Heterogeneous photo catalytic process using TiO$_2$ for removing Levetiracetam in water – A study

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Abstract: Of late, 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. 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, Levetiracetam (LEV) removal was investigated employing a UV/ TiO$_2$ based photo reactor. Three parameters were included in the study. The parameters include initial concentrations of LEV ranging between 50 and 100 mg/L, reaction time between 10 and 30 min, the photo catalyst concentration viz., TiO$_2$ dosage between 500 and 1000 mg/L. The experimental data was used for performing the further analysis and was done using MINITAB software. An empirical equation was obtained correlating the LEV removal and the three parameters considered in the study.

Keywords: Pharmaceutical Contaminants; Levetiracetam; Photo-catalysis; 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 Levetiracetam. Further Levetiracetam 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 Levetiracetam (LEV) removal was investigated employing a UV/ TiO$_2$ based photo reactor. Three parameters were included in the study. The parameters include initial concentrations of LEV ranging between 50 and 100 mg/L, reaction time between 10 and 30 min, the photo catalyst concentration viz., TiO$_2$ 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 Levetiracetam removal and the three parameters considered in the study.

2. METHODOLOGY

The chemicals were all of laboratory grade purity. In this study Levetiracetam (LEV) removal was investigated employing a UV/ TiO\textsubscript{2} based photo reactor purchased from M/s Heber Scientific, Chennai. 365 nm UV radiations were used for the degradation of Levetiracetam. Three parameters were included in the study. The parameters include initial concentrations of LEV ranging between 50 and 100 mg/L, reaction time between 10 and 30 min, the photo catalyst concentration viz., TiO\textsubscript{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 (Equation 3.2). UV-VIS spectrometer (254 nm) was used for measuring the Levetiracetam concentration.

3. RESULTS AND DISCUSSION

3.1. LEV 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 3.2). The elimination of LEV varied between 32 and 55% for the various combinations of the selected three parameters in this study.

| Initial LEV Conc. (mg/L) | Time (min) | Photo catalyst TiO\textsubscript{2} concentration (mg/L) | LEV removal (%) |
|-------------------------|------------|--------------------------------------------------------|-----------------|
| 75                      | 20         | 750                                                    | 32              |
| 75                      | 20         | 750                                                    | 45              |
| 100                     | 30         | 500                                                    | 54              |
| 75                      | 10         | 750                                                    | 47              |
| 75                      | 20         | 750                                                    | 49              |
| 50                      | 10         | 500                                                    | 38              |
| 75                      | 20         | 1000                                                   | 43              |
| 75                      | 20         | 500                                                    | 51              |
| 75                      | 20         | 750                                                    | 36              |
| 50                      | 20         | 750                                                    | 42              |
| 75                      | 30         | 750                                                    | 48              |
| 100                     | 20         | 750                                                    | 48              |
| 100                     | 30         | 1000                                                   | 51              |
| 50                      | 10         | 1000                                                   | 37              |
| 100                     | 10         | 1000                                                   | 34              |
| 100                     | 10         | 500                                                    | 41              |
| 50                      | 30         | 500                                                    | 48              |
| 50                      | 30         | 1000                                                   | 55              |
| 75                      | 20         | 750                                                    | 42              |
| 75                      | 20         | 750                                                    | 38              |
3.2 Regression equation for LEV Removal

\[ \text{LEV Removal} = 42.3 + 0.361 \times \text{Contaminant conc} \left( \frac{mg}{L} \right) - 0.75 \times \text{Time (min)} - 0.00073 \times \text{Contaminant conc} \left( \frac{mg}{L} \right) \\
\times \text{Contaminant conc} \left( \frac{mg}{L} \right) + 0.000025 \times \text{TiO2} \left( \frac{mg}{L} \right) \times \text{TiO2} \left( \frac{mg}{L} \right) \\
+ 0.0205 \times \text{Time (min)} \times \text{Time (min)} - 0.000320 \times \text{Contaminant conc} \left( \frac{mg}{L} \right) \\
\times \text{TiO2} \left( \frac{mg}{L} \right) + 0.00100 \times \text{Contaminant conc} \left( \frac{mg}{L} \right) \times \text{Time (min)} \\
+ 0.000600 \times \text{TiO2} \left( \frac{mg}{L} \right) \times \text{Time (min)} \]

3.3 LEV removal for change in LEV concentration and TiO2

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

Figure 1 (a) Response surface for LEV removal for change in LEV and TiO2

By observing the response surface plot (Figure 1 (a)), it can be inferred that the LEV removal strongly depends on the factors like LEV concentration and TiO2. It was observed that as the photo catalyst concentration increases the LEV removal varies depending upon the initial concentration of LEV and needs to be studied further. Maximum removal of around 48% was observed when the TiO2 concentration was 500 mg/L. Further the removal is more when the contaminant concentration is at 100 mg/L and is found to be 50%. As the contaminant concentration decreases to 50 mg/L, the LEV removal decreases to 42%, and this needs to be studied further.

3.4 LEV removal for change in LEV concentration and Time

Figure 1 (b) Response surface for LEV removal for change in LEV and Time
By observing the response surface plot (Figure 1 (b)), it can be inferred that the LEV removal strongly depends on the factors like LEV concentration and reaction time. As the reaction time increases the overall LEV removal increases in general. Around 52% removal of LEV was observed for a reaction time of about 30 min.

3.5 LEV removal for change in Time and TiO₂

By observing the response surface plot (Figure 1 (c)), it can be inferred that the LEV removal strongly depends on the factors like TiO₂ and reaction time. As the reaction time increases the overall LEV removal increases in general. Around 50% removal of LEV 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, Levetiracetam (LEV) removal was investigated employing a UV/ TiO₂ based photo reactor. Three parameters were included in the study and include concentrations of contaminants, reaction time and TiO₂ dosage. The experimental data was used for performing the regression analysis and was performed using Minitab software. An empirical equation was obtained correlating the Levetiracetam removal and the three parameters considered in the study. From the work, it was found that LEV percentage removal was dominated by all the three parameters which are considered in this work. At time and photo catalyst dosage considered in this study (i.e. 30 min and 500 mg/L) a maximum LEV removal of 52% was observed from the study. From this study it was found that the UV/ TiO₂ system employed in this study is versatile and can be used for treating various emerging contaminants.

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