Use of TiO₂ for removing emerging contaminant in water – Amoxicillin as a case study

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Abstract: In the recent years, evidence of pharmaceutical contaminant in water having deteriorating effects on various species is well documented. The concentration of these pollutants range from ng/L in surface water to mg/L in pharmaceutical industry effluent. Treatment of highly concentrated pharmaceutical industrial effluent is a feasible option when compared to the treatment of dilute surface water. In this work, treatment of pharmaceutical industry effluent containing critical pharmaceutical contaminants (PC) Amoxicillin employing a photocatalytic system was investigated. Chosen factors include concentrations of contaminants (50 – 100 mg/L), TiO₂ dosage (500 – 1000 mg/L) and reaction time (10- 30 min). MINITAB software was employed to perform the standard regression analysis and the corresponding second-order polynomial equation was constructed between the chosen response (contaminant removal) and the three factors. Results indicate that studied emerging contaminant removal depends on the dosage of photocatalyst and the time employed in the reactor

Keywords: Pharmaceutical Contaminants; Metformin; Amoxicillin; Photocatalysis; Response surface methodology.

1. Introduction:
There is strong evidence that presence of emerging contaminants in environment including pharmaceutical compounds at very dilute concentration have deteriorating effects on various species [1]. In general the concentration of these pollutants detected in environment ranges between ng/L to μg/L [2], but their concentration is elevated (mg/L) in the point sources including pharmaceutical industrial effluent. In India, highest concentration of Ciproflaxin (31 mg/L) was reported by Larsson et al. [3] in the effluent from a generic medicine production centre in Hyderabad. To improve the removal of these emerging contaminants, pre-treatment of the highly concentrated pharmaceutical wastewater can be done before it is let into a domestic waste water treatment plant [4, 5]. Many studies have found that the advanced oxidation process was a feasible process to remove these recalcitrant contaminants [6,7]. In this work, treatment of synthetic pharmaceutical industry effluent containing critical pharmaceutical contaminants (PC) Amoxicillin employing a photocatalytic system was investigated

In Coimbatore, a reconnaissance survey was conducted, and it was found that most of the hospitals are discharging their hospital effluent water without much treatment into the municipal wastewater collection system. The most prescribed active pharmaceutical ingredient (API) in these hospitals include Amoxicillin trihydrate (AMX) in combination with other drugs. In a study by Chinnaiyan et al [8], AMX was found to be critical pharmaceutical contaminants for Indian environment. Hence, in this study, Amoxicillin was chosen as the contaminant. Amoxicillin trihydrate (C₁₆H₂₅N₃O₈S) is a widely used antibiotic. It has a molecular weight of 419.4 g/ mol and is soluble in water (3000mg/L).

The purpose of this study is to examine the suitability of heterogeneous photocatalytic system employing UV/ TiO₂ as a pre-treatment option for treating the artificial pharmaceutical wastewater
containing Amoxicillin trihydrate. The influence of Amoxicillin concentration, photocatalytic reaction time and photocatalyst concentration on the removal of the contaminant was investigated using the response surface methodology.

2. Materials and Methods

2.1 Reagents
All chemicals are of laboratory grade purity and are purchased from local vendor.

2.2 Experimental design
Design of experiment employing response surface methodology was used to perform standard regression analysis. The three factors chosen are initial contaminant concentration (X₁), TiO₂ concentration (X₂), and reaction time (X₃). Amoxicillin removal was chosen as the response. The levels of the factors considered are shown in Table 1. Regression analysis was performed using MINITAB software.

|Factor             | Levels used, actual (Coded) |
|-------------------|-----------------------------|
|                  | Low (-1) | Medium (0) | High(+1) |
| X₁ = Contaminant concentration (mg/L) | 50      | 75       | 100      |
| X₂ = TiO₂ concentration (mg/L)        | 500     | 750      | 1000     |
| X₃ = Reaction time (min)              | 10      | 20       | 30       |

2.3 Photocatalytic systems
Experiments were conducted employing the photoreactor procured from M/s Heber Scientific, Chennai. The reactor configuration is shown in Fig 1. UV radiation (365 nm) was emitted for the degradation of Amoxicillin.

