# Supplementary Information

# High-efficient Recovery of Vanadium and Chromium: Optimized by Response Surface Methodology

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**Experimental design and optimization method**

The adoption of RSM to optimize a known process is easy practica1 and economica1. Successful RSM optimizations usually consist of three steps . The first step was to design appropriate experiments to efficiently assess the model parameters. The second step was to develop a polynomial model that can be applied to the experimental data through regression and to verify the model's suitability by applying a statistical test (e.g., *lack-of-fit* or *F-test*) [1-3]. The final step was to determine the values of factors that result in the best conditions. A first or second-order polynomial was usually used for RSM analysis, and a second order polynomial was preferred for responses that include a curvature. The general form of such a polynomial is as follows：

$$y=a_0+\sum_{i=1}^{k} a_i x_i + \sum_{i=1}^{k} a_{ii} x_i^2 + \sum_{i=1}^{k}\sum_{j=1}^{k} a_{ij} x_i x_j^2 + \varepsilon(i<j) \quad (1)$$

Where $y$ is the predicted response, $a_0$ is a constant, $a_i$ is the $i$ th linear coefficient, $a_{ii}$ is the $i$ th quadratic coefficient, $a_{ij}$ is the $i$ th interaction coefficient, $x_i$ is an independent variable, $k$ is the number of factors, and $\varepsilon$ is the associated error.

The coefficients of the model were predicted using regression. Details of the parameter estimations for such a model have been reported previously [1-3]. Central composite design (CCD), which was utilized in this study, was the most popular second-order experimental design and was an efficient approach to providing sufficient information to test the fitness of a model. The CCD approach did not require numerous design points; therefore, it saved the expense and time associated with completing experiments. Many experiments in which CCD had been applied had included three sets: (1) factional factorial runs ($2^{k-1}$), which studied factors at -1 (minimum) and +1 (maximum) levels; (2) center-point runs, which examined factors at a center point of a design space and aided in the understanding of curvature and data replication to evaluate pure errors; and (3) axial or star-point runs (2k), which set a1l factors to 0 (i.e., the center point), except for one factor with values of $+\alpha$ and $-\alpha$ [1-3].

In this study, the Design-Expert software (Version 8.0.6) was used to design the experiments. CCD was applied to investigate the impact of process parameters on the leaching efficiency of vanadium from vanadium-chromium residue. The experiment results were incorporated to determine an empirical equation that could predict the optimal operating conditions. The operation factors included the mass ratio of NaOH to vanadium-chromium residue, volume ratio of $H_2O_2$ to mass of vanadium-chromium residue, reaction time, reaction temperature, stirring rate and liquid-to-solid ratio. The satisfaction degree of the polynomial equation developed through a regression of Equation (1) was assessed on the basis of $R^2$ and $R_{Adj}^2$. $R^2$ was a measurement of the amount of variation around the mean, it was determined for a model using Equation (2). $R_{Adj}^2$ was a measurement is a measurement of the amount of variation around the mean; it was determined by experiments and was regulated for the number of terms in the model using Equation (3).

$$R^2=1-\frac{S_{residual}}{S_{model}-S_{residual}} \quad (2)$$

$$R_{adj}^2=1-\frac{S_{residual}\ /\ Z_{residual}}{(S_{model}+S_{residual})\ /\ (Z_{model}+Z_{residual})} \quad (3)$$

Where $S$ is the sum of squares and $Z$ is the degrees of freedom. The statistical importance of the model was verified with adequate precision using Equation (4) and Equation (5). These equations were used to determine the signal-to-noise ratio.

$$\text{Adequate precision}=\frac{\max \hat{y} - \min \hat{y}}{\sqrt{\overline{V}(\hat{y})}} \quad (4)$$

$$\overline{V}(\hat{y})=\frac{1}{n}\sum_{i=1}^{n} V(\hat{y})=\frac{p\sigma^2}{n} \quad (5)$$

Where $\hat{y}$ is the predicted response, $p$ is the number of model parameters. $\sigma^2$ is the residual mean square, and $n$ is the number of experiments.

## Analysis of the adequacy of the fitted model

Experiments were performed to evaluate the effect of process variables on the leaching efficiency; these experiments were based on the design matrix of CCD by using six replicated points. The design points and experimental results of leaching efficiency were presented in ***Table S1***.

