ID Project

N. 1826

PRIMA programme is supported by Horizon 2020, the European Union's Framework Programme for Research and Innovation

SAFE

Sustainable water reuse practices improving safety in agriculture, food and environment

Deliverable: 1.6 - Validated model able to predict any behaviour in consequence of specific process conditions.

Work Package: WP1

Task 1.5 – Modelling

Antonio Zuorro

Monica Brienza

Vittoria Sapone

Due date of deliverable: 30.11.2023

Actual submission date: 30.11.2023

Deliverables	**Number**	1.6	**Title:**	Validate model able to predict any behaviour in consequence of specific process conditions
Work Package	**Number**	1	**Title:**	Sustainable and nature-based solutions as applied innovative technologies for wastewater treatment
Due date of deliverable	**Contractual**	30/11/2023	**Actual**	30/11/2023
Version number	1			
Format	pdf			
Creation date				
Version date				
Type	**X R**	☐ **DEM**	☐ **DEC**	☐ **OTHER**
Dissemination Level	☐ **PU Public**		X **CO Confidential**	
Target groups (if public)	X Scientific Community (Higher education, Research) ☐ General Public ☐ Investors		☐ Industry ☐ Policy makers ☐ Other	☐ Civil Society ☐ Medias
Responsible authors	**Name:**	Antonio Zuorro	E-mail:	Antonio.zuorro@uniroma1.it
	Partner:			

Rights	**Copyright “SAFE Consortium”. During the drafting process, access is generally limited to the SAFE Partners.**
Brief Description	The work addresses the significant need for a robust predictive model in the dynamic context of the SAFE project, focused on sustainable practices in agriculture and the food sector. The document represents a critical phase in the project's development, validating a comprehensive predictive model to anticipate outcomes in different scenarios. The SAFE project aims to revolutionize agricultural practices to enhance sustainability and resilience. Concurrently, the study explores the use of soils derived from volcanic ash for the adsorption of trimethoprim, a pollutant commonly found in wastewater. The research provides valuable insights into efficient and environmentally sound water treatment strategies. Overall, the document marks a significant milestone in the SAFE project's journey, connecting scientific research with practical applications for informed decision-making and transformative outcomes in sustainable agriculture and the food sector

Keywords	Model; adsorption, RSM, volcanic ash, wastewater treatment		
Version log Revision history			
Rev. No.	**Issue Date**	**Modified By**	**Comments**

LIST OF TABLES

LIST OF FIGURES

ABBREVIATIONS

TRM

Trimethoprim

CCD

Central Composite Design

C

concentration

T

contact time

S

stirring speed

R

solid-to-liquid ratio

EXECUTIVE SUMMARY

This work addresses the imperative need for a robust and predictive model within the dynamic context of the SAFE project, focusing on agriculture and food enterprises' sustainable practices. The deliverable represents a critical phase in the project's evolution, emphasizing the validation of a comprehensive model designed to forecast outcomes across diverse scenarios. As the SAFE project aims to revolutionize agriculture practices, the intricate processes involved necessitate a nuanced understanding. The validated predictive model scrutinized in this deliverable encapsulates the complex interplay of factors within these processes, offering a tool to anticipate outcomes under varying conditions. The overarching goal is to instigate transformative changes in agriculture and food enterprises, enhancing sustainability and resilience. In tandem, the study delves into utilizing volcanic ash-derived soils for the adsorption of trimethoprim, a common antibiotic pollutant in wastewater. The research presents a comprehensive exploration of process modeling and optimization techniques to address the pressing need for mitigating pharmaceutical pollution in aquatic systems. Through a Central Composite Design, the study evaluates the effects of key factors on trimethoprim removal, providing valuable insights for efficient and environmentally sound water treatment strategies. The deliverable marks a significant milestone in the SAFE project's journey by aligning scientific endeavors with practical applications. The validated predictive model and the innovative wastewater treatment approach contribute to informed decision-making and transformative outcomes in sustainable agriculture and food enterprises.

