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Photocatalytic treatment of amiodarone and levetiracetam in pharmaceutical industry effluent: process optimization using response surface methodology

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ABSTRACT

In this work, the treatment of synthetic pharmaceutical industry effluent containing two critical pharmaceutical contaminants, viz. amiodarone (AMD) and levetiracetam (LEV) was investigated employing heterogeneous photocatalytic system. Response surface methodology (RSM) was used to model and optimize the process variables. Photoreactor (500 mL), immersion lamp emitting ultraviolet rays at 365 nm (125 W) and TiO_2 as photocatalyst, was employed and four variables, viz. initial concentrations of AMD and LEV, pH, photocatalyst concentration and reaction time, were considered in this study. The influence of the chosen variables on the removal of contaminants was evaluated using RSM. Regression analysis revealed that removal of both AMD and LEV was influenced by all the four variables. It was found that the maximum removal of AMD was 67.6% and LEV was 92.7% under the optimum conditions. Characteristics experiments indicate that the removal by $^{\bullet}OH$ was the major mechanism in the degradation process. Lesser adsorption of AMD and LEV on the surface of TiO_2 and the insignificant removal of these contaminants when acetonitrile was the solvent suggested that heterogeneous photocatalytic effect plays a significant role in the removal process. More than 50% mineralization indicates that the heterogeneous photocatalytic system was capable of oxidizing the synthetic pharmaceutical industrial effluent containing AMD and LEV and could be effectively used to pre-treat the pharmaceutical effluent.

Keywords: Pharmaceutical contaminants; Design of experiment; MINITAB; Titanium dioxide; Adsorption; Optimum condition

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1. Introduction

There is increasing evidence that occurrence of emerging contaminants like pharmaceutical and personal care products (PPCPs) in the aquatic environment, even at low concentrations, could have harmful effects on the aquatic species [1]. Studies to map these emerging contaminants have been reported from all over the world [2]. This trace level mapping was essentially possible due to advancements in detection techniques such as liquid chromatography aided with mass spectroscopy which can detect multiple compounds in a single analysis. Within PPCPs, the focus is on pharmaceutical contaminants (PCs), owing to its bioactive nature [3]. The major source of these PCs in the environment include discharge of untreated or partially treated effluents from pharmaceutical industries, hospitals and other nonpoint sources emissions from household levels. Effluent discharge from pharmaceutical industries is a significant contributor as contaminants, in higher concentrations are released into the domestic wastewater drain without complete removal of these emerging contaminants [4,5]. Literature indicates

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that, more than 50% of the pharmaceutical effluents was discharged without any specific treatment [6]. Earlier studies show that the removal efficiency of these contaminants through domestic wastewater treatment plants (WWTPs) is very low, as these conventional treatment plants are not designed to eliminate these contaminants [1,3]. Though these pollutants are detected at very low concentrations (ng L^{-1} to μg L^{-1}) in natural water sources [7,8] their levels are quite high in the effluent discharges from industries. The highest concentration of ciprofloxacin (31 mg L^{-1}) was detected in the effluent from a generic medicine production centre in Hyderabad, India [4]. To improve the removal of these emerging contaminants, pre-treatment of the highly concentrated pharmaceutical wastewater can be done before it is let into domestic WWTPs [5].

Several studies have been reported on the removal of specific PCs employing different processes in prototype reactors [9,10]. Among these different processes, advanced oxidation processes (AOPs) are reported to be a feasible and sustainable technology for the removal of these emerging contaminants [11–13]. In AOPs, hydroxyl radicals are generated, which facilitate the removal of these recalcitrant contaminants. Among the AOPs, heterogeneous photocatalysis employing ultraviolet (UV) light (λ < 387 nm) and a photocatalyst was widely used. Though immense research is on the development of new nano material, these newly synthesised materials could not still replace TiO_2, as a photocatalyst in commercial operation plants. TiO_2 was very commonly adopted at pilot scale and treatment plants as it is found to be cost effective and the removal achieved is very good [14]. In recent years, combinations of two or more treatment process are also studied for the removal of pharmaceutical wastewater [15]. Different contaminants could be simultaneously removed in above multiple reactors, but the efficiency of the process varies with change in other system parameters like pH, reaction time which needs further investigation. Artificial neural networking and response surface methodology (RSM) are widely employed in investigating the influence of different independent variables on chosen response. In specific, RSM has attracted attention in recent times than the conventional experiments due to vast reduction in the number of experiments required [16]. Further, RSM is widely employed for optimisation of process parameters in treating contaminants in water [17].

Among the numerous pharmaceutical compounds manufactured in India, amiodarone HCl (AMD) and levetiracetam (LEV) are widely prescribed and produced. These compounds are studied as emerging contaminants in water [3,18] and are reported as critical pharmaceutical contaminant for the Indian environment [19]. For this reason, these two pharmaceutical compounds belonging to two different categories of drugs were selected for study in this work. AMD HCl ($C_{25}H_{30}ClI_2NO_3$) is an antiarrhythmic drug widely prescribed for treating irregular heartbeats. The molecular weight of AMD is 681.8 g mol^{-1} and its solubility is 700 mg L^{-1} in water. LEV is an anticonvulsant and it is used to treat seizure disorders in combination with other medicines. The molecular weight of LEV is 170.2 g mol^{-1} and it is readily soluble in water (1.04 × 106 mg L^{-1}). The presence of emerging PCs including AMD and LEV were earlier reported in domestic and hospital wastewaters [20,21].

Literature on degradation of AMD and LEV are scarce. Helbling et al. [20] studied microbial degradation of levetiracetam and other xenobiotics in a batch reactor seeded with activated sludge to identify the transformation products. Based on our understanding, till date no work has been carried out on the removal of AMD and LEV from synthetic pharmaceutical wastewater by employing AOP process and optimisation of variables using RSM.

The objective of this work is to investigate the removal of amiodarone HCl and levetiracetam from synthetic pharmaceutical industry effluent by employing the AOP process using UV/TiO_2 in a batch photoreactor. RSM was employed to study the influence of four variables (contaminant concentration, concentration of photocatalyst, pH and reaction duration). Further, the outcome of the study will be used for establishing a pilot scale treatment plant proposed at Coimbatore.

2. Materials and methods

2.1. Reagents

Amiodarone HCl (98%), levetiracetam (98%) and TiO_2 (anatase 99%, <25 nm) were purchased from Sigma Aldrich Chemical Pvt. Ltd., (Bangalore, India). Carbinol, acetonitrile, sodium hydroxide and sulphuric acid were procured from Merck Life Science Pvt. Ltd., (Mumbai, India). The procured chemicals were all utilised without any further processing and purification. Stock solution of standards and synthetic pharmaceutical wastewater samples were prepared using deionised water.