**Table S1** CCD experimental matrix and experimental results for this study

| Run | $m_{NaOH}/m_{residue}$ | $V_{H2O2}/m_{residue}$ | Reaction time/ min | Reaction temperature/ °C | Stirring rate/ rpm | Liquid to solid mass ratio | Leaching efficiency/ % | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | Vanadium | Chromium |
| 1 | 0.2 | 0.6 | 60 | 60 | 500 | 4 | 59.68 | 49.21 |
| 2 | 0.3 | 1 | 90 | 30 | 700 | 3 | 77.67 | 40.70 |
| 3 | 1 | 0.2 | 90 | 90 | 300 | 6 | 55.15 | 19.76 |
| 4 | 1 | 1 | 30 | 30 | 300 | 6 | 96.46 | 32.93 |
| 5 | 0.6 | 0.6 | 60 | 60 | 500 | 4 | 93.70 | 52.97 |
| 6 | 0.6 | 0.6 | 60 | 60 | 500 | 4 | 93.70 | 52.97 |
| 7 | 1 | 0.2 | 30 | 90 | 300 | 3 | 75.82 | 22.74 |
| 8 | 0.2 | 1 | 30 | 30 | 300 | 3 | 51.63 | 34.41 |
| 9 | 0.6 | 0.6 | 60 | 60 | 500 | 6 | 93.76 | 52.30 |
| 10 | 1 | 1 | 30 | 90 | 700 | 6 | 58.86 | 55.28 |
| 11 | 0.6 | 0.2 | 60 | 60 | 500 | 4 | 49.98 | 18.53 |
| 12 | 1 | 0.2 | 90 | 90 | 700 | 3 | 67.43 | 24.37 |
| 13 | 0.6 | 0.6 | 90 | 60 | 500 | 4 | 56.10 | 58.57 |
| 14 | 0.2 | 0.2 | 90 | 90 | 300 | 3 | 2.46 | 18.18 |
| 15 | 0.2 | 0.2 | 30 | 90 | 700 | 6 | 6.88 | 19.85 |
| 16 | 0.6 | 0.6 | 60 | 60 | 500 | 4 | 63.00 | 59.44 |
| 17 | 1 | 0.2 | 90 | 90 | 300 | 3 | 66.24 | 22.46 |
| 18 | 0.2 | 0.2 | 30 | 30 | 300 | 6 | 14.35 | 6.63 |
| 19 | 0.6 | 0.6 | 60 | 90 | 500 | 4 | 97.23 | 54.83 |
| 20 | 0.2 | 0.2 | 90 | 30 | 700 | 6 | 15.95 | 8.00 |
| 21 | 1 | 0.2 | 30 | 30 | 700 | 6 | 32.30 | 11.80 |
| 22 | 0.6 | 0.6 | 60 | 60 | 700 | 4 | 61.12 | 53.58 |
| 23 | 0.6 | 1 | 60 | 60 | 500 | 4 | 68.53 | 71.63 |
| 24 | 0.2 | 1 | 30 | 90 | 300 | 6 | 9.91 | 71.04 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 25 | 0.6 | 0.6 | 30 | 60 | 500 | 4 | 63.02 | 58.79 |
| 26 | 0.2 | 1 | 90 | 90 | 700 | 6 | 1.88 | 55.49 |
| 27 | 0.6 | 0.6 | 60 | 60 | 500 | 4 | 59.86 | 58.63 |
| 28 | 0.6 | 0.6 | 60 | 60 | 300 | 4 | 71.30 | 57.04 |
| 29 | 0.2 | 1 | 30 | 90 | 700 | 3 | 23.86 | 68.09 |
| 30 | 0.2 | 0.2 | 30 | 30 | 700 | 3 | 16.05 | 6.12 |
| 31 | 1 | 0.2 | 90 | 30 | 300 | 3 | 39.61 | 12.15 |
| 32 | 0.6 | 0.6 | 60 | 60 | 500 | 4 | 64.88 | 63.57 |
| 33 | 1 | 1 | 90 | 30 | 700 | 6 | 65.93 | 57.01 |
| 34 | 1 | 1 | 90 | 90 | 300 | 3 | 70.23 | 75.93 |
| 35 | 0.6 | 0.6 | 60 | 60 | 500 | 4 | 68.00 | 61.54 |
| 36 | 0.2 | 1 | 90 | 30 | 300 | 6 | 33.89 | 38.50 |
| 37 | 1 | 0.6 | 60 | 60 | 500 | 4 | 69.00 | 66.70 |
| 38 | 0.6 | 0.6 | 60 | 30 | 500 | 4 | 55.18 | 35.66 |
| 39 | 1 | 1 | 30 | 30 | 700 | 3 | 69.28 | 53.64 |
| 40 | 0.6 | 0.6 | 60 | 60 | 500 | 3 | 71.37 | 58.54 |

