This research investigated design of experiment for the optimization of the experimental parameters of the photocatalytic degradation of VAT yellow dye using dye concentration (mg/L), catalyst dosage (mg/L), pH and time of exposure (minutes) as experimental factors. Stock solution of vat yellow dye was prepared (0.00001M) and serial dilution was used to prepare twenty seven (27) different concentrations of the dye solution which were subjected to photocatalytic degradation in a photo reactor using a ultraviolet light source under ambient environmental condition. The absorbances of these solutions before and after photo degradation were taken to obtain different percentage degradation for each experimental run. Analysis of these results was carried out using minitab18 computer software. The result revealed the best conditions for the photodegradation as (20mg/l) (dye concentration), (2mg/L) (catalyst dosage), 3.39 pH and 45 minutes (time of exposure). This was confirmed experimentally after the optimization to prove that minitab18 software is highly effective for the optimization of photodegradation of tannery and textile effluent containing reactive red dye.

KEYWORDS
Photocatalytic, Parameter, Dye, Minitab18 and Optimization.

1. INTRODUCTION

Different techniques such as biological detoxification, pyrolysis, biosorption, complexation, precipitation, solvent extraction, physicochemical remediation, phytochemical remediation, microbial remediation, ion-exchange, membrane processes, adsorption using activated carbon, coagulation and others have been used for the treatment of effluents (Goncalves et al, 2019). These techniques are not capable of destroying the dye components of the effluents which may be carcinogenic and highly toxic if absorbed by human through consumption of food or water contaminated by the effluent (Halmann, 2002). Advanced oxidation processes (AOPs) have been developed and used to destroy the dye components of these effluents in a process known as photodegradation (Finar, 2001).

Effluents from textile and leather industries contain high level contaminants of unconsumed dyes, surfactants and trace metals. (Gilws, 2015). This constitutes a major source of environmental pollution which is indeed a National threat (IUPAC, 1996). Heterogeneous photocatalysis via combination of titanium (IV) oxide and hydrogen peroxide as photocatalysts and ultra-violet light is considered one of the most promising advanced oxidation processes for destruction of dye components in water soluble organic pollutants (Fujishima et al., 2019). In this research, design of experiment was used to optimize the photocatalytic degradation of vat yellow dye (Hallas, 2010). Optimization is a way of adjusting controllable variables in any process to find out the suitable factors level that gives the best possible outcome (response) (Grigg, 2001). Design of experiment is a statistical based structural approach to processes that will quickly yield significant increase in product quality. It is aimed at designing and developing process in shorter time and get maximum result (Fox and Dulay, 2020). The basic principles of design of experiment (DOE) involves: randomization, replication and blocking. It includes the steps for planning and analyzing an experiment.

1.1 Statement of Research Problem

This research is aimed at subjecting vat yellow dye used in leather and textile industries to photodegradation using TiO2 and hydrogen peroxides as catalysts in order to eliminate dye concentrations from industrial effluents and optimization of their photodegradation parameters.

1.2 Justification of the Study

Discharge of textile and tannery untreated effluents to the environment and water bodies poses a threat to the environment and aquatic lives, hence the need for the degradation of these dyes using an economical and more environmentally friendly method.

1.3 Aim And Objectives

The aim of the study is to carry out photocatalytic degradation of VAT YELLOW dyes used in Textile and Leather industries, using design of experiment.

The aim was achieved by the following objectives:

(1) Characterizing the dyes using Thinlayer chromatography, UV-visible spectrophotometry, Fourier Transform infrared Spectrophotometry (FTIR) and Gas Chromatography Mass Spectrometry, GCMS.

(2) Carrying out degradation studies on the dyes based on the following operational parameters; dye concentration (mg/L), catalyst loading (mg/L), time of irradiation (min), and pH of the dye.

(3) Studying the inter-dependence of these variables and how they
affect degradation of the dyes using design of experiment.

(4) Determination of the optimized operational parameters.
(5) Experimental confirmation of the optimized conditions.