1. Introduction

In the dynamic realm of the SAFE project, the need for a robust and predictive model to discern and anticipate diverse behaviours resulting from specific process conditions becomes paramount. This deliverable represents a pivotal phase in the project's evolution, focusing on the validation of a comprehensive model designed to forecast outcomes across a spectrum of scenarios. As the SAFE project endeavours to innovate sustainable practices in agriculture and food enterprises, the intricacies of various processes demand a nuanced understanding. The predictive model under scrutiny aims to encapsulate the intricate interplay of factors within these processes, offering a tool to foresee and comprehend outcomes under diverse conditions. The overarching goal of the SAFE project is to instigate transformative changes in agriculture and food enterprises, fostering sustainability and resilience. The ability to validate a predictive model aligned with this ambition is fundamental. It not only augments the project's scientific underpinnings but also positions it strategically to navigate and optimize myriad processes critical to its success. Validation, a crucial aspect of model development, poses unique challenges in the context of the SAFE project. The intricacies of agricultural and food-related processes introduce a myriad of variables, necessitating a meticulous validation process. This deliverable strives to surmount these challenges, ensuring that the model's predictions align with real-world observations, thus enhancing its reliability and applicability. The successful validation of this predictive model holds the promise of being a linchpin for decision-making within the SAFE project.

By providing a tool capable of foreseeing the consequences of specific process conditions, the model becomes an invaluable asset. Its validated predictions can guide strategic choices, optimize resource utilization, and ultimately contribute to the overarching objectives of sustainability, productivity, and resilience championed by the SAFE project. This deliverable encompasses a multifaceted approach, integrating theoretical frameworks, empirical data, and real-world observations to validate the model's predictive capabilities comprehensively. Through rigorous validation protocols and scenario-based assessments, the deliverable aims to fortify the model's reliability, ensuring its utility as a dynamic and adaptive tool within the evolving landscape of the SAFE project. In essence, the validation of this predictive model marks a significant milestone in the SAFE project's journey, aligning its scientific endeavours with practical applications. It underscores the commitment to precision, innovation, and sustainability, setting the stage for informed decision-making and transformative outcomes in the realm of sustainable agriculture and food enterprises.

By delving into existing research and studies, Sapienza collected data that allowed the development of our robust model to be applied to the SAFE project data. In particular, the model was built using a specific case study. The treatment of wastewater by adsorption with volcanic ash has been improved. In the case in question the pollutant to be removed is trimethoprim (TRM). It is a medication belonging to the antibiotic class, widely used in the treatment of bacterial infections, particularly urinary tract infections. Its action aims to inhibit the growth and reproduction of bacteria, making it effective against a range of pathogens. However, its ubiquity in medical use raises significant questions regarding its impact on the aquatic environment. Trimethoprim, once administered, can persist in the human body for extended periods. This persistence is not limited to the human context but extends to wastewater effluents, as a fraction of the drug can be excreted through urine in an active form. This persistence characteristic increases the risk of contamination of water resources and surrounding soil. Trimethoprim, when released into the aquatic environment through domestic or hospital wastewater, can interact with microorganisms in water bodies. Its presence can trigger antibiotic resistance among aquatic bacteria, potentially contributing to the development of resistant strains. This can have significant implications for the ability to treat bacterial infections, both in human and animal contexts. The entry of trimethoprim into the water can generate negative effects on aquatic fauna and soil microorganisms. Its antibacterial action can alter the ecological balance, influencing the composition of microbial communities in aquatic systems. Furthermore, the presence of trimethoprim can affect the growth of algae and other aquatic organisms, with potential repercussions on the entire ecosystem. Trimethoprim falls into the category of emerging pharmaceutical pollutants, an increasingly recognized and studied phenomenon in the context of water pollution. These drugs, once released into the environment, can interact in complex ways, posing significant challenges for the sustainable management of water resources.

This study delves into the promising avenue of utilizing volcanic ash-derived soils for the adsorption of trimethoprim, presenting a comprehensive exploration of process modelling and optimization techniques. By investigating the efficacy of volcanic ash-derived soils in the removal of trimethoprim, this research aims to contribute to the development of efficient and environmentally sound water treatment strategies, addressing the pressing need for mitigating pharmaceutical pollution in aquatic systems.

