was assessed with the absorbance at 542 nm.

Dye abatement efficiency (DAE %) was calculated using the following

\[
\text{DAE} = 100 \times \frac{(A_a - A_b)}{A_a} \quad (1)
\]

Where A_a and A_b were the absorbance of dye solution before electrocoagulation and at time t, respectively.
Phytoxicity Investigation

Dye components can influence the entire photosynthesis process and eventually inhibit plant growth, even at very low concentrations in water, and dye degradation releases a range of intermediate products that must be non-toxic to the environment. To determine the likelihood of the treated water being reused, a phytoxicity study was conducted on the growth of V. radiata seeds using a 150mg.L⁻¹ Yellow 10gw dye solution, a treated dye solution with Al and Cu, and tap water as a control. Twenty sterilized seeds were placed in a 250 mL beaker with 150 g autoclaved soil and exposed to sunlight after being soaked in 0.1 percent (w/v) mercuric chloride and then splashed three times with distilled water to remove any traces of mercury.

With an equal volume of treated, untreated Yellow 10gw aqueous solution and tap water, the seed germination and plant growth were studied. Germination percentage, root, and shoot length were calculated after 10 days, and the results were compared to the control

\[
\text{% of Germination} = \frac{\text{number of seeds germinated}}{\text{Total number of seeds sown}} \times 100
\]

... (2)

RESULTS AND DISCUSSION

The effects of various parameters on the percentage of color removal of the Yellow 10gw dye aqueous solution were determined using analysis of variance (ANOVA). The p-value associated with the F statistics is used to assess if they are high enough to establish statistical significance (Kalivel et al. 2020). The regression model equation fitted by the curve is a second-order polynomial equation for the percentage color removal of Yellow 10gw dye aqueous solution as a function of pH(X1), NaCl (X2), current density (X3), and contact time (X4) (Kunasekarn et al. 2017).

\[
Y_i = b_0 + \sum b_i x_i + \sum b_{ij} x_i^2 + \sum \sum b_{ij} x_i x_j \quad \ldots (3)
\]

Where \(Y_i\) is the amount of efficiency of removing the dye

\[b_0 = \text{Constant coefficient}\]

\[b_i = \text{Regression coefficients for linear effects}\]

\[b_{ij} = \text{Interaction coefficients and } x_i, x_j \text{ are the parameters.}\]

When comparing pH to time, the \(r^2\) value was 0.312, which was significant at \(P < 0.05\). In the current study, this method was used to measure the effectiveness of adsorption of the Yellow 10Gw dye solution under a variety of conditions, including pH, NaCl, current density, and contact time.

From Table 1, we found no statistically significant (p > 0.05) differences in pH for Cu electrodes. Therefore, we could not conclude that the model explains variation in the operational behaviors such as pH, NaCl, contact time, and current density.

Table 1: pH with Time in Cu electrodes.

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>Df</th>
<th>Mean Square</th>
<th>F-value</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-Time</td>
<td>1.016E-07</td>
<td>1</td>
<td>1.016E-07</td>
<td>0.5654</td>
<td>0.4613</td>
</tr>
<tr>
<td>A²</td>
<td>1.428E-07</td>
<td>1</td>
<td>1.428E-07</td>
<td>0.7951</td>
<td>0.3837</td>
</tr>
<tr>
<td>AB</td>
<td>4.185E-07</td>
<td>1</td>
<td>4.185E-07</td>
<td>2.33</td>
<td>0.1434</td>
</tr>
<tr>
<td>A-pH</td>
<td>4.870E-07</td>
<td>1</td>
<td>4.870E-07</td>
<td>2.71</td>
<td>0.1161</td>
</tr>
<tr>
<td>B²</td>
<td>7.492E-07</td>
<td>1</td>
<td>7.492E-07</td>
<td>4.17</td>
<td>0.0553</td>
</tr>
<tr>
<td>Model</td>
<td>1.615E-06</td>
<td>5</td>
<td>3.230E-07</td>
<td>1.80</td>
<td>0.1615</td>
</tr>
<tr>
<td>Residual</td>
<td>3.413E-06</td>
<td>19</td>
<td>1.796E-07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>5.028E-06</td>
<td>24</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
time period. Therefore, there is enough evidence to say that the model explains variation in the operational behaviors such as pH, NaCl, contact time, and current density.

Fig. 2 suggests that some of the variations in the response are due to contact time. As the pattern is quite random, this indicates that a linear regression model is appropriate for Al electrodes.

The F-value of 2.90 indicates that it is statistically significant at the 5% level.

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**Phytotoxicity study on V. radiata**

When comparing Yellow 10gw dye solution with treated dye solution utilizing Al, Cu in this study, the value of $r^2$ was 0.378 (significant at $P > 0.05$). We discovered that plant’s root and shoot length grown in Yellow 10gw dye solution treated with Al electrodes resulted in increased length of both.

According to Fig. 3 and 4, Al electrodes were the best when compared to other electrodes.
Table 2: pH with contact time in Al electrodes.

