Photocatalytic Degradation of AO7 Aqueous Solution Using Ag/CeO₂ Catalyst: Modeling of Process Parameters Using Response Surface Methodology

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Abstract. In the present study, photocatalytic degradation of Acid Orange 7 (AO7) aqueous solution using Ag/CeO₂ catalyst with the presence of UV light was evaluated. The effect of process parameters such as pH, initial dye concentration and Ag/CeO₂ dosage were investigated using response surface methodology (RSM) based on three levels of Box-Behnken Design. The effect of process parameters and their binary interactions were analyzed using the polynomial regression model. The experimental data and ANOVA analysis showed that the determination coefficient (R²) and adjusted determination coefficient (R²_adj) were 0.9580 and 0.9161, respectively, demonstrating that the model was significant. The response surface plot was successfully established the interaction effect of process parameters on the photocatalytic degradation of AO7 aqueous solution.

1. Introduction

The textile industry generates a large volume (during dyeing and finishing processes) of coloured effluents every year and causing intense water pollution in the environment. The resulted effluent is due to the usage of colouring substance such as synthetic organic dyes. The most important class of synthetic organic dyes which have been used in this industry are azo, anthraquinone and phthalocyanine dyes [1]. Among all these dye classes, azo dye has been strictly restricted in a few countries such as India, China and Europe countries. This restriction not only because of the aesthetic reasons, however, it is due to these dye class and their breakdown products might release harmful aromatic amines which are highly toxic [2], mutagenic and carcinogenic [3]. Therefore, an appropriate treatment technology in decolorizing and mineralizing these dyes should be applied prior discharge to the environment.

Many research have revealed that azo dyes can be decolourized by advanced oxidation processes (AOPs), involving the generation of hydroxyl radicals (·OH). It is now well established that photocatalysis under UV or solar light on a semiconductor surface is an attractive of AOPs processes. The (·OH) radicals are generated when the UV or visible light irradiates on the surface of semiconductor or photocatalyst material. This radicals are very strong oxidizing agents which has potential to break molecular structure for almost all organic pollutants such as azo dye. The intermediate products can be further oxidized and mineralized to produce CO₂ and H₂O [4].
Recently, Cerium oxide (CeO$_2$) demonstrates good potential as photocatalyst material besides TiO$_2$. This rare earth metal oxide has good criterion to act as a good metal oxide semiconductor and has similar properties like TiO$_2$ such as wide bandgap (2.9 – 3.2 eV) and highly stable [5]. The CeO$_2$ has been widely used in many fields such as fuel cells, oxygen sensors, oxygen permeation membrane, catalysis and biomedical. In catalytic application, CeO$_2$ has been used as a three-way automotive catalyst (TWCs), catalyst in steam reforming of ethanol for producing H$_2$ and photocatalyst as well [6]. The widespread application of CeO$_2$ in catalysis is mainly originated from the outstanding its redox properties. This property is associated with the unique excellent ability of this catalyst to easily transform between III and IV oxidation states and leads to the formation of oxygen vacancies within the crystal structure [7]. However, the main drawback of this material is its wide band-gap property which leads to the limited absorption of the visible light region. Thus, a simple approach can be applied in extending the catalyst absorption toward the visible region is by doping this material with a noble metal such as silver (Ag), gold (Au), platinum (Pt) and palladium (Pd) [8]. Doping technique can narrower the bandgap of CeO$_2$ and consequently enhance its photocatalytic performance. Recently, Ag has been studied exhibits surface plasmon resonance (SPR) under visible light region which can enhance the light absorption of metal oxide through scattering, absorption enhancement and hot-electron injection [9].

Despite of all the success studies, the study of degradation of Acid Orange 7 (AO7) using Ag/CeO$_2$ catalyst via photocatalysis process has still been limited. Besides, the photocatalytic degradation of pollutants was greatly affected by different process parameters including pH, initial concentration of pollutant and catalyst dosage. Thus, the aim of this study was to evaluate the effects of process parameter such as pH, initial dye concentration and Ag/CeO$_2$ dosage on the photocatalytic degradation of Acid Orange 7 (AO7) aqueous solution using response surface methodology (RSM) based on three levels Box-Behnken Design (BBD).