2.2. Experimental design

The complete set of experiments for the removal of AMD and LEV were performed in a lab scale batch photoreactor. Design of experiments (DoE) using face centred central composite design (FCCD) was employed in this study to reduce the number of experimental runs required. DoE is a statistical technique that allows simultaneous variation number of independent factors while keeping the number of experiments to minimum. In the analysis presented here, the term factor refers to the independent variable whose levels are changed in the experiments and response refers to the dependent variable that is measured during or after the experiment. RSM is a technique in DoE that enables us to generate a polynomial equation by regression analysis that relates the factors and responses. These models are useful in determining the main and the interaction effects of the factors on the responses as well as for optimizing the levels of the factors to obtain desired values of the responses. Main effects refer to how a response varies when a factor is changed. When the variation in a response (Y) to a change in factor (X_1) is affected by the level of another factor (X_2) it is said to have an interaction effect between X_1 and X_2 on the response, Y. FCCD is a class of RSM design that provides relatively high quality predictions over the entire design space. The factors considered include pollutant concentration (X_1), pH (X_2), photocatalyst TiO_2 concentration (X_3), reaction time (X_4) as the independent variables. The ranges considered for each variable are presented in Table 1 based on the literature review [4]. PCs like amoxicillin, carbamazepine, clofibric acid and triclosan have been investigated in the range of 2.5–50 mg L^{-1} in previous studies under different treatment processes [5,22].

DoE for the RSM was generated using MINITAB software with four factors and a total of 31 experiments was arrived. The order in which the experiments were conducted were randomized to ensure that the effect of unknown or uncontrolled extraneous variables that were not considered in the design do not bias the experiment. The response considered for the FCCD design includes the removal percentage of AMD and LEV with respect to its initial concentration. The average percentage removal from 3 trials was reported as the removal percentage. *T*-test was used to determine the statistical significance of each factor considered and analysis of variance (ANOVA) was used to determine the overall fit of model.

2.3. Photocatalytic systems

The reactor used for performing the photocatalytic experiments was purchased from M s^{-1} Heber Scientific, Chennai (Fig. 1). 125 W UV lamp emitting UV radiation predominantly at 365 nm was used for the study. The UV lamp was placed inside the Quartz immersion vessel. Synthetic pharmaceutical wastewater containing AMD/LEV was prepared in laboratory using standard stock solution. Further the pH of the sample was adjusted for each trial as per requirement using either dilute NaOH or H_2SO_4. Preliminary adsorption experiments were conducted between contaminants (50 mg L^{-1}) and photocatalyst (1,250 mg L^{-1}) for duration of 24 h under constant magnetic stirring in dark condition. The equilibrium time for the adsorption process was found to be 15 min and less than 5% removal of contaminants was observed through adsorption process. Therefore, in all the photocatalytic experiments, initial stirring process was eliminated. 200 ml of the synthetic wastewater was taken, TiO_2 was added at appropriate concentration and the sample was transferred into the borosilicate reaction vessel of the reactor. Continuous agitation was given to the sample with the aid of air pump and magnetic stirrer.

2.4. Analysis

AMD and LEV concentration of the synthetic wastewater sample was analysed by collecting 30 mL of the sample

Table 1
Levels of factors for the FCCD design

Factor	Levels used, actual (coded)		
	Low (–1)	Medium (0)	High (+1)
X_1 = contaminant concentration (mg L^{-1})	10	30	50
X_2 = pH	3	7	11
X_3 = TiO_2 concentration (mg L^{-1})	250	750	1,250
X_4 = reaction time	30	90	150

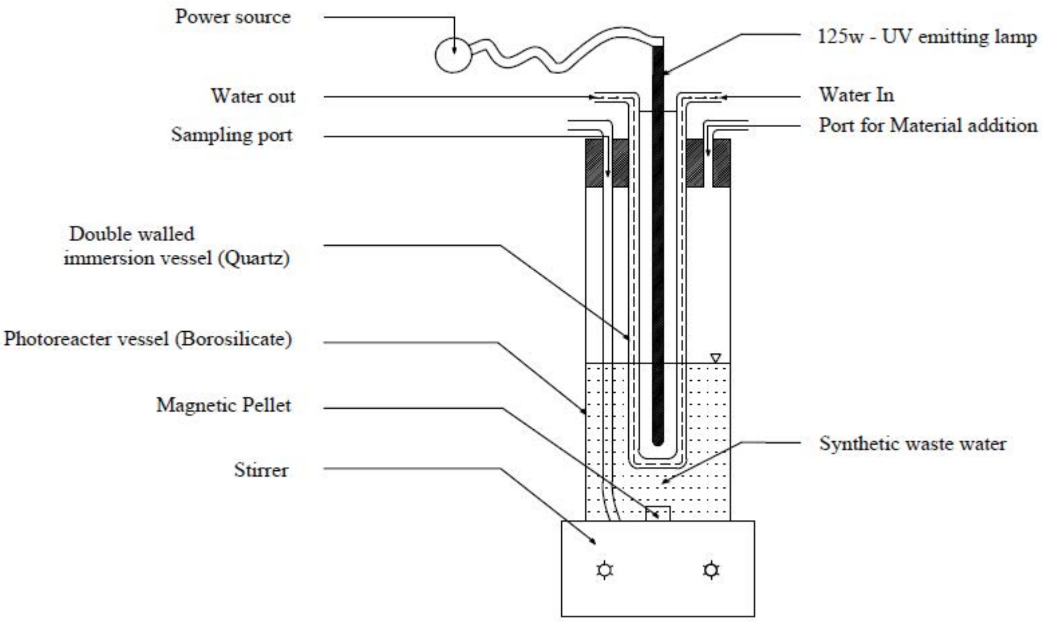

Fig. 1. Photoreactor setup.

during the start and the end of the photocatalysis experiment. For removing the TiO_2 particles, the collected samples were centrifuged for 5 min @ 1,000 rpm, followed by the extraction of the supernatant and filtered using 0.45 µm filtered paper. The clear filtrate was analysed for AMD and LEV concentrations using UV-VIS spectrometer (Perkin Elmer (lndia) Pvt. Ltd., Chennai, India, Lambda 35 instrument). The maximum absorbance for AMD and LEV was found to occur at 241 and 209 nm, respectively. The mineralisation of AMD and LEV was analysed by determining the total organic carbon (TOC) with the use of TOC analyser (Shimadzu, Japan).

3. Results and discussion

3.1. AMD and LEV degradation

Based on DoE run order generated for FCCD design from MINITAB, the experiments were performed for the different combination of the chosen factors. AMD and LEV removals along with final pH were evaluated for the 31 experiments and the data's are presented in Table 2. The removal percentage for AMD ranged from 29.4 to 63.1 whereas for LEV, it was found to be varying between 43.3 and 86.7 for different run order. The degradation results are in good agreement with similar studies on other PCs [23].

