A study on emerging contaminant amiodarone removal in water - experimental investigations and modeling

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Abstract: In the recent times, pharmaceutical contaminants in water are posing a negative impact on the environment. In India, pharmaceutical contaminant Ciproflaxin was detected at a highest concentration of 31 mg/L from the wastewater effluent of bulk pharmaceutical production plant located in Hyderabad. To increase the overall removal of these emerging pharmaceutical contaminants pre-treatment of strong pharmaceutical wastewater at a higher concentration can be done. In this study one of the critical pharmaceutical contaminant in India, Amiodarone (AMD) removal was investigated employing a UV/TiO2 based photoreactor. Three parameters were included in the study. The parameters include initial concentrations of AMD ranging between 50 and 100 mg/L, reaction time between 10 and 30 min, the photocatalyst concentration viz., TiO2 dosage between 500 and 1000 mg/L. The experimental data was used for performing the regression analysis and was done using MINITAB software. An empirical equation was obtained correlating the Amiodarone removal and the three parameters considered in the study.

Keywords: Pharmaceutical Contaminants; Amiodarone, Photocatalysis; Response surface methodology.

1. Introduction

In the recent times, pharmaceutical contaminants in water are posing a negative impact on the environment [1]. In India, pharmaceutical contaminant Ciproflaxin was detected at a highest concentration of 31 mg/L from the wastewater effluent of bulk pharmaceutical production plant located in Hyderabad [2]. One of the widely prescribed active pharmaceutical ingredients (API) in India is found to be Amiodarone. Further Amiodarone is found to be one of the critical pharmaceutical contaminant in India [3]. Different treatment techniques are available to treat these emerging contaminants but efficiency of removal, development of harmful by-products, cost of treatment are some of the challenges in addressing these emerging contaminant removal from the environment [4,5,6,7]. To increase the overall removal of these emerging pharmaceutical contaminants pre-treatment of strong pharmaceutical wastewater at a higher concentration can be done [8]. In this study Amiodarone (AMD) removal was investigated employing a UV/TiO2 based photoreactor. Three parameters were included in the study. The parameters include initial concentrations of AMD ranging between 50 and 100 mg/L, reaction time between 10 and 30 min, the photocatalyst concentration viz., TiO2 dosage between 500 and 1000 mg/L. Design of experiment was used for designing the experiment. The experimental data was used for performing the regression analysis and was performed using MINITAB software. For the regression analysis, response surface
methodology was used. An empirical equation was obtained correlating the Amiodarone removal and
the three parameters considered in the study.

2. Methodology

The chemicals were all of laboratory grade purity. In this study Amiodarone (AMD) removal was
investigated employing a UV/ TiO$_2$ based photoreactor purchased from M/s Heber Scientific, Chennai.
365 nm UV radiations were used for the degradation of Amiodarone. Three parameters were included
in the study. The parameters include initial concentrations of AMD ranging between 50 and 100 mg/L,
reaction time between 10 and 30 min, the photocatalyst concentration viz., TiO$_2$ dosage between 500
and 1000 mg/L. Design of experiment (DoE) was used for designing the experiment. The experimental
data was used for performing the regression analysis and was performed using MINITAB software.
For the regression analysis, response surface methodology was used. An empirical equation was
obtained correlating the Amiodarone removal and the three parameters considered in the study (Eqn
1). UV-VIS spectrometer (254 nm) was used for measuring the Amiodarone concentration.

3. Results and Discussion

3.1. AMD removal

The parameters varied through the design of experiment and the results obtained from the experiments
are represented in Table 1. Analysis was done using the results and equation obtained is presented in
equation 1. The elimination of AMD varied between 26 and 52% for the various combination of the
selected three parameters in this study.