2. Methods

2.1. Photocatalytic degradation of AO7 aqueous solution

In this study, the Ag/CeO$_2$ catalyst was synthesized as been described in our previous work [10]. All the photocatalytic degradation experiments were carried out in a 200 mL beaker as a reaction vessel under UV irradiation whereas the emission power and wavelength of UV lamp were 2.5 Watts and 253.7 nm, respectively. The photocatalytic system was also equipped with a magnetic stirrer and UV resistance box. The UV lamp was located at the top of the resistance box with a distance of 0.20 m from the reaction vessel.

For a typical catalytic process, a certain quantity of Ag/CeO$_2$ catalyst was added to a 100 mL of AO7 aqueous solution with certain concentration and pH. Prior to the photocatalytic degradation experiments, the suspension was agitated for 30 min in the dark condition to achieve the adsorption-desorption equilibrium. Subsequently, the suspension was irradiated for 120 min in the resistance box. During the process, 3 mL of sample was withdrawn and filtered through 0.22 μm syringe filter (PVDF) at 30 min of interval time. The absorbance of the filtrate was then determined at the maximum wavelength ($\lambda_{\text{max}}$) of 486 nm using Lambda 25 UV-VIS Spectrophotometer (Perkin Elmer, USA). Then, the concentration of the sample was determined based on the standard calibration curve. Meanwhile, the removal performance for AO7 aqueous solution was calculated as follows: $(C_i - C)/C_i \times 100$, where $C_i$ is the initial concentration of AO7 aqueous solution and $C$ is the concentration of AO7 aqueous solution after irradiation.

2.2. Experimental design

Response surface methodology was applied to determine the effect of three input variables or process parameters: pH (A), initial concentration of AO7 (B) and Ag/CeO$_2$ dosage (C) on the photocatalytic degradation of AO7 (%) (response). The individual and interaction effects of these process parameters on the photocatalytic degradation of AO7 solution (%) were investigated using
Box-Behnken Design (BBD) approach. The total of 15 experiments (runs) were established based on this approach with three factors and three levels. The coded levels with their values are -1 (3, 5, 0.50), 0 (4, 20, 0.75) and +1 (5, 35, 1.00) for pH, initial concentration of AO7 (ppm) and Ag/CeO$_2$ dosage (g/L), respectively. Meanwhile, the actual BBD experimental design matric is shown in Table 1. The experimental design and all the statistical analyses and plots were performed using Minitab®19 software. Analysis of variance (ANOVA) was utilized to evaluate the significance and adequacy of the regression model on the response.

Table 1. BBD matric response.

| Run | pH | Initial concentration of AO7 (ppm) | Ag/CeO$_2$ dosage (g/L) | Photocatalytic degradation of AO7 (%) |
|-----|----|-----------------------------------|-------------------------|-------------------------------------|
|     | Coded values | Uncoded values | Coded values | Uncoded values | Coded values | Uncoded values | Experimental response |
| 1   | -1  | 3          | 0          | 20         | 1          | 1          | 99.26 |
| 2   | 0   | 4          | 1          | 35         | -1         | 0.5        | 77.67 |
| 3   | 0   | 4          | -1         | 5          | 1          | 1          | 76.51 |
| 4   | 0   | 4          | -1         | 5          | -1         | 0.5        | 97.31 |
| 5   | 0   | 4          | 1          | 35         | 1          | 1          | 63.42 |
| 6   | 1   | 5          | -1         | 5          | 0          | 0.75       | 79.57 |
| 7   | 0   | 4          | 0          | 20         | 0          | 0.75       | 94.09 |
| 8   | 0   | 4          | 0          | 20         | 0          | 0.75       | 84.56 |
| 9   | -1  | 3          | 1          | 35         | 0          | 0.75       | 97.43 |
| 10  | 0   | 4          | 0          | 20         | 0          | 0.75       | 97.41 |
| 11  | 1   | 5          | 0          | 20         | -1         | 0.5        | 87.41 |
| 12  | -1  | 3          | -1         | 5          | 0          | 0.75       | 94.88 |
| 13  | 1   | 5          | 1          | 35         | 0          | 0.75       | 64.32 |
| 14  | -1  | 3          | 0          | 20         | -1         | 0.5        | 99.02 |
| 15  | 1   | 5          | 0          | 20         | 1          | 1          | 66.32 |