3.2. Statistical analysis

MINITAB software was employed to perform the standard regression analysis and the corresponding second-order polynomial equation was constructed between the chosen response (AMD/LEV removal) and the four factors. The regression equations were obtained from the ANOVA for different responses. A statistical significance level of 90% was used for constructing the regression equations. The obtained regression equations for AMD and LEV removal are shown in Eqs. (1) and (2), respectively. A quantitative measure of this statistical significance of each term

Table 2
DoE for AMD and LEV removal using four factor FCCD

Run order	Contaminant concentration (mg L^{-1})	Initial pH	TiO_2 (mg L^{-1})	Time (min)	AMD removal (%)	Final pH (AMD run)	LEV removal (%)	Final pH (LEV run)
1	10	11	250	150	63.1	9.5	86.7	8.9
2	30	7	750	90	56.5	6.3	77.9	6.5
3	30	7	750	90	57.6	6.6	79.2	6.5
4	10	11	1,250	30	50.7	10.1	71.0	10.7
5	30	3	750	90	44.4	3.6	62.3	3.5
6	30	7	750	90	56.4	6.8	77.8	6.4
7	50	11	1,250	150	48.3	9.5	68.7	9.2
8	50	11	250	30	42.8	10.4	61.1	10.7
9	30	7	750	150	56.7	5.9	78.8	6.3
10	10	7	750	90	59.7	6.2	82.6	6.5
11	30	7	750	90	56.6	6.3	78.1	6.6
12	10	3	1,250	150	55.7	3.7	77.7	3.6
13	10	3	1,250	30	38.6	3.4	55.1	3.5
14	30	11	750	90	55.9	10.5	77.2	10.7
15	30	7	250	90	51.6	6.2	71.5	6.8
16	50	7	750	90	53.6	6.4	74.3	6.5
17	30	7	1,250	90	61.5	5.8	84.5	6.1
18	50	11	1,250	30	35.9	9.6	51.3	9.4
19	10	3	250	30	37.6	3.3	53.9	3.6
20	50	3	1,250	150	59.1	3.7	81.4	3.5
21	50	3	1,250	30	36.7	3.1	52.5	3.4
22	50	3	250	150	45.2	3.3	64.3	3.2
23	30	7	750	90	58.1	6.3	80.0	6.6
24	10	11	1,250	150	56.6	9.1	79.4	9.4
25	50	3	250	30	29.4	3.3	43.3	3.4
26	10	3	250	150	52.6	3.6	73.4	3.8
27	30	7	750	30	54.0	6.6	74.5	6.3
28	30	7	750	90	57.5	6.1	79.0	6.4
29	10	11	250	30	48.4	10.3	66.1	10.1
30	50	11	250	150	46.3	10.5	66.1	10.2
31	30	7	750	90	54.5	6.1	75.4	6.4

(representing factors or factor combinations) is the *p*-value associated with the test statistic used. If the *p*-value of the coefficient is less than a chosen α level 0.1, the relationship between the term and the response is statistically significant. The terms that have high *p*-value do not significantly influence the response and hence can be removed from the model. Statistically significant terms influencing the removal for AMD and LEV are presented in Tables 3 and 4, respectively. The coefficient of each term in the model represent the magnitude of change in response if there is a unit change in the term, provided all other terms are held constant.

3.2.1. AMD removal

The R^2 value obtained for AMD removal was 89.57% (adjusted R^2 was 85.78%) by considering only the significant terms. Higher R^2 for the AMD removal indicates that around 89% of the variation in the removal could be justified by the combination of selected factors and their interactions in the regression model. Further it also indicates that the obtained regression model was a good predictor of AMD removal and the model can be utilised for predicting and optimizing the AMD removal within the boundary conditions. Though it was found that all the chosen four factors were significant in the removal of AMD, by comparing the *p*-value (Table 3), the factor contaminant concentration has a negative interaction with the AMD removal. This indicates that AMD removal decreases as the initial contaminant concentration increases and vice versa [24].

$$\text{AMD removal (\%)} = 0.8 - 0109X_1 + 11.23X_2 + 0.0104X_3 + 0.1628X_4 - 0.5876X_2^2 - 0.0245X_1X_2 - 0.0011X_2X_3 - 0.0088X_2X_4 \quad (1)$$

3.2.2. LEV removal

Similar analysis was performed on the data pertaining to LEV removal. The R^2 value obtained for LEV removal was 89.66% (adjusted R^2 was 85.9%) by considering only the significant terms. In this case, again all the chosen four factors were significant in the removal of LEV (Table 4). The factor contaminant concentration has a negative interaction with the LEV removal.

$$\text{LEV removal (\%)} = 7.77 - 0.025X_1 + 13.99X_2 + 0.0129X_3 + 0.211X_4 - 0.7363X_2^2 - 0.0293X_1X_2 - 0.0013X_2X_3 - 0.0106\,X_2X_4 \quad (2)$$

Analysing the initial and final pH of various run order for AMD and LEV experiments it was found that there was an insignificant change from the initial pH.

3.3. Effect of contaminant concentration and pH on contaminant removal

The response surface and contour plot of AMD removal and LEV removal vs. contaminant concentration and pH were presented in Figs. 2a and b, respectively. It was observed in general that as initial contaminant concentration increases, the removal decreases for both the chosen contaminants. The results are good in agreement with earlier studies as literature indicates that under similar operating conditions, the degradation rate diminishes at higher concentration of contaminant. Maximum removal occurs at an initial concentration of 10 mg L^{-1}. With respect to pH, AMD and LEV removal increases as the pH increase and maximum removal occurs when the pH is between 7 and 9. Further increase in pH results in decreased the removal of contaminants. Literature suggests that reduction in degradation at acidic pH may be due to lesser amount of hydroxyl ions which are needed for the hydroxyl radical formation, whereas diminishing degradation at alkaline pH range could be due to scavenging of hydroxyl radicals.