2. Material and methods

A Central Composite Design (CCD) was used to evaluate the effects of initial antibiotic concentration (C), contact time (T), stirring speed (S) and solid-to-liquid ratio (R) on TRM removal. The CCD consisted of a full two-level factorial design (24 points), eight axial points at a distance ±α from the central point and six replicates at the center of the domain. The value of α was taken as (24)1/4 = 2 to ensure the orthogonality and rotatability of the design [..]. Factor levels were chosen on the basis of preliminary experiments and the need to cover a range of values of practical interest. They are reported in real and dimensionless coded values in Table 1. The coded values (xi) were calculated from the real ones (Xi) using the following equation:

$$x_i = \frac{X_i - X_{i,0}}{\Delta X_i}$$

where X_i,0 is the central point value of the i-th factor and ΔX_i is the step change value. The percentage of antibiotic removal from the aqueous solution was taken as the response variable (y). It was calculated as:

$$y = 100\frac{c_0 - c}{c_0}$$

where C_0 is the initial TRM concentration in the liquid and C is the concentration at the end of the adsorption process. The overall experimental design consisted of 30 runs, which were performed in random order to minimize the effects of uncontrolled factors (Table 2). For the statistical analysis of the results, the Design-Expert® software (version 7.0.0, Stat-Ease, Inc., Minneapolis, MN, USA) was used.

Table 1. Real and coded values of factors for the CCD

Factor	**Factor level**					**Unit**
	−α	−1	0	+1	+α	
Initial TRM concentration (C)	2	4	6	8	10	mg/L
Contact time (T)	5	20	35	50	65	min
Stirring speed (S)	300	450	600	750	900	rpm
Solid-to-liquid ratio (R)	0.01	0.02	0.03	0.04	0.05	g/mL

Table 2. Experimental design layout. xi are the dimensionless coded values for the i-th factor, y is the observed response, SO is the standard order and RO is the run order of experiments.

SO	RO	Factor level				y
		x_1	x_2	x_3	x_4	
1	22	–1	–1	–1	–1	51.66
2	26	+1	–1	–1	–1	44.08
3	3	–1	+1	–1	–1	62.17
4	29	+1	+1	–1	–1	59.15
5	7	–1	–1	+1	–1	56.52
6	24	+1	–1	+1	–1	52.44
7	18	–1	+1	+1	–1	69.73
8	8	+1	+1	+1	–1	56.74
9	14	–1	–1	–1	+1	64.26
10	20	+1	–1	–1	+1	56.58
11	4	–1	+1	–1	+1	72.95
12	21	+1	+1	–1	+1	69.94
13	30	–1	–1	+1	+1	65.08
14	1	+1	–1	+1	+1	57.86
15	25	–1	+1	+1	+1	72.08
16	13	+1	+1	+1	+1	73.14
17	11	–2	0	0	0	67.22
18	16	+2	0	0	0	65.96
19	12	0	–2	0	0	34.87
29	17	0	+2	0	0	75.75
21	15	0	0	–2	0	61.29
22	19	0	0	+2	0	71.88
23	10	0	0	0	–2	46.45
24	6	0	0	0	+2	73.74
25	23	0	0	0	0	69.92
26	2	0	0	0	0	63.53
27	5	0	0	0	0	68.29
28	28	0	0	0	0	71.19
29	27	0	0	0	0	68.27
30	9	0	0	0	0	73.33

3. Results

Several polynomials, including linear, two-factor interaction, quadratic and cubic models, were tested for their ability to fit the data listed in Table 2. The best result was obtained with a full quadratic model containing linear, quadratic and interaction terms:

$$y = a_0 + \sum_{i=1}^{4} a_i\, x_i + \sum_{i=1}^{4} a_{ii}\, x_i^2 + \sum_{i=1}^{4} \sum_{j=i+1}^{3} a_{ij} x_i x_j$$

where y is the response, xi are the coded independent variables, a0 is the intercept and a i, a_{ii} and a_{ij} are the linear, quadratic and interaction coefficients. The model was then reduced to include only the statistically significant terms. To this end, a stepwise procedure with entrance and removal levels of 0.1 was used. This procedure led to the following equation:

$$y = a_0 + a_1 x_1 + a_2 x_2 + a_3 x_3 + a_4 x_4 + a_{22} x_2^2 + a_{44} x_4^2$$

Statistical analysis by ANOVA indicated that the model was statistically significant ($p < 0.0001$) while the lack-of-fit was not ($p = 0.3599$) (Table 3). Furthermore, internally studentized residuals were randomly scattered between −3 and +3, with no outliers detected (Fig. 1).