1.4 Significance of Research
The significance of the research is that environment pollution is a Global issue and it requires serious attention.

1.5 Scope of The Study
The research work is limited to VAT YELLOW dye commonly used in textile and leather industries. Characterization of the dyes and photodegradation studies of the dye and optimization of their process parameters using design of experiment.

2. LITERATURE REVIEW
Advanced oxidation processes (AOPs), uniting together ozone and high output ultraviolet technologies, in conjunction with hydrogen peroxide and catalyst are successfully used to decompose many toxic and bio-resistant organic pollutants in aqueous solution to acceptable levels, without producing additional hazardous by-products or sludge which require further treatment. Advanced oxidation processes involve the generation of hydroxyl (OH*) radicals which oxidize the pollutants (Gordon and Gregory, 2018). The hydroxyl radical is able to oxidize and mineralize almost every organic molecule, yielding CO2 and inorganic ions as shown below:

*OH + RH → R* + H2O
R* + O2 → RO2
RO2 → Products and CO2

TiO2-based photocatalysis appears as the most emerging destructive technology (Goncalves et al., 2019). The key advantage is that it can be carried out under ambient conditions (atmospheric oxygen is used as oxidant) and may lead to complete mineralization of organic carbon into CO2. Moreover, TiO2 photocatalyst is largely available, inexpensive, and non-toxic and shows relatively high chemical stability (Grifinth, 2012).

2.1 Degradation Studies
Chemical reaction involves kinetics which make use of traditional one-factor-at-a-time (OFAT) approach, examining the effect of parameters such as initial concentration of target compound, degradation time, catalyst dose and characteristics, pH, temperature, UV light source and intensity. If the factors involved in the process are independent (which is rarely the situation) the most common practice is OFAT while holding all others constant. However, the result of this univariate analysis shows inadequate optimization towards response(s) (Gewald, 2016).

2.2 Materials and Equipment

2.2.1 Materials
The materials and chemicals used for this research were sodium hydroxide, hydrochloric acid, tetraoxosulphate VI acid, sodium nitrite, titanium IV oxide. VAT YELLOW dye.

2.2.2 Equipment
The equipment used were: Mercury bulb (25W). B22, 220 – 240V, Jenway UV-Visible spectrophotometer model 6305, digital pH meter model Jenway 3505, 78HW – 1 magnetic stirrer, electronic digital weighing balance, Shimadzu FTIR – 8400S Fourier transformed Infrared spectrophotometer, photoreactor, equipped with heat suction fan (model 361KL – 04W – B69, 12V DC, 0.56A, DC Brushless, Gas chromatography and Mass spectrophotometer, melting point apparatus (Gallenkamp).

3. METHODOLOGY

3.1 Characterization of The Dye
➢ Purification of the dyes
➢ Determination of Melting Point
➢ Percentage Yield

3.2 Ultra-violet-visible Spectroscopy
The wavelength of maximum absorption \( \lambda_{\text{max}} \) of the dyes produced who measured using JENWAY 6305 UV-visible spectrophotometer.

3.3 Fourier Transform Infra-red (FTIR) Measurement
The infrared peaks of the dye was determined using FTIR – 8400 series.

3.4 Gas-chromatography-mass Spectrophotometry Measurement
The structural elucidation of the dye was studied by the use of gas-chromatography – mass spectrophotometry.
3.6 Design of Experiment Using Box Behnken Design

Number of experimental runs = \(2k (k-1) + C_o\)

\[ N = 2k (k-1) + C_o \]

Where

- \(N\) = number of experimental runs,
- \(k\) = number of factors,
- \(C_o\) = centre point

For the ten dyes, the factors used were:

- Dye Concentration (mg/L)
- Catalysts loading (mg/L)
- Time of irradiation (min)
- pH

Exposure for dye concentration of 10 mg/L and a catalyst loading of 1 mg/L. The plot indicates that greater than 70% degradation was obtained at the pH range of about 3.0 to 5.0 at the time of exposure of 60 to 80 minutes. This represents the optimum conditions for the performances of the catalyst, when the active sites were fully utilized for photodegradation reaction.