3.4. Effect of contaminant concentration and TiO_2 on contaminant removal

The effects of contaminant concentration and TiO_2 on AMD and LEV removal were studied using the contour

Table 3
Regression coefficients for AMD removal

Term	Coefficient	*p*-value[a]
Constant	0.8	0.000
Contaminant concentration	–0.0109	0.000
pH	11.23	0.002
TiO_2	0.0104	0.067
Time	0.1628	0.000
pH × pH	–0.5876	0.000
Contaminant concentration × pH	–0.0245	0.023
pH × TiO_2	–0.0011	0.014
pH × Time	–0.0088	0.016
R-Sq = 89.57%	*R*-Sq(adj) = 85.78%	

[a] Factors for which *p*-value is less than the chosen level of significance (0.1)

Table 4
Regression coefficients for LEV removal

Term	Coefficient	*p*-value[a]
Constant	7.77	0.000
Contaminant concentration	–0.025	0.000
pH	13.99	0.001
TiO_2	0.0129	0.057
Time	0.211	0.000
pH × pH	–0.7363	0.000
Contaminant concentration × pH	–0.0293	0.033
pH × TiO_2	–0.0013	0.02
pH × Time	–0.0106	0.022
R-Sq = 89.66%	*R*-Sq(adj) = 85.9%	

[a] Factors for which *p*-value is less than the chosen level of significance (0.1)

plot (Figs. 3a and b, respectively). It was observed that, the concentration of TiO_2 increases, the removal of AMD and LEV increases. This increased photocatalytic activity could be attributed to the increase in catalyst active sites as TiO_2 concentration increases. Literature suggests that this phenomenon occurs up to a certain limit and beyond that the photocatalytic activity decreases. The reduction in photocatalytic reaction could be due to light scattering effect, particle agglomeration which effectively reduces the surface of catalyst [25]. Higher removal of Amoxicillin with higher loading of TiO_2 up to 1.5 g L^{-1} was reported in earlier study [23]. Maximum removal of AMD (60%) occurs for a TiO_2 concentration of 700 mg L^{-1} when the initial contaminant concentration is at 10 mg L^{-1}. With increase in contaminant concentration, the TiO_2 concentration required to maintain the equivalent removal also increases. Similar trend is observed for LEV removal, and a maximum removal of more than 84% is observed.

3.5. Effect of contaminant concentration and time on contaminant removal

The contour plot of AMD removal and LEV removal vs. contaminant concentration and time was presented in Figs. 4a and b, respectively. It was observed that the higher reaction time improves the removal of both AMD and LEV as the initial contaminant concentration increases. More than 65% removal for AMD and 90% removal of LEV were observed for the reaction time of 150 min and for an initial contaminant concentration of 10 mg L^{-1}.

3.6. Effect of pH and TiO_2 on contaminant removal

The effect of pH and TiO_2 on AMD and LEV removal was studied using the contour plot (Figs. 5a and b, respectively). The removal of AMD was found to be maximum (>57%) when the pH is between 7 and 9, while the TiO_2 is between 900 and 1,200 mg L^{-1}. With respect to the LEV removal, the maximum removal (>76%) was reported when the pH is between 6 and 10, while the TiO_2 is between 300 and 1,200 mg L^{-1}. In general it was observed that the higher concentration of catalyst improves the AMD and LEV removal in a wider pH range.

3.7. Effect of pH and time on contaminant removal

The contour plot of AMD removal and LEV removal vs. pH and time was presented in Figs. 6a and b, respectively. The removal of AMD was found to be maximum (60%) when the pH is between 6.5 and 9, while the time is between 125 and 150 min. With respect to the LEV removal, the maximum removal (>85%) was reported when the pH is between 6.5 and 8, while the time is between 140 and 150 min. Higher reaction time improves the removal of AMD and LEV in a wider pH range.

3.8. Effect of TiO_2 and time on contaminant removal

The effects of TiO_2 and time on AMD and LEV removal were studied using the contour plot (Figs. 7a and b, respectively). It was observed that the higher concentration of TiO_2 and higher reaction time, improved the removal

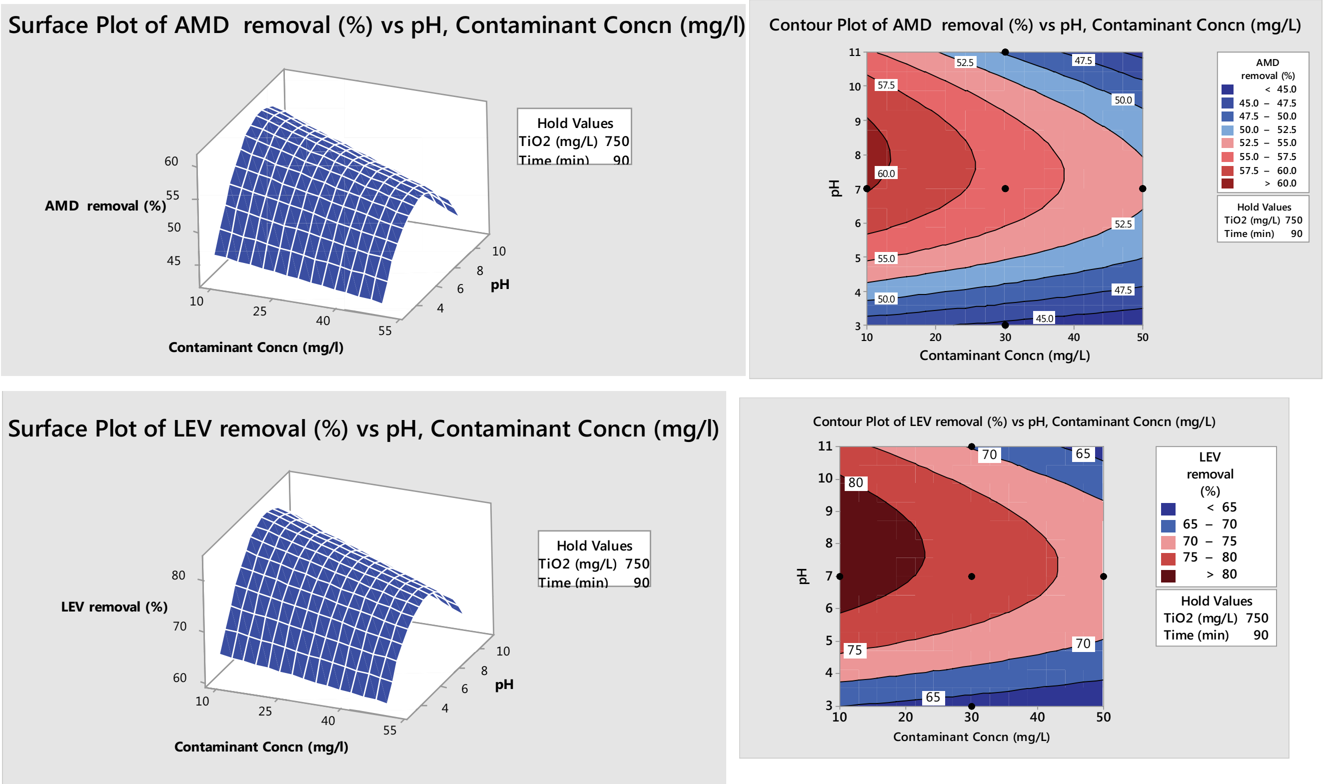

Fig. 2. Response surface and contour plot of contaminant concentration (a) pH vs. AMD removal and (b) pH vs. LEV removal.

of contaminants. The removal of AMD was found to be maximum (62%) when the TiO_2 is between 800 and 1,200 mg L^{-1}, while the time is between 125 and 150 min. With respect to the LEV removal, maximum removal (>85%) was reported when the TiO_2 is between 500 and 1,200 mg L^{-1}, while the time is between 125 and 150 min.