Table 3. Analysis of variance for the reduced quadratic model (DF: degrees of freedom; SS: sum of squares; MS: mean squares; F: F-value; p: p-value).

Source	**DF**	**SS**	**MS**	***F***	***p***
Regression	6	2527.71	421.29	93.32	<0.0001
Residual error	23	345.49	15.02		
Lack-of-fit	18	290.19	16.12	1.46	0.360
Pure error	5	55.30	11.06		
Total	29	2873.20			

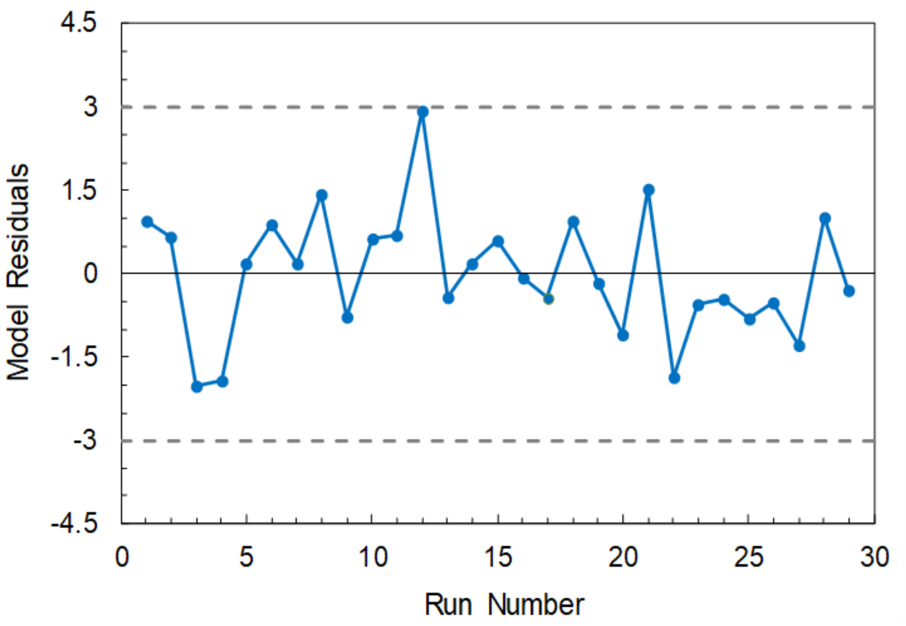


Fig. 1. Studentized model residuals as a function of run number.

The estimated coefficients together with their standard errors, t statistics and p-values, are reported in Table 4.

Table 4. Estimated model coefficients

Coefficient	**Term**	**Value**
a_0	Intercept	67.63
a_1	C	–1.96
a_2	T	7.05
a_3	S	1.83
a_4	R	5.58
a_{22}	T × T	–3.36
a_{44}	R × R	–2.17

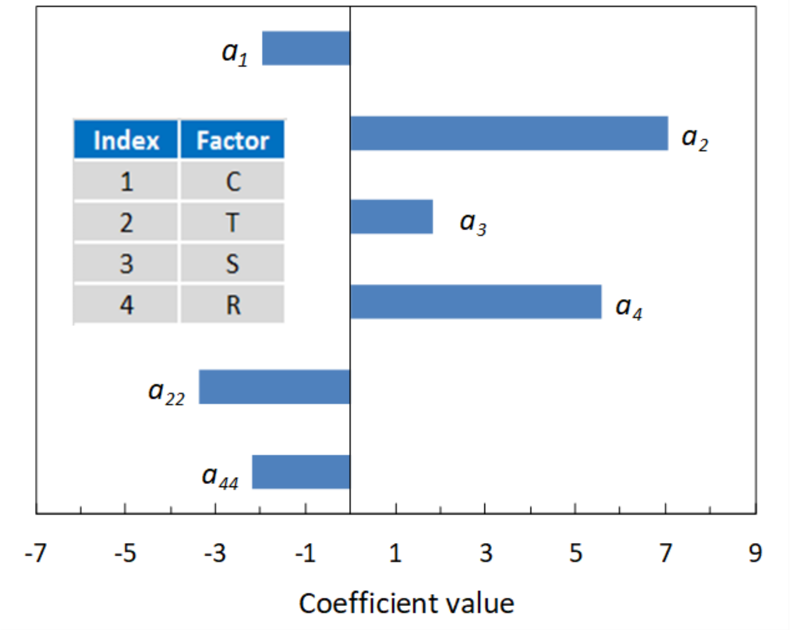
The Fig. 2 shows the Pareto chart for the reduced model coefficients. Inspection of the diagram reveals that:

a) All the factors had a significant effect on TRM removal. Two of them, T and R, affected the process response through both a linear and a quadratic term, while C and S had only a linear effect;

b) Concerning the linear terms, the initial antibiotic concentration (C) made a negative contribution to the response variable, i.e., an increase in its value had a negative effect on the removal efficiency;

c) Linear effects of the other factors were positive and increased in in the order: S < R < T;

d) There were no interactions between factors, indicating that each factor exerted its effect independently of the others.



Index	Factor
1	C
2	T
3	S
4	R

Fig. 2. Pareto chart for the model coefficients

To better appreciate the effects of the investigated factors, an analysis of perturbation and response surface plots was carried out. Perturbation plots were generated by changing the value of each factor over the range [–1, 1], while setting the other factors to their central values (0). They are shown in Fig. 3, from which it can be seen the non-monotonic variation of the response variable with contact time (T) and solvent-to-liquid ratio (R), consistently with the presence of non-zero quadratic terms in the model equation. For the initial antibiotic concentration (C) and stirring speed (S), the sign and value of the slope of the corresponding lines provide a clear indication of their effects on the removal efficiency. Some representative response surface and contour plots are presented in Figs. 4 and 5. These plots allow a simple visualization of the combined effects of two factors and are usually obtained by setting the remaining factors at their central values. The curvature of the response surfaces reflects the presence of non-linear terms in the model equation and their shape provides more detailed information on the model structure.