This graph illustrates the contour plot of degradation versus pH and catalyst loading for the dye concentrates of 10 mg/L and time of exposure of 45 minutes. Greater than 70% degradation was obtained at pH of 3.5 to 4.0 and catalyst loading of 1.4 to 1.5 g/L.

This graph illustrates the contour plot of percentage degradation against pH and dye concentration for catalyst loading of 1 mg/L and time of exposure of 45 minutes. Greater than 70% degradation was obtained at pH of 3.5 to 4.5 at dye concentration of about 15 mg/L.

Figure 1: Contour Plot of % Degradation versus pH, Catalyst loading
Figure 2: Contour Plot of % Degradation versus pH, Dye concentration

Table 1: Box-Beckken Design of Experiment for the VAT YELLOW Dye

<table>
<thead>
<tr>
<th>Run Order</th>
<th>Dye Concentration (mg/L)</th>
<th>Catalyst loading (mg/L)</th>
<th>pH</th>
<th>Time (min)</th>
<th>Absorbance Initial</th>
<th>Absorbance final</th>
<th>Degradation (%)</th>
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<tbody>
<tr>
<td>1</td>
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<td>0.200</td>
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<td>2</td>
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<tr>
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<td>3.39</td>
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<tr>
<td>4</td>
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<td>0.176</td>
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<tr>
<td>5</td>
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<td>2</td>
<td>3.39</td>
<td>45</td>
<td>0.304</td>
<td>0.200</td>
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</tr>
<tr>
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<td>3.39</td>
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<td>0.201</td>
<td>0.201</td>
<td>0.000</td>
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<tr>
<td>7</td>
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<td>0.135</td>
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<tr>
<td>20</td>
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<td>45</td>
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<td>0.134</td>
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<td>3.39</td>
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<tr>
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<td>45</td>
<td>0.701</td>
<td>0.610</td>
<td>12.981</td>
</tr>
</tbody>
</table>

Figure 3: Response Optimization for Dye
Table 2: Experimental Confirmation of Each of The Optimized Results

<table>
<thead>
<tr>
<th>Dye</th>
<th>Dye Conc. (mg/L)</th>
<th>Catalyst Loading (mg/L)</th>
<th>pH</th>
<th>Time (min)</th>
<th>Initial Absorbance</th>
<th>Final Absorbance</th>
<th>% Degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>20</td>
<td>2.0</td>
<td>3.21</td>
<td>45</td>
<td>0.911</td>
<td>0.009</td>
<td>99.012</td>
</tr>
</tbody>
</table>

4. DISCUSSIONS

Figures 1, 2, and 3 showed plots of standardization residual against observation order. It helped to show whether the fit is uniformly good or different for lower or higher values of the residual. Residual plots are the best single check for violation of assumptions, such as:

i. Variance not being constant across the explanatory variables.
ii. Fitted relationships being non-linear.
iii. Random variation not having a normal distribution

Residuals are random variables and arc functions of data. Examining residuals is a key part of all statistical modeling including Design of Experiments (DOE’s). Residual tell us how well or otherwise the model fits the data. One problem with using residuals is that their values depend on the scale and units used. Since the residuals are in units of the dependent variable Y there are no cut-off points for defining what a “large” residual is. The problem is overcome by using standardized residuals. They are calculated by residual divided by standard error of the residual. The standard error of each residual is different, and using standardized residuals helps one to get round the problem.

5. CONCLUSION

The photocatalytic degradation of vat yellow dye using UV light as radiation source and TiO₂ as photocatalyst had been achieved using Minitab 18 software to carry out the experimental design.

SUMMARY AND RECOMMENDATION

This work revealed the optimization of process parameters namely dye concentration (mg/L), catalyst loading (mg/L), time of irradiation (mins) and pH of Vat Yellow dye. Ultraviolet light was used to investigate the photodegradation using Titanium oxide TiO₂ as photocatalyst.

REFERENCES