3.9. Optimization of AMD and LEV removal

The contour plots were overlaid to locate the possible experimental conditions for maximum removal of both the contaminants. Considering the percentage removal of AMD ranged from 29.4 to 63.1 and that of LEV between 43.3 and

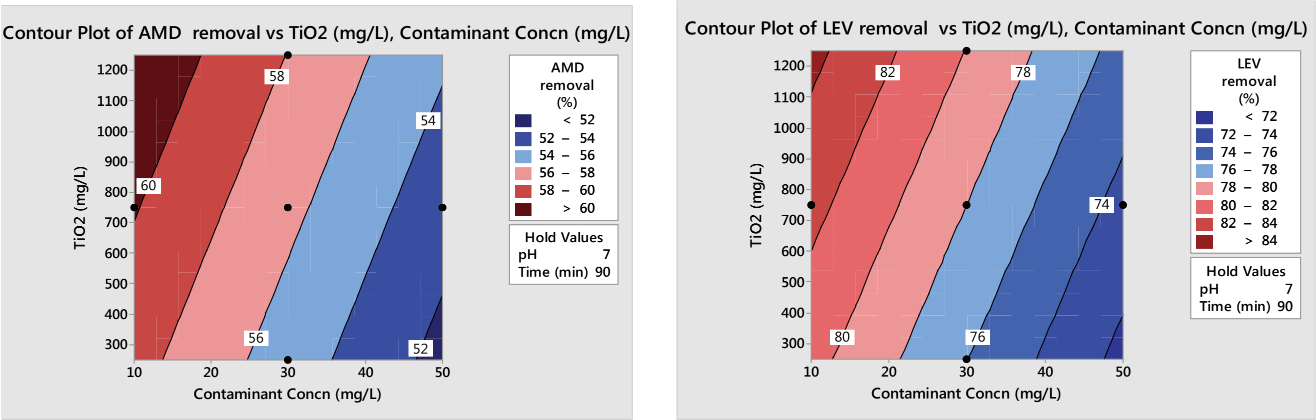

Fig. 3. Contour plot of contaminant concentration (a) TiO_2 vs. AMD and (b) TiO_2 vs. LEV removal.

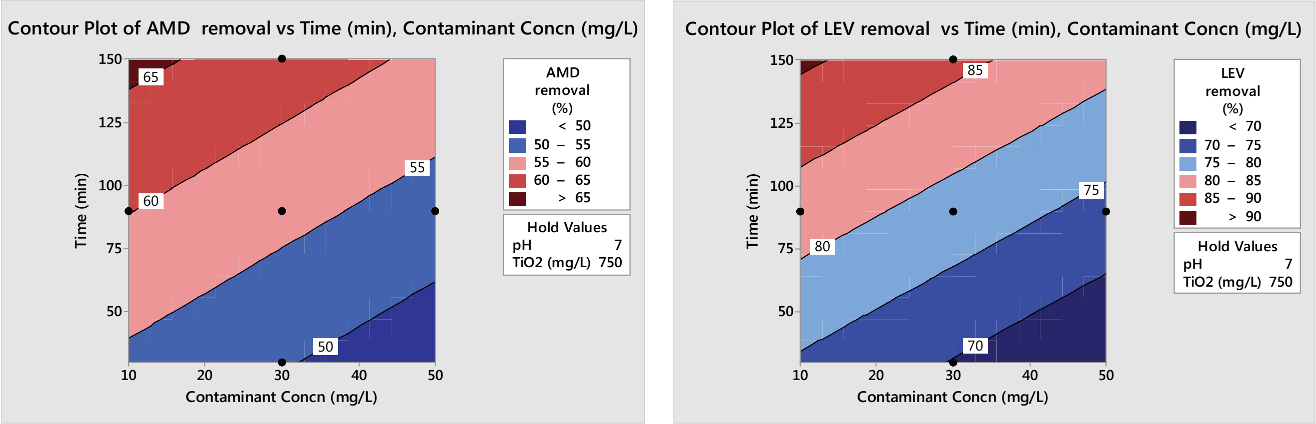

Fig. 4. Contour plot of contaminant concentration (a) time vs. AMD and (b) time vs. LEV removal.

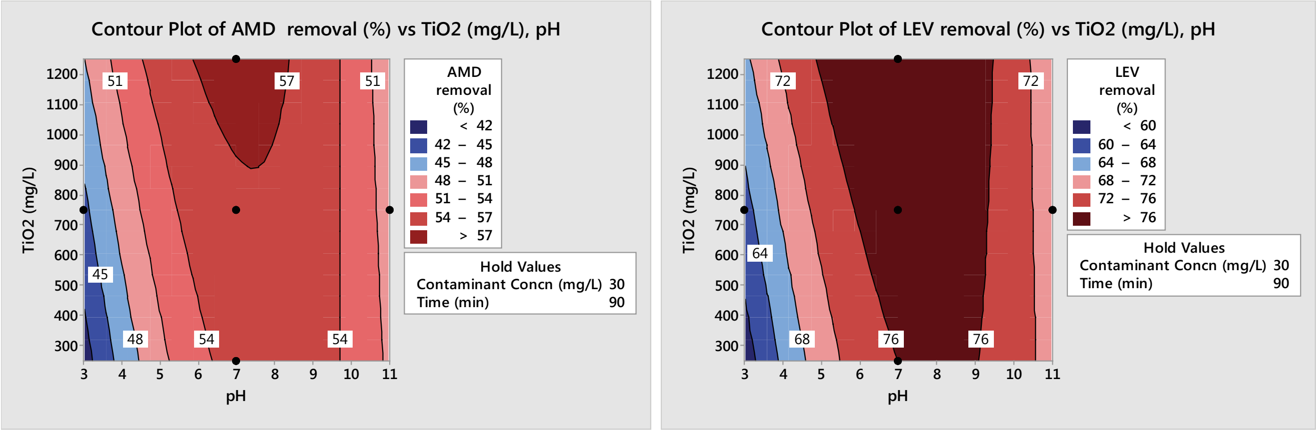

Fig. 5. Contour plot of (a) pH and TiO_2 vs. AMD and (b) pH and TiO_2 vs. LEV removal.

