

## Supplementary file

For

### Dynamics of textile effluent degradation in falling film photoreactor at pilot scale: special attention towards inorganic pollution

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**Statistic modelling support, 2 Tables and 2 Figures**

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### **pH zero point charge (pH<sub>zpc</sub>) determination**

pH at zero point charge (pH<sub>zpc</sub>) of the used catalyst was determined using a Titrand 905 automated titrating analyzer (Metrohm, Herisau, Switzerland) according to the following set up: 0.02 g of the catalyst was immersed in 200 mL of NaCl solution at different concentrations (0.1, 0.01 and 0.001 M) under rigorous stirring at a speed of 300 rpm. The automated titrating system injected small volumes of NaOH and HCl solutions at 0.04 and 0.01 M concentrations, respectively. pH variations were monitored by the system, and the surface charge  $\sigma(C/m^2)$  was plotted Vs.  $\Delta pH = pH_i - pH_f$  and the pH<sub>zpc</sub> value was then determined. According to the results (data not shown), the surface of the catalyst presented a high concentration of cationic charges, which was confirmed by the value of pH<sub>zpc</sub> = 4.322.

### **Statistic modelling annex: Optimization of the MB degradation using RSM approach**

In the present study, a five level, four parameters CCRD was investigated for the degradation of MB in a falling film heterogeneous photocatalytic reactor according to the RSM approach. The elaborated experimental matrix was indicated in the section 2.3. ANOVA test was elaborated (See Supplementary file, Table S1) to have a better understanding on the statistical significance of the followed variables and the difference between experimental data and predicted responses as well as the determination of the second order polynomial equation. To apprehend the importance of the parameters coefficients in the empirical regression model, namely linear, square and interaction patterns, Fischer and probability test were also established (See supplementary file, Table S2).

The second order polynomial equation related to the discoloration percentage of methylene blue in aqueous solution under UV-radiation in falling film reactor is presented by the following equation:

*Percentage*(%)

$$\begin{aligned} &= 45.3 + 0.940 X_1 + 0.134 X_2 - 38.7 X_3 + 0.0295 X_4 - 0.008491 X_1^2 \\ &- 0.004025 X_2^2 - 176.1 X_3^2 - 0.000104 X_4^2 - 0.000022 X_1X_2 \\ &+ 0.063 X_1X_3 + 0.000573 X_1X_4 + 0.111 X_2X_3 + 0.000443 X_2X_4 \\ &+ 0.0995 X_3X_4 \end{aligned}$$

(Eq.S1)

By investigating the significance of the parameters coefficients in the latter equation, the positive and negative signs indicated synergistic and antagonist effects of the variables, respectively. For example, in case of a single variation, the initial concentration of MB, zinc and flow rate seem to increase the degradation rate, in opposition to the concentration of salt, which its increase imputed the decrease in the degradation rate of MB. Furthermore, statistical significance of the parameter using ANOVA test showed that both linear and quadratic variation presented low  $p$ -values and high  $F$ -values, which confirms their statistical substantiality ( $p < 0.05$ ). However, for two-way interaction condition, some parameters were found to be less suitable with the experimental data, namely  $X_1X_2$ ,  $X_1X_3$  and  $X_2X_3$ , and presented high  $p$ -values ( $p > 0.05$ ) and low  $F$ -values (0.00; 0.62 and 2.77, respectively). These results suggest that a simultaneous variation of these parameters do not have a significant effect on the degradation rate of MB (Table S1).

Considering the previous results, the empirical equation could be simplified and presented as follows:

*Percentage (%)*

$$\begin{aligned} &= 45.3 + 0.940 X_1 + 0.134 X_2 - 38.7 X_3 + 0.0295 X_4 - 0.008491 X_1^2 \\ &- 0.004025 X_2^2 - 176.1 X_3^2 - 0.000104 X_4^2 + 0.000573 X_1 X_4 \\ &+ 0.000443 X_2 X_4 + 0.0995 X_3 X_4 \end{aligned}$$

(Eq. S2)

The lack of fit (LOF) was calculated in order to predict the non-suitability of the design of experiment for fitting the experimental data (Azzaz et al., 2016). The LOF *P*-value was found to be very small (9.451E-05) and did not exceed the acceptable minimum of 0.05. However, ANOVA test related to the new regression equation presented a high determination coefficients ( $R^2 = 0.9879$  and  $R^2$  (adjusted) = 0.9773) thus confirming the good fitting of the model to the experimental data. This finding could be due to the very low experimental error, especially at the central point experiments, compared to the relatively high modelling error. Similar results were found by Berkani et al. (Berkani et al., 2015) when investigating the degradation of basic red 46 from aqueous solution using  $TiO_2$  as a photocatalyst and by Körbahti and Rauf (Körbahti and Rauf 2008) when studying the removal of toluidine blue from aqueous solution using  $V_2O_5/TiO_2$  catalyst. These results were confirmed by the normal probability plot (See Supplementary file, S3), as the experimental data presented a linear partition and a low deviation amount around the mean curve, which indicates a good normal error distribution of the given model.