2.4 Analysis
The concentration of Amoxicillin was measured using UV-VIS spectrometer by calibrating with known standards. For measuring the absorbance the detector was set at 254 nm.
3. Results and Discussion

3.1 AMX removal

The experimental results of the DoE are shown in Table 2. Regression analysis was performed using the results and equation obtained is presented in Eqn 1. The removal of AMX varied between 43 and 68% for the different combination of the chosen three factors. The results obtained are comparable to earlier studies [9,10]

| Contaminant Conc. (mg/L) | TiO₂ (mg/l) | Time (min) | AMX removal (%) |
|--------------------------|-------------|------------|-----------------|
| 75                       | 750         | 20         | 51              |
| 75                       | 750         | 20         | 47              |
| 100                      | 500         | 30         | 59              |
| 75                       | 750         | 10         | 55              |
| 75                       | 750         | 20         | 54              |
| 50                       | 500         | 10         | 43              |
| 75                       | 1000        | 20         | 66              |
| 75                       | 500         | 20         | 52              |
| 75                       | 750         | 20         | 59              |
| 50                       | 750         | 20         | 51              |
| 75                       | 750         | 30         | 68              |
| 100                      | 750         | 20         | 59              |
| 100                      | 1000        | 30         | 76              |
| 50                       | 1000        | 10         | 49              |
| 100                      | 1000        | 10         | 67              |
| 100                      | 500         | 10         | 55              |
| 50                       | 500         | 30         | 54              |
| 50                       | 1000        | 30         | 57              |
| 75                       | 750         | 20         | 52              |
| 75                       | 750         | 20         | 48              |

Equation 1:

\[
AMX\text{Removal} = 47.2 + 0.499AMX\text{conc(mg/L)} - 0.058TiO₂(mg/L) - 1.18T\text{ime(min)} \\
- 0.003AMX\text{conc(mg/L)}*AMX\text{conc(mg/L)} - 0.001TiO₂(mg/L)*TiO₂(mg/L) \\
+ 0.044T\text{ime(min)}*T\text{ime(min)} + 0.004AMX\text{conc(mg/L)}*TiO₂(mg/L) \\
- 0.003AMX\text{conc(mg/L)}*T\text{ime(min)} + 0.001TiO₂(mg/L)*T\text{ime(min)}
\] (1)

3.2 Response surface plot

To study the interaction between the factors considered, response surface plot (RSP) were generated (Figure 2 a to c) from the model equations,

Analysing the response surface plot (Fig 2a), it was found that there is a strong interaction between the factors AMX concentration and TiO₂ with respect to the response AMX removal. For the same initial concentration, the AMX removal increases as photocatalyst concentration increases. Maximum removal of around 70% was observed when the TiO₂ concentration was 1000 mg/L.

Analysing the response surface plot (Fig 2b), it was found that there is a strong interaction between the factors AMX concentration and time with respect to the response AMX removal. For the same initial concentration, the AMX removal increases as time increases. Maximum removal of around 65% was observed when the reaction time was maintained at 30 min.
Analysing the response surface plot (Fig 2c), it was found that there is a strong interaction between the factors TiO2 and time with respect to the response AMX removal. The removal is found to increase as the TiO2 increases. Similar trend is observed for the factor time and maximum removal of 70% was observed at a reaction period of 30 min.
4. Conclusion
The synthetic pharmaceutical wastewater containing Amoxicillin was pre treated using UV/ TiO$_2$ heterogeneous photocatalytic system. Influence of initial amoxicillin concentration, time and TiO$_2$ concentration was studied using response surface methodology. Standard regression analysis was performed and a model was created between AMX removal and the three chosen factors. Analysing the response surface plots it was found the AMX removal was influenced by all the chosen three factors. Maximum removal of 70% was observed at a reaction period of 30 min and when the TiO$_2$ concentration is at 1000 mg/L, indicating that the heterogeneous photocatalytic system can be suitably employed for the pre treatment of the pharmaceutical effluent.

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