86.7 under different conditions maintained during the test, at least 55% combined removal of AMD and LEV was considered as the optimum condition (Figs. S1a–c, Figs. S1 and S2). The white region in the graph indicates the feasible region satisfying the conditions of the test. In order to optimise all the variables considered, response optimiser tool of MINITAB was made use of, and the optimum conditions corresponding to the highest removal of both AMD and LEV removal were evaluated (Fig. S2a). It was observed that the maximum removal of AMD was 67.6% and that of LEV was around 92.7% at the optimum conditions of the four factors considered in this design (contaminant concentration = 10 mg L^{-1}, pH = 7.3, TiO$_2$ dosage = 1,250 mg L^{-1} and reaction time = 150 min). Taking it into account the reality that the initial contaminant concentration of AMD and LEV can differ in the realistic field conditions, this variable was varied and the corresponding optimum conditions were predicted. The results are presented in Table 5 (Figs. S2b–d).

In order to validate the empirical model obtained, confirmatory experiments were performed. In the validation experiment, all the variables were retained at their respective optimum condition. Results obtained from the experiment and predicted values from the model are tabulated (Table 6). In case of AMD removal the deviation from the predicted

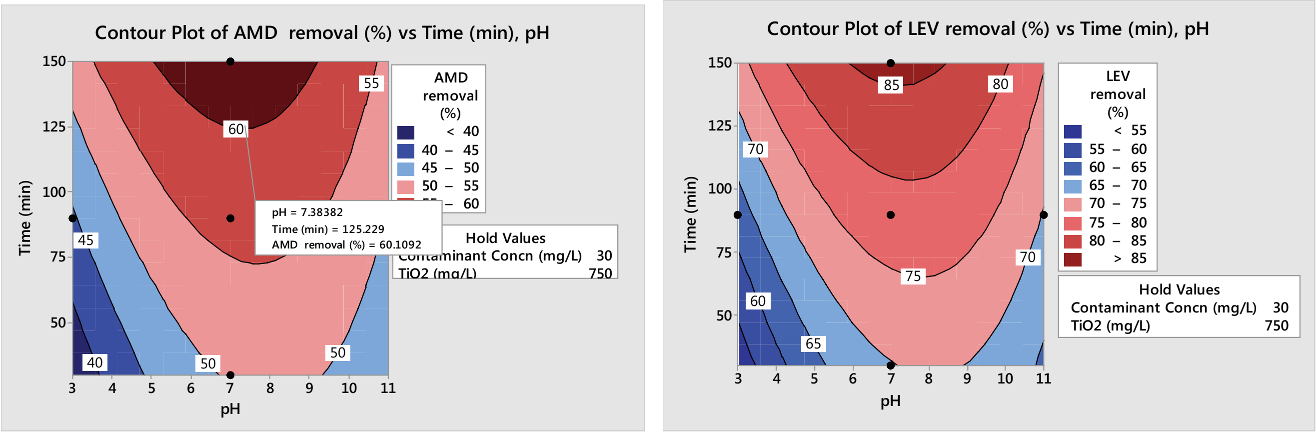

Fig. 6. Contour plot of (a) pH and time vs. AMD and (b) pH and time vs. LEV removal.

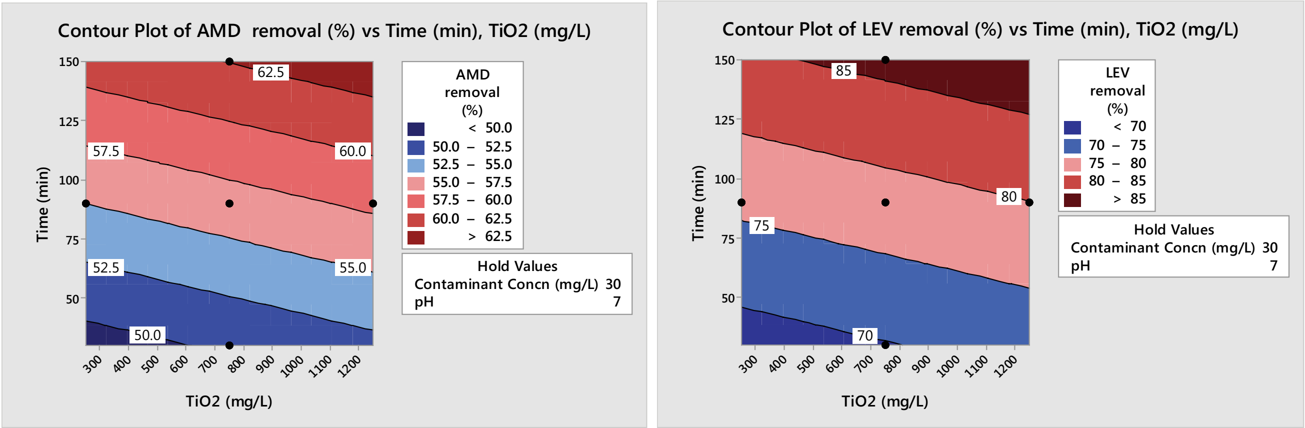

Fig. 7. Contour plot of (a) TiO$_2$ and time vs. AMD and (b) TiO$_2$ and time vs. LEV removal.

Table 5
Optimum system parameters for removal of AMD and LEV at varying initial concentration

Contaminant concentration (mg L^{-1})	Optimum system conditions			Contaminant removal (%)	
	pH	TiO$_2$ (mg L^{-1})	Reaction time (min)	AMD	LEV
10–20	7.3	1,250	150	67.6	92.7
21–30	6.8	1,250	150	63.5	87.7
31–40	6.6	1,250	150	62.5	86.2
41–50	6.3	1,250	150	61.2	84.4

Table 6
Experimental and predicted values for AMD and LEV removal

Experimental conditions	Contaminants	Observed removal (%)	Predicted removal (%)	Change (%)
AMD and LEV concentration – 10 mg L^{-1}, pH – 7.3, TiO_2 concentration – 1,250 mg L^{-1}, reaction time – 150 min	AMD	63.4	67.6	6.6
	LEV	88.3	92.7	5.0

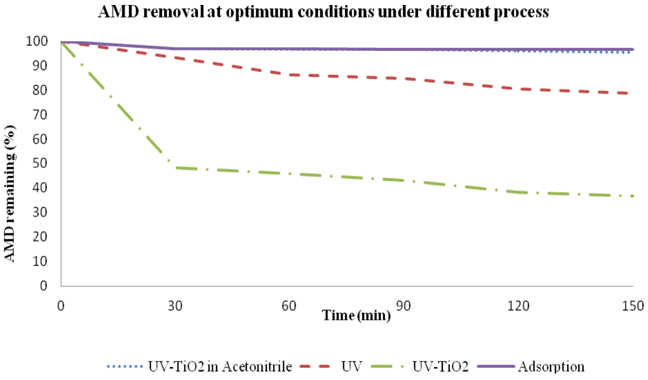

Fig. 8. AMD removal at optimum conditions under different processes.