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>Df</th>
<th>Mean Square</th>
<th>F-value</th>
<th>p-value</th>
<th>significant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>2.161E-06</td>
<td>5</td>
<td>4.322E-07</td>
<td>2.90</td>
<td>0.0411</td>
<td>significant</td>
</tr>
<tr>
<td>A-pH</td>
<td>4.532E-07</td>
<td>1</td>
<td>4.532E-07</td>
<td>3.04</td>
<td>0.0971</td>
<td></td>
</tr>
<tr>
<td>B-Time</td>
<td>1.974E-07</td>
<td>1</td>
<td>1.974E-07</td>
<td>1.33</td>
<td>0.2637</td>
<td></td>
</tr>
<tr>
<td>AB</td>
<td>1.889E-08</td>
<td>1</td>
<td>1.889E-08</td>
<td>0.1269</td>
<td>0.7256</td>
<td></td>
</tr>
<tr>
<td>A²</td>
<td>6.453E-07</td>
<td>1</td>
<td>6.453E-07</td>
<td>4.34</td>
<td>0.0511</td>
<td></td>
</tr>
<tr>
<td>B²</td>
<td>1.064E-06</td>
<td>1</td>
<td>1.064E-06</td>
<td>7.15</td>
<td>0.0150</td>
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</tr>
<tr>
<td>Residual</td>
<td>2.828E-06</td>
<td>19</td>
<td>1.488E-07</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>4.989E-06</td>
<td>24</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

XPS Analysis of Sludge

Al and Cu XPS survey spectra as well as high-resolution core line spectra [(Al, Al2p) and (Cu, Cu2p³)] (a-d) are given in Fig. 5. It has been claimed that the capacity of Al to generate dimeric, trimeric, and polynuclear hydrolysis products can be formed during the anodization process (Saha et al. 2015, Jeurgens et al. 2002, Liu et al. 2016).

However, the development of different forms of M(OH)n is dependent on various factors, including the composition of the anode metal during anodization, hydroxides from the cathode, and so on. This study contributes to a better understanding of the electrochemistry of metal hydroxide
Table 3: Overall statistics and analysis of variance.

Descriptive statistics for phytotoxicity of Yellow 10gw dye solution treated dye solution using Al

<table>
<thead>
<tr>
<th>Sample Size</th>
<th>Mean</th>
<th>Standard Deviation</th>
<th>SE of Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Germination</td>
<td>86.028</td>
<td>30.90759</td>
<td>9.77384</td>
</tr>
<tr>
<td>Stem</td>
<td>39.609</td>
<td>31.82887</td>
<td>10.06517</td>
</tr>
</tbody>
</table>

ANOVA for phytotoxicity of Yellow 10gw dye solution Vs treated dye solution using Al

<table>
<thead>
<tr>
<th>Source</th>
<th>df</th>
<th>Sum of Squares</th>
<th>Mean Square</th>
<th>F Value</th>
<th>Prob &gt; F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model1</td>
<td>10</td>
<td>773.6178</td>
<td>10773.6178</td>
<td>10.94682</td>
<td>0.00391</td>
</tr>
<tr>
<td>Error</td>
<td>18</td>
<td>17715.20085</td>
<td>984.17783</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>19</td>
<td>28488.81866</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fit statistics

<table>
<thead>
<tr>
<th>R-Square</th>
<th>Coeff Var</th>
<th>Root MSE</th>
<th>Data Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.37817</td>
<td>0.4994</td>
<td>31.37161</td>
<td>62.8185</td>
</tr>
</tbody>
</table>

Fig. 5: Al and Cu XPS survey spectra and high-resolution core line spectra [(Al, Al2p) and (Cu, Cu2p3)].
formations, as well as a better understanding of the different types of metal hydroxides that are produced, which aids in the coagulation of dye molecules and the evaluation of the electrodes' efficacy in the removal of dye pollutants. From the high-resolution core spectra of Al2p, the binding energy value of Al as gibbsite 74.4 eV [γ-Al(OH)3], bayerite [Al(OH)3] 75.0 eV [Al(OH)3], Boehmite [AlO(OH)] 73.9 eV and pseudoboehmite [AlO(OH)] 74.3 eV were found and it was noteworthy to conclude that there are four types of hydroxides of Al formed, such as [Al(OH)3] gibbsite, [Al(OH)3] bayerite, [AlO(OH)] boehmite and [AlO(OH)] pseudoboehmite.

XPS analysis of copper electrodes revealed a binding energy value of 934.06 eV for copper in its +2 oxidation state, showing that the metal hydroxide as flocs formed in the EC operation with copper was Cu(OH)2, which was supported by published work (Kloprogge et al. 2006). The efficacy of Al metal over Cu was substantiated by XPS studies of the respective sludge in the process.

CONCLUSION

The percentage of Yellow 10gw dye removed from aqueous solution using Cu and Al electrodes in the EC method exhibits a linear relationship with pH, electrolyte concentration, contact time, and current density, and with a substantial interaction between the amount of adsorbent and dye concentration. The use of Al exhibited better results in the germination, root, and shoot length of V.radiata than the dye solution used with Cu electrodes in comparison to the control in the phytotoxicity study of V.radiata with treated dye solutions. The improved performance of Al was demonstrated by XPS analysis of the corresponding sludge, which revealed four different types of hydroxides as adsorbents in the Al process versus just one hydroxide from the process used with copper electrodes.

REFERENCES