| Initial AMD Conc. (mg/L) | Time (min) | Photocatalyst TiO$_2$ concentration (mg/L) | AMD removal (%) |
|-------------------------|------------|--------------------------------------------|-----------------|
| 75                      | 20         | 750                                        | 26              |
| 75                      | 20         | 750                                        | 35              |
| 100                     | 30         | 500                                        | 31              |
| 75                      | 10         | 750                                        | 35              |
| 75                      | 20         | 750                                        | 44              |
| 50                      | 10         | 500                                        | 37              |
| 75                      | 20         | 1000                                       | 46              |
| 75                      | 20         | 500                                        | 48              |
| 75                      | 20         | 750                                        | 48              |
| 50                      | 20         | 750                                        | 37              |
| 75                      | 30         | 750                                        | 52              |
| 100                     | 20         | 750                                        | 43              |
| 100                     | 30         | 1000                                       | 47              |
| 50                      | 10         | 1000                                       | 24              |
| 100                     | 10         | 1000                                       | 29              |
| 100                     | 10         | 500                                        | 36              |
| 50                      | 30         | 500                                        | 47              |
| 50                      | 30         | 1000                                       | 51              |
| 75                      | 20         | 750                                        | 48              |
| 75                      | 20         | 750                                        | 33              |
Equation 1:

\[
\text{AMD removal} = 61.3 + 0.77 \text{Contaminant conc}(mg/L) - 0.152 \text{TiO}_2 (mg/L) \\
+ 0.07 \text{Time (min)} - 0.00560 \text{Contaminant conc}(mg/L) \\
\times \text{Contaminant conc}(mg/L) + 0.000056 \text{TiO}_2 (mg/L) \times \text{TiO}_2 (mg/L) \\
+ 0.000360 \text{Contaminant conc}(mg/L) \times \text{TiO}_2 (mg/L) \\
- 0.0120 \text{Contaminant conc}(mg/L) \times \text{Time(min)} + 0.00200 \text{TiO}_2 (mg/L) \\
\times \text{Time(min)}
\]

3.2. AMD removal for change in AMD concentration and TiO\(_2\)

The effect of different parameters on the AMD removal is studied through the response surface plot (RSP) which was obtained from MINITAB from equation 1 (Figure 1(a) to 1(c)).

![Surface Plot of AMD removal vs TiO\(_2\) (mg/L), Contaminant conc(mg/L)](image)

**Figure 1(a).** Response surface for AMD removal for change in AMD and TiO\(_2\)

By observing the response surface plot (Figure 1a), it can be inferred that the AMD removal strongly depends on the factors like AMD concentration and TiO\(_2\). It was observed that as the photocatalyst concentration increases the AMD removal increases. Maximum removal of around 42% was observed when the TiO\(_2\) concentration was 1000 mg/L. Further the removal is more when the contaminant concentration is at 50 mg/L and is found to be 42%. As the contaminant concentration increases to 100 mg/L, the AMD removal decreases to 35%.

3.3. AMD removal for change in AMD concentration and Time

By observing the response surface plot (Figure 1b), it can be inferred that the AMD removal strongly depends on the factors like AMD concentration and reaction time. As the reaction time increases the overall AMD removal increases in general. Around 45% removal of AMD was observed for a reaction time of about 30 min.
By observing the response surface plot (Figure 1c), it can be inferred that the AMD removal strongly depends on the factors like TiO$_2$ and reaction time. As the reaction time increases the overall AMD removal increases in general. Around 50% removal of AMD was observed for a reaction time of about 30 min.
4. Conclusion

In this study pre treatment of one of the critical pharmaceutical contaminant in India, Amiodarone (AMD) removal was investigated employing a UV/ TiO$_2$ based photoreactor. Three parameters were included in the study and include concentrations of contaminants, reaction time and TiO$_2$ dosage. The experimental data was used for performing the regression analysis and was performed using MINITAB software. An empirical equation was obtained correlating the Amiodarone removal and the three parameters considered in the study. From the work, it was found that AMD percentage removal was dominated by all the three parameters which are considered in this work. At highest time and photocatalyst dosage considered in this study (i.e 30 min and 1000 mg/L) a maximum AMD removal of 50% was observed from the study. From this study it was found that the UV/ TiO$_2$ system employed in this study is versatile and can be used for treating various emerging contaminants.

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