**S1 – Table:** Analysis of variance (ANOVA) for central composite design of MB degradation in falling film photoreactor in presence of an inorganic pollution (DF: Degree of Freedom; Adj SS: Adjusted Sum of Square; Adj MS: Adjusted Mean Square; F: Fischer coefficient; P: Probability; X<sub>1</sub>: MB concentration (mg/L), X<sub>2</sub>: Zinc concentration (g/L), X<sub>3</sub>: NaCl concentration (Mole), X<sub>4</sub>: Solution flowrate (mL/min))

<b>Source</b>	<b>DF</b>	<b>Adj SS</b>	<b>Adj MS</b>	<b>F</b>	<b>P</b>
<b>Regression</b>	14	7252.16	518.01	19.06	0.000
<b>Linear</b>	4	7427.83	1856.56	64.04	0.000
<b>X<sub>1</sub></b>	1	2421.08	2421.08	83.5	0.000
<b>X<sub>2</sub></b>	1	191.84	191.84	6.61	0.000
<b>X<sub>3</sub></b>	1	517.37	517.37	17.84	0.000
<b>X<sub>4</sub></b>	1	4297.53	4297.53	148.21	0.000
<b>Square</b>	4	289.53	72.384	2.5	0.000
<b>X<sub>1</sub><sup>2</sup></b>	1	63.95	63.95	6.03	0.000
<b>X<sub>2</sub><sup>2</sup></b>	1	0.98	0.98	0.21	0.000
<b>X<sub>3</sub><sup>2</sup></b>	1	1.06	1.06	0.04	0.000
<b>X<sub>4</sub><sup>2</sup></b>	1	228.66	228.66	7.89	0.000
<b>Interaction</b>	6	19.19	3.198	0.11	0.000
<b>X<sub>1</sub>X<sub>2</sub></b>	1	3.02	3.02	0.10	0.978

<b>X<sub>1</sub>X<sub>3</sub></b>	1	3.08	3.08	0.11	0.742
<b>X<sub>1</sub>X<sub>4</sub></b>	1	0.41	0.41	0.01	0.000
<b>X<sub>2</sub>X<sub>3</sub></b>	1	1.43	1.43	0.05	0.490
<b>X<sub>2</sub>X<sub>4</sub></b>	1	0.21	0.21	0.01	0.000
<b>X<sub>3</sub>X<sub>4</sub></b>	1	11.04	11.04	0.38	0.000
<b>Residual Error</b>	16	88.89	5.56	-	-
<b>Lack of fit</b>	10	87.64	8.76	41.88	9.451E-05
<b>Pure Error</b>	6	1.26	0.21	-	-
<b>Total</b>	30	7341.05	-	-	-

**S2 – Table:** Factors and comparison between observed and predicted by central composite design approach of MB degradation ( $X_1$ : MB concentration (mg/L),  $X_2$ : Zinc concentration (g/L),  $X_3$ : NaCl concentration (Mole),  $X_4$ : Solution flowrate (mL/min)).

Rank of Test	Test Variables				Response	
	$X_1$	$X_2$	$X_3$	$X_4$	(Percentage (%))	
					Observed (%)	Calculated (%)
<b>1</b>	75	60	0.250	750	79.27	78.16
<b>2</b>	125	60	0.250	750	62.57	62.44
<b>3</b>	75	120	0.250	750	60.95	64.20
<b>4</b>	125	120	0.250	750	49.89	48.42
<b>5</b>	75	60	0.500	750	58.93	56.97
<b>6</b>	125	60	0.500	750	42.27	42.04
<b>7</b>	75	120	0.500	750	45.15	44.68
<b>8</b>	125	120	0.500	750	30.48	29.68
<b>9</b>	75	60	0.250	1250	35.58	36.29
<b>10</b>	125	60	0.250	1250	33.16	34.89
<b>11</b>	75	120	0.250	1250	34.12	35.61