3. Results and discussion

3.1. Model development and analysis

A quadratic polynomial model was selected to develop the empirical relationship between the coded factors and the response. To achieve the reasonable accuracy of the correctly predicted model, the Box-Cox power transformation ($\lambda = -2$) with the stepwise method (to improve the fitting of the model) was used to check the suitability of the regression model. Table 2 lists the results of ANOVA for the photocatalytic degradation of AO7 aqueous solution. This table only shows significant terms such as A, B, C, B$^2$, C$^2$, AB and AC for the response and the insignificant terms were excluded. The p-value of the model is less than 0.05 (at 95% confidence level) which signifies this model is statistically significant [11]. Thus, all three process parameters do affect the photocatalytic degradation of AO7 aqueous solution.

The determination coefficient ($R^2 = 0.9580$) and adjusted determination coefficient ($R^2_{adj} = 0.9161$) of the statistical summary were found to be highest for the quadratic model for the photocatalytic degradation of AO7 aqueous solution. Both of these coefficient values indicate this model adequately represents a good correlation between the actual and predicted values of photocatalytic degradation of AO7 aqueous solution with the process parameters. The model with coded three factors can be written in Equation 1. Figure 1(a) and Figure 1(b) show normal probability plots of residual and residual versus fitted value plot, respectively. Both figures show the residuals are normally distributed whereas
the points in Figure 1(a) generally form a straight line and the points in Figure 1(b) displays a random pattern for both sides of zero [11].

### Table 2. ANOVA results of the response surface quadratic model for the photocatalytic degradation of AO7 aqueous solution.

| Source                | Df | F-Value | P-Value |
|-----------------------|----|---------|---------|
| Model                 | 7  | 22.83   | 0.000   |
| A – pH (A)            | 1  | 61.38   | 0.000   |
| B – Initial concentration of AO7 | 1  | 25.07   | 0.002   |
| C – Ag/CeO2 dosage   | 1  | 32.01   | 0.001   |
| B²                    | 1  | 17.77   | 0.004   |
| C²                    | 1  | 6.24    | 0.041   |
| AB                    | 1  | 8.61    | 0.022   |
| AC                    | 1  | 10.10   | 0.016   |
| Lack of Fit          | 5  | 0.59    | 0.725   |
| Total                | 14 |         |         |

Photocatalytic degradation of AO7 (%): \[ -4.71 \times 10^4 + 6.00 \times 10^5 A + 1.00 \times 10^5 B + 7.40 \times 10^4 C - 0.00 B^2 - 3.16 \times 10^4 C^2 - 1.00 \times 10^6 AB - 9.70 \times 10^5 AC \] (1)

**Figure 1.** Residual plots for photocatalytic degradation of AO7 aqueous solution (a) normal probability plots of residuals and (b) residuals versus fits plots.

3.2. **Effect of process parameters on photocatalytic degradation of AO7 aqueous solution**