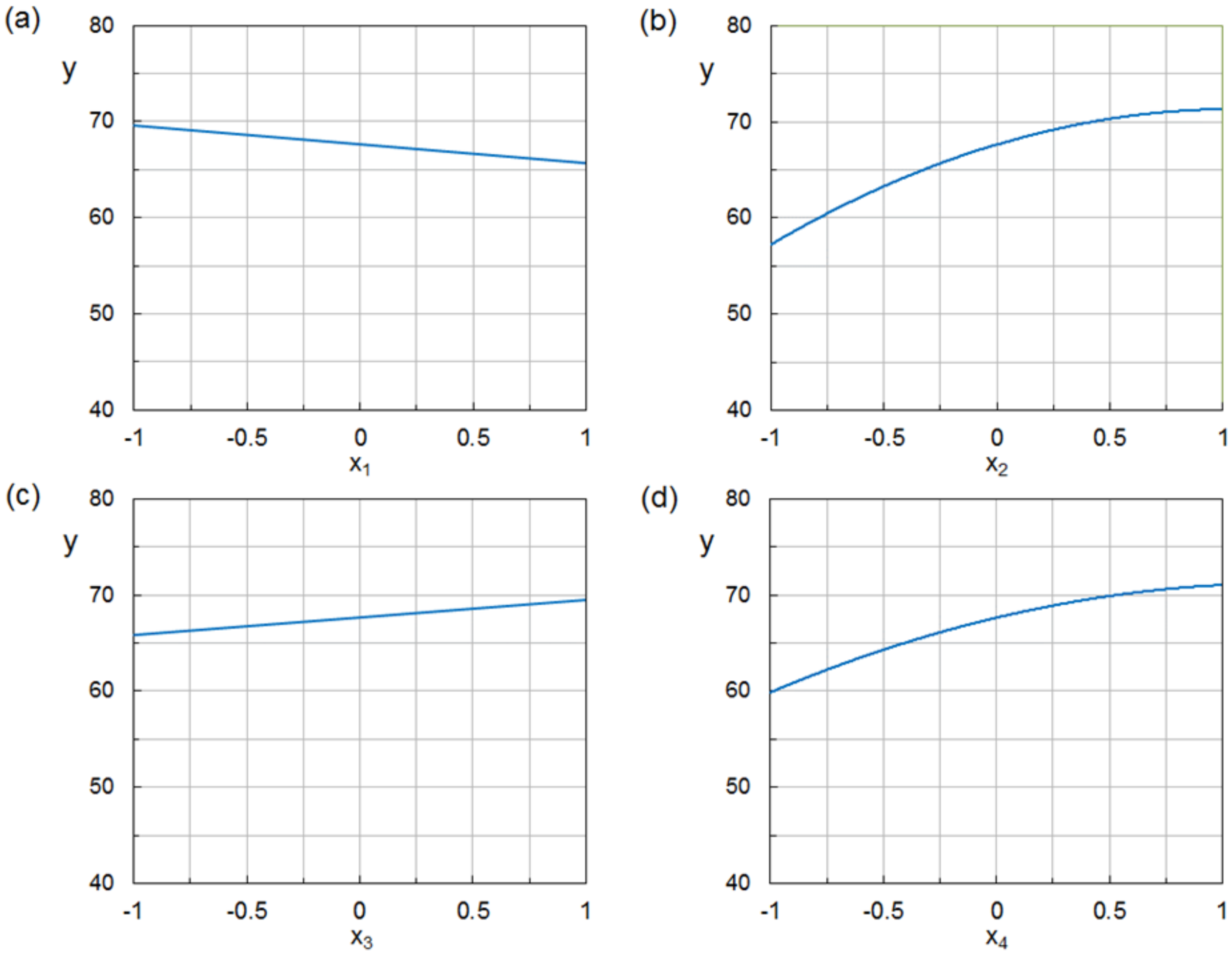
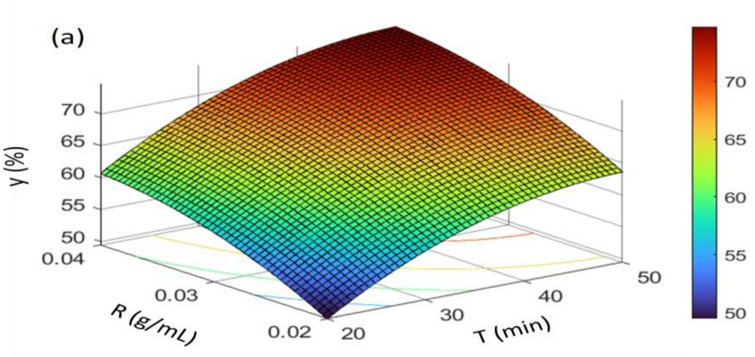


Fig. 3. Perturbation plots for: (a) initial TRM concentration; (b) contact time; (c) stirring speed; and (d) solid-to-liquid ratio. Each diagram was plotted by keeping the levels of the other three factors at their central value



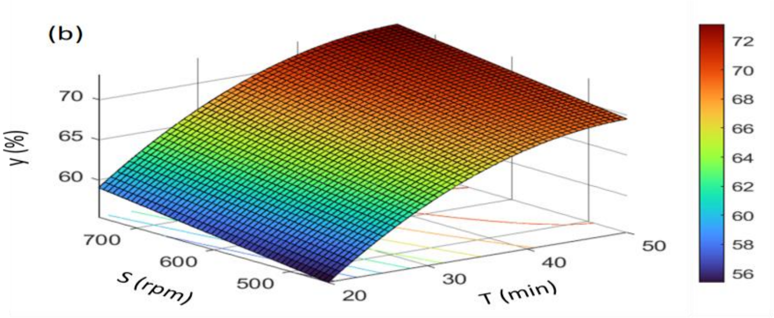


Fig. 4. Response surface plots showing the effects on TRM removal of: (a) contact time (T) and solid-to-liquid ratio (R); (b) contact time (T) and stirring speed (S). For each plot, the levels of the other factors were set at their central values (C = 6 mg/L; T = 35 min; S = 600 rpm; R = 0.03 g/mL).