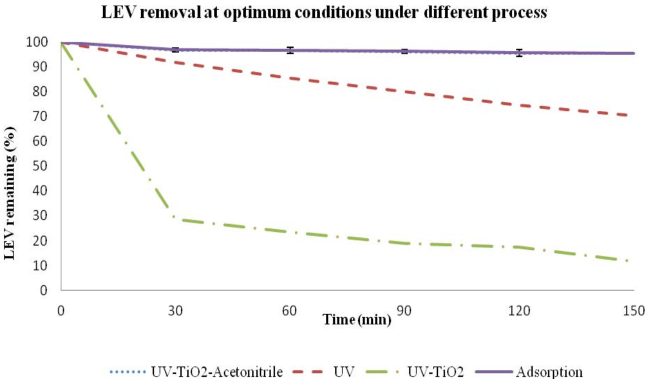

Fig. 9. LEV removal at optimum conditions under different processes.

value was found to be 6.6%, whereas for LEV it was around 5.0%. Observed removal was lower than the predicted removal; however the variation was found to be less than 10%, indicating that the regression models was developed for the removal of AMD and LEV removal are working well.

3.10. *Photocatalytic degradation characteristics of AMD and LEV under optimal system conditions*

In order to characterise the photocatalytic degradation of AMD and LEV, separate experiments were conducted to evaluate the removal by adsorption, photolytic and photocatalysis process (Figs. 8 and 9). The initial contaminant concentration was maintained at 10 mg L^{-1} and other variables were maintained at the optimum level (pH = 7.3, TiO_2 concentration = 1,250 mg L^{-1} and reaction time = 150 min). It was observed that the removal of AMD and LEV by the adsorption process was only about 3.6% and 4.7%. Additional experiments were conducted to assess the photolytic removal of AMD and LEV in the presence of a UV source without the presence of photocatalyst TiO_2. About 21% removal of AMD and 29% removal of LEV were observed. It has been reported that the removal of PCs is dominated by the OH^- radical oxidation pathway rather than by photolysis [26,27]. Lower removal of the contaminants due to adsorption and photolytic process indicates that TiO_2 plays a major role as a photocatalyst in the removal process, through the generation of the hydroxyl radical ($OH^\bullet$). Significance of the role of the $OH^\bullet$ radical can be ascertained by using a non-aqueous solvent like acetonitrile, which eliminates radical generation in the reaction mechanism. Additional experiments were performed by replacing the solvent water with acetonitrile. It was found that there was a negligible removal of AMD and LEV.

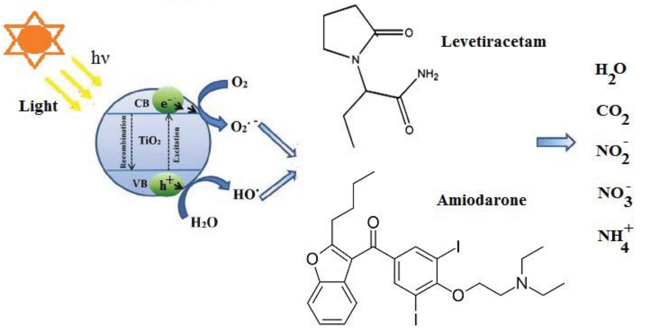

Fig. 10. Schematic diagram of photocatalytic degradation mechanisms of AMD and LEV.

These findings indicates that the $OH^\bullet$ radical plays a major role in the removal of both AMD and LEV and photocatalysis is the dominant process effecting this removal when compared to photolytic and adsorption processes. The schematic photocatalytic degradation mechanism of AMD and LEV is shown in Fig. 10.

To study the extent of mineralization of AMD and LEV under the photocatalysis process, TOC and COD were measured. The samples were tested under optimum conditions with an initial contaminant concentration of 10 mg L^{-1}. It is found that in the case of AMD, the reduction in COD and TOC was about 61.3% and 57.6% respectively, whereas for LEV, the reduction in COD and TOC was about 84.1% and 75.8%, respectively towards the end of reaction time (150 min). Removal of AMD and mineralization was found to be comparatively less when compared to that of LEV, although more than 50% mineralization could be achieved. Earlier studies have reported 50%–81% removal of TOC for other PCs in a reaction period ranging between 80 and 240 min [28–30].

4. Conclusions

Heterogeneous photocatalytic treatment of synthetic pharmaceutical industrial wastewater containing AMD and LEV was performed using a prototype photoreactor. The percentage removal of AMD ranged between 29.3% and 63.1%, whereas that of LEV varied between 43.3% and 86.6% under various experimental conditions employed in the investigation. Regression analysis was performed using the MINITAB software and equations to predict contaminant removal were developed. The R^2 value was close to 90%. It was observed that all the four chosen variables influenced the removal of AMD and LEV individually and also in combination. It was also observed that maximum removal of AMD was 67.6% and that of LEV was around 92.7% under the optimum conditions concerning the four variables considered in this design (contaminant concentration = 10 mg L^{-1}, pH = 7.3, TiO_2 concentration = 1,250 mg L^{-1} and reaction time = 150 min). The regression model developed for the removal of AMD and LEV was validated by performing confirmatory experiments. Investigations into the degradation characteristics indicate that there is very little removal of AMD and LEV through adsorption and photolytic process. Lower adsorption of AMD and LEV onto the surface of TiO_2 and negligible removal of contaminants observed when acetonitrile was employed as the solvent indicate that OH^- radical removal could be the major pathway in the degradation process. This suggests that heterogeneous photocatalytic effect plays a significant role in the removal of both these contaminants. Mineralization of the contaminants was confirmed from the COD and TOC experiments. Thus, the heterogeneous photocatalytic system employing 125 W-UV lamp and TiO_2 was capable of oxidizing and mineralizing more than 50% of the synthetic pharmaceutical industrial effluent containing AMD and LEV and could be effectively used to pre treat the pharmaceutical effluent.