In this study, the interactions between the model terms (process parameters) were expressed by 2D contour plot as the graphical representation. This plot is necessary to test the interactions between the process parameters in order to determine the significance of the model equation. Besides, it also would allow a better understanding of the optimum level of each process parameter and the optimum level of photocatalytic degradation of AO7 aqueous solution as the response [13]. The contour plots of the interaction between pH and initial concentration of AO7 (at a constant Ag/CeO2 dosage) and; pH and Ag/CeO2 dosage (at a constant initial concentration of AO7) on the degradation efficiency are shown in Figure 2(a) and (b), respectively. Both figures, Figure 2(a) and (b) demonstrate the similar pattern of contour plot which the degradation efficiency approaches the maximum level with decreasing of pH. When the pH decrease from 5 to 3, the degradation efficiency was increased from 65 to >90%. However, the trend goes downward after the optimum points of both parameters for both figures. This can be explained by the point zero charge (pZC) of Ag/CeO2 and the ionization of AO7 molecules in aqueous solution. Since the pZC of Ag/CeO2 is 6.7 – 8.6 [14], the catalyst surface is positively charged (adsorption of anionic molecules is favorable) when the AO7 aqueous solution was at pH < 6.7 and is negatively charged (adsorption of cationic molecules is favorable) when the pH > 8.6. This results
showed that decreasing pH greatly affect the degradation efficiency. Therefore, the best photocatalytic degradation of AO7 aqueous solution could be observed at pH 3 – 3.5 with the range of initial concentration of AO7 and Ag/CeO2 dosage were 5.0 – 25 ppm and 0.5 – 0.8 g/L, respectively.

In Figure 2(b), it was observed at the range of 5 – 35 ppm, the degradation efficiency decreased as the initial concentration of AO7 increased. The reason behind this behaviour is due to at high initial concentration of AO7, more AO7 molecules were adsorbed on the surface of Ag/CeO2 catalyst to occupy the active sites and resulted in the fewer active site for adsorption of hydroxyl ions [14-15]. Therefore, the generation of •OH radicals would be decreased and led to low degradation efficiency. Besides, as the initial concentration of AO7 increased, the amount of UV light could reach the catalyst surface became lesser due to more AO7 molecules were adsorbed. Hence, led to decreasing of the amount of catalyst activated by photo or light. From this figure, it is clearly demonstrated that the range of initial concentration was almost completely degraded for the range of 5.0 – 25 ppm. This may be attributed to the active sites of the catalyst required was more than adequate [8].

Meanwhile, for the effect of Ag/CeO2 dosage, the degradation efficiency was increased with the increased amount of catalyst. This can be explained due to the availability of active sites, the number of electron-hole pairs generated and the penetration of UV light into the AO7 aqueous solution. However, excess amount of catalyst (>0.8 g/L of Ag/CeO2) probably showed decreasing in degradation efficiency which may result in an unfavorable light scattering and reduction of light
penetration into the AO7 aqueous solution due to an increase in the turbidity of aqueous solution [8, 16].

Figure 2(c) shows the contour plot of the interaction between initial concentration of AO7 and Ag/CeO2 dosage at a constant pH on the degradation efficiency. It was observed that the degradation efficiency found to be optimum at 20 ppm and ~0.7 g/L for initial concentration of AO7 and Ag/CeO2 dosage, respectively. However, both initial concentration of AO7 and Ag/CeO2 dosage beyond the range of 0.5 – 0.75 g/L and ~5 – 25 ppm, respectively, resulted in a decrease in degradation efficiency (<90%). This lead to the conclusion that the interaction effect of the initial concentration of AO7 and Ag/CeO2 dosage beyond the optimum value cannot enhance the efficiency of photocatalytic degradation of AO7 aqueous solution.

4. Conclusion

In this present study, RSM based on three levels of Box-Behnken design was significant in analyzing the effect of process parameters such as pH, initial concentration of AO7 and Ag/CeO2 dosage on the photocatalytic degradation of AO7 aqueous solution. The results demonstrated that all these three process parameters have a strong effect on the photocatalytic degradation of AO7 aqueous solution and this degradation efficiency can be adequately modeled. The model fitted very well to the experimental data by considering the values of determination coefficient (R²) and adjusted determination coefficient (R² adj). The response surface plot was successfully utilized to accesses the significant interaction effect of the process parameters on the photocatalytic degradation of AO7. The best photocatalytic degradation of AO7 aqueous solution could be observed at pH 3 – 3.5 with the range of the initial concentration of AO7 and Ag/CeO2 dosage were 5.0 – 25 ppm and 0.5 – 0.8 g/L, respectively.

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