<b>12</b>	125	120	0.250	1250	32.27	34.15
<b>13</b>	75	60	0.500	1250	24.81	27.55
<b>14</b>	125	60	0.500	1250	30.27	26.94
<b>15</b>	75	120	0.500	1250	28.48	28.53
<b>16</b>	125	120	0.500	1250	25.48	27.86
<b>17</b>	50	90	0.375	1000	49.32	47.54
<b>18</b>	150	90	0.375	1000	30.57	31.14
<b>19</b>	100	30	0.375	1000	51.23	52.60
<b>20</b>	100	150	0.375	1000	42.14	39.56
<b>21</b>	100	90	0.125	1000	65.90	63.30
<b>22</b>	100	90	0.625	1000	34.44	35.83
<b>23</b>	100	90	0.375	500	54.43	56.47
<b>24</b>	100	90	0.375	1500	16.02	12.77
<b>25</b>	100	90	0.375	1000	60.24	60.57
<b>26</b>	100	90	0.375	1000	60.48	60.57
<b>27</b>	100	90	0.375	1000	60.18	60.57
<b>28</b>	100	90	0.375	1000	61.17	60.57
<b>29</b>	100	90	0.375	1000	60.39	60.57

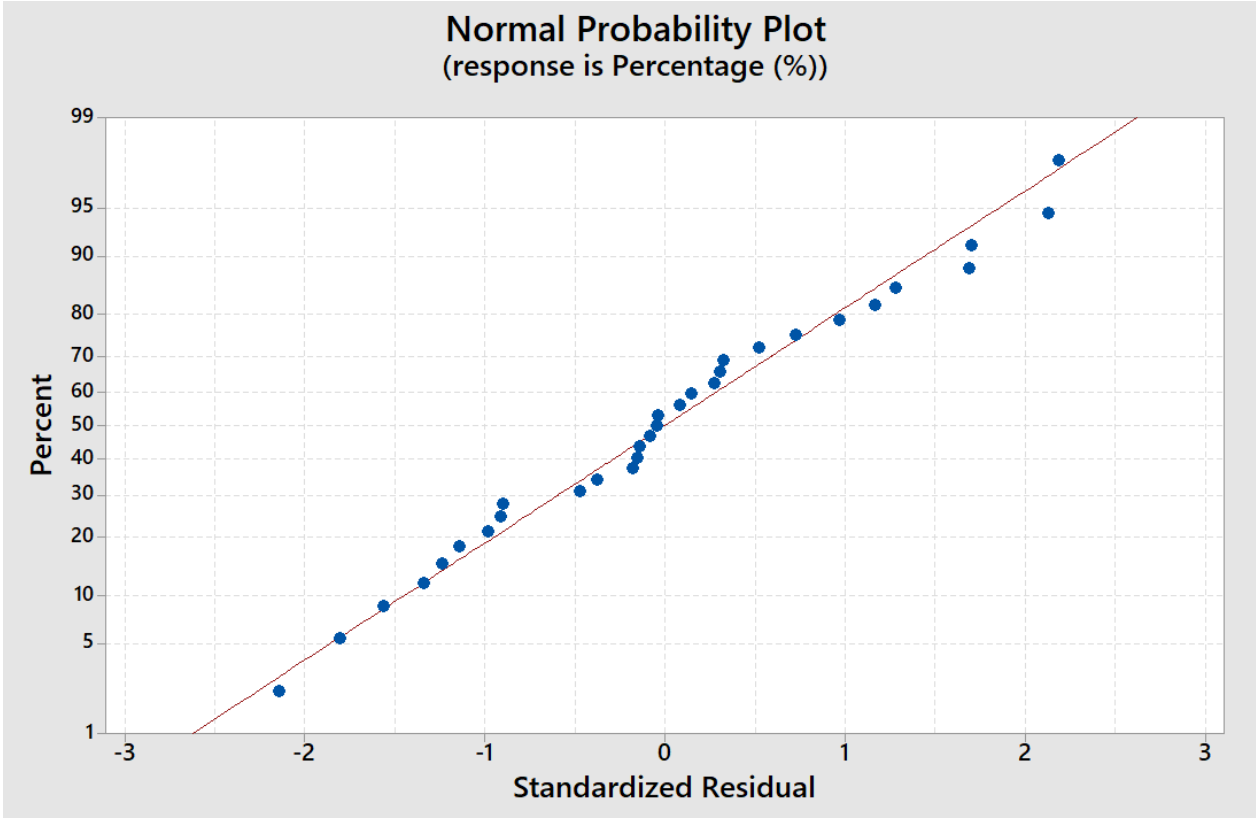


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<b>30</b>	100	90	0.375	1000	61.28	60.57
<b>31</b>	100	90	0.375	1000	60.27	60.57

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S3 – Figure: Normal probability plot between residual and error percentages



**S4 – Figure:** Desirability function of the studied model and the corresponding optimal point (Goal = maximal discoloration percentage (85.92%); Desirability = 1.000)