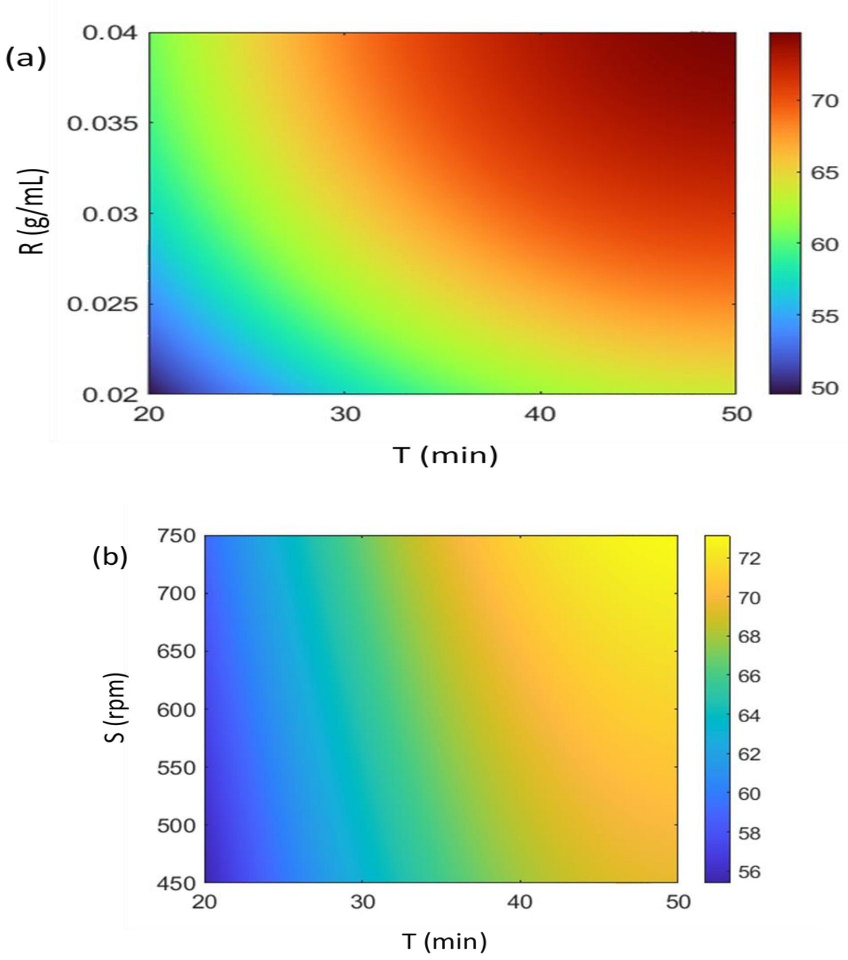


Fig. 5. Contour plots showing the effects on TRM removal of: (a) contact time (T) and solid-to-liquid ratio (R); (b) contact time (T) and stirring speed (S). For each plot, the levels of the other factors were set at their central values (C = 6 mg/L; T = 35 min; S = 600 rpm; R = 0.03 g/mL).

4. Conclusions

The reduced model coefficients revealed that all four factors (initial antibiotic concentration, contact time, solvent-to-liquid ratio, and stirring speed) had a significant effect on tetracycline removal (TRM). The contact time and solvent-to-liquid ratio both affected the process response through both linear and quadratic terms, while the initial antibiotic concentration and stirring speed had only a linear effect.

The initial antibiotic concentration had a negative effect on the removal efficiency, while the other factors had positive effects. The magnitude of the positive effects increased in the order: stirring speed < solvent-to-liquid ratio < contact time.

There were no interactions between factors, indicating that each factor exerted its effect independently of the others.

Perturbation plots showed that the response variable varied non-monotonically with contact time and solvent-to-liquid ratio, consistent with the presence of non-zero quadratic terms in the model equation. For the initial antibiotic concentration and stirring speed, the sign and value of the slope of the corresponding lines provided a clear indication of their effects on the removal efficiency.

Response surface and contour plots allowed a simple visualization of the combined effects of two factors. The curvature of the response surfaces reflected the presence of non-linear terms in the model equation and their shape provided more detailed information on the model structure.

The model can be applied on any case considered by SAFE project.