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Supplementary information

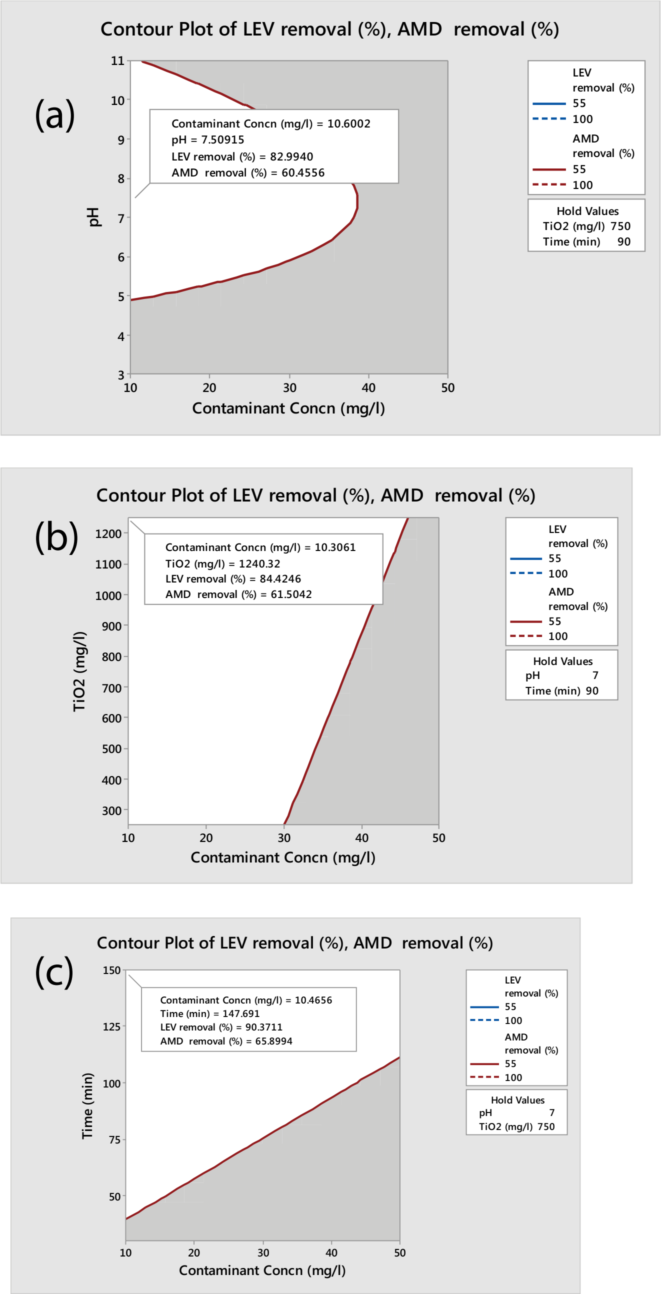

Fig. S1. Overlaid contour plot for optimum removal of AMD and LEV with variable as (a) contaminant concentration and pH, (b) contaminant and TiO_2 concentration and (c) contaminant concentration and time.

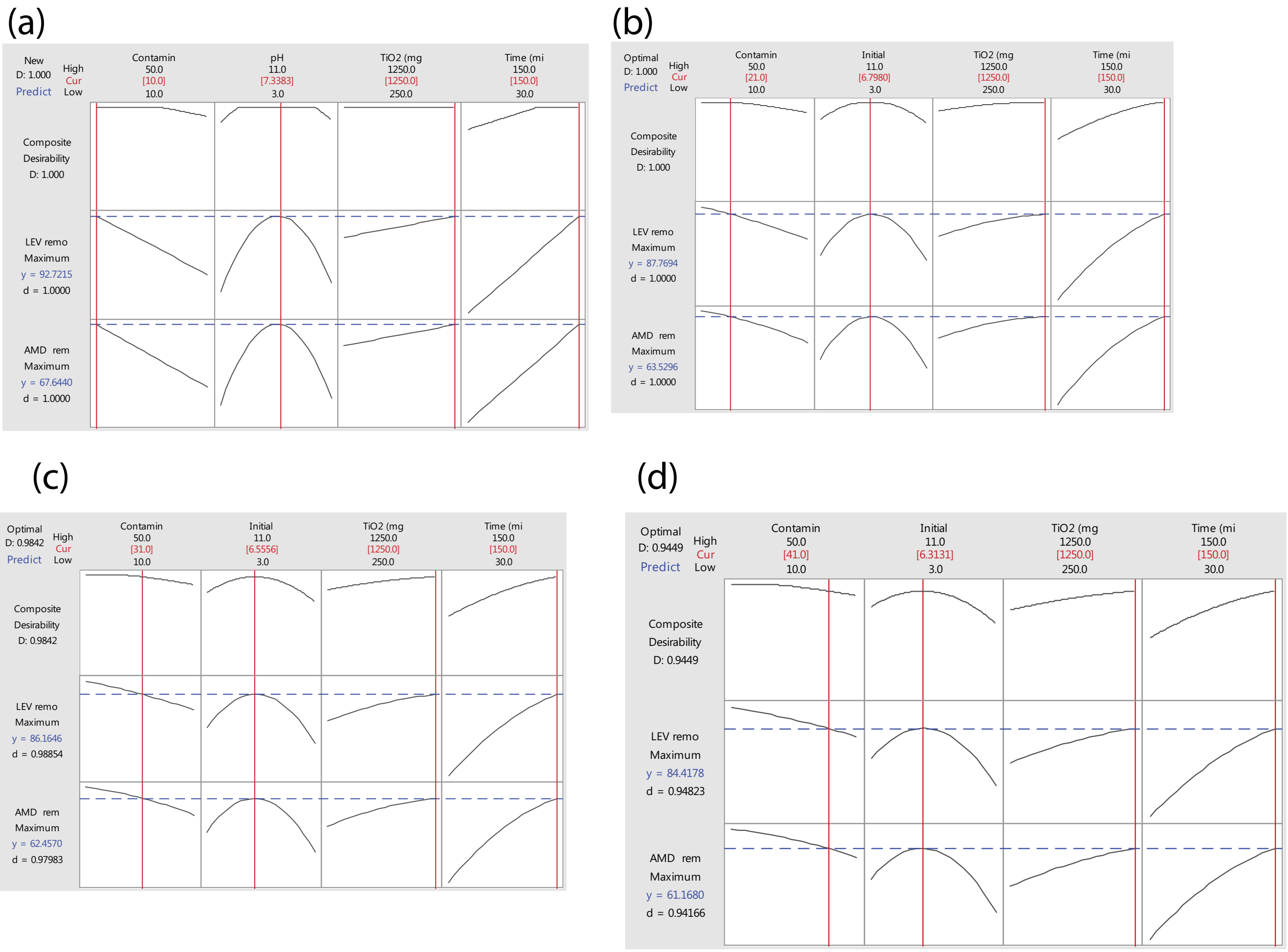

Fig. S2. Response optimiser plot for maximum removal of AMD and LEV for contaminant concentration varying between (a) 10 and 20 mg L^{-1}, (b) 21 and 30 mg L^{-1}, (c) 31 and 40 mg L^{-1} and (d) 41 and 50 mg L^{-1}.