Three-dimensional plots were utilized to study the interaction between factors on a particular response. In such plots, two factors were varied while keeping the other four constant at the middle of the variable's range. ***Figure S1*** and ***Figure S3*** showed the joint effect of the mass ratio of NaOH to vanadium-chromium residue to other factors on the leaching efficiency of vanadium. The leaching efficiency of vanadium was increased with the increasing of mass ratio of NaOH. As the mass ratio of NaOH held constant, increasing of reaction temperature also increased the leaching efficiency of vanadium, while other factor had no significant effect on leaching efficiency of vanadium. Actually reaction temperature was a very important factor affected the leaching process, while the results showed in ***Figure S3*** was not consistent with the research before and also the common results. Leaching efficiency of vanadium was mainly kept stable no matter what other factors changed except mass ratio of NaOH to vanadium-chromium residue. Also the results showed in ***Figure S4*** implied that the leaching process was not affected significant by stirring rate and liquid-to-solid ratio while other factors held constant. It was only need to choose an appropriate stirring rate and liquid-to-solid ration during the leaching efficiency upon the energy consumption and economical effective during the whole leaching process. Results showed in ***Figure S2*** indicated that reaction time was not significant factors affect leaching process of vanadium whether other factor changes.

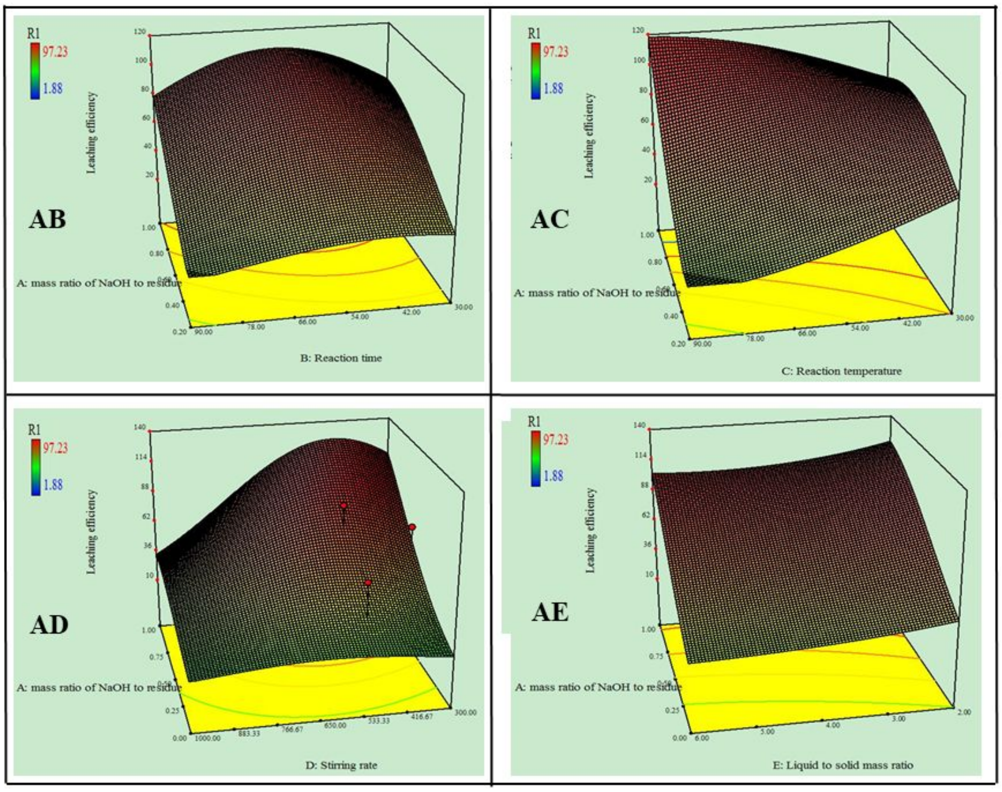


***Figure S1*** Response surface plots for factors (A to B, C, D and E)

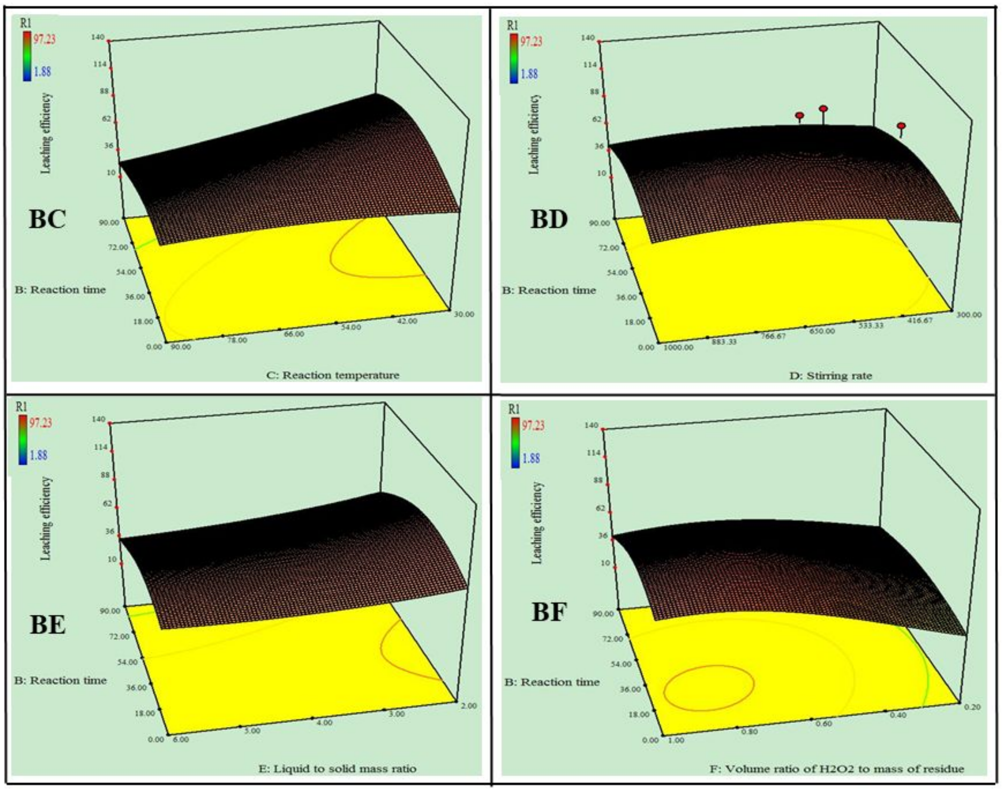


***Figure S2*** Response surface plots for factors (B to C, D, E and F)

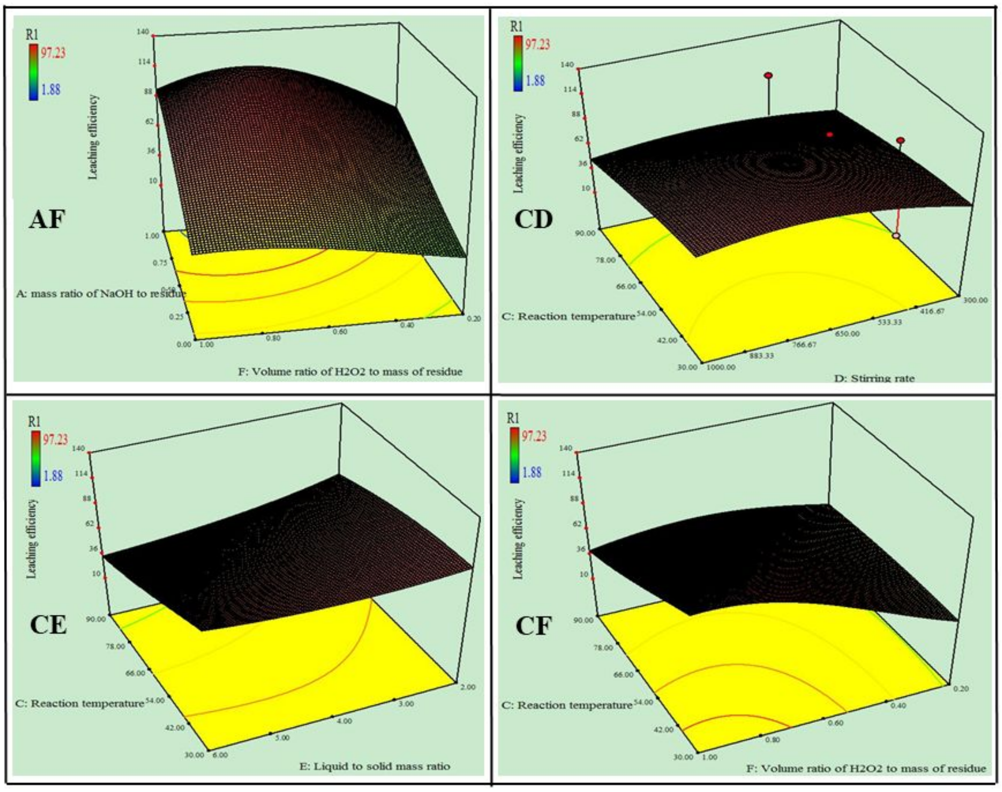


***Figure S3*** Response surface plots for factors (A to F and C to D, E and F)

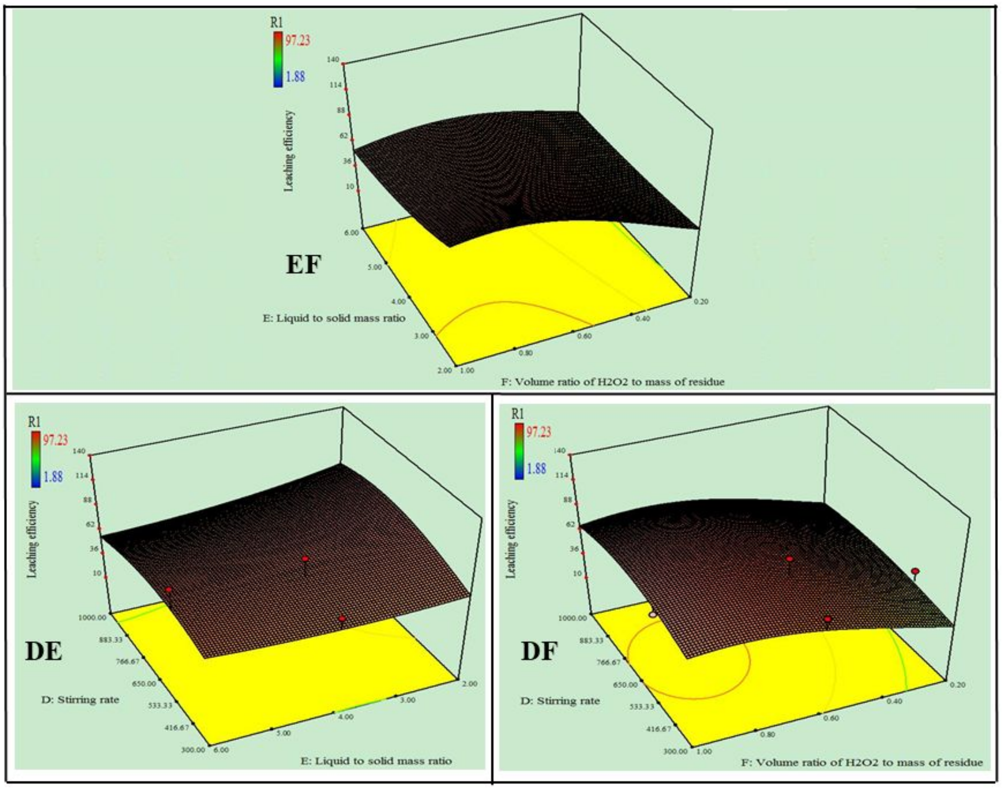


***Figure S4*** Response surface plots for factors (D to E, F and E to F)

***Figure S5*** and ***Figure S7*** showed the joint effect of the mass ratio of NaOH to vanadium-chromium residue to other factors on the leaching efficiency of chromium. The leaching efficiency of chromium was increased with the increase of mass ratio of NaOH. As the mass ratio of NaOH held constant, increasing of reaction temperature and volume ratio of $H_2O_2$ to mass of vanadium-chromium residue also increased the leaching efficiency of chromium, while other factor had no significant effect on leaching efficiency of chromium. Actually reaction temperature was a very important factor affected the leaching process, while the results showed in Figure 8 was not consistent with the research before and also the common results. Leaching efficiency of chromium was mainly kept stable no matter what other factors changed except volume ratio of $H_2O_2$ to mass of vanadium-chromium residue. Also the results showed in ***Figure S8*** implied that the leaching process was not affected significant by stirring rate and liquid-to-solid ratio while other factors held constant. It was only need to choose an appropriate stirring rate and liquid-to-solid ration during the leaching efficiency upon the energy consumption and economical effective during the whole leaching process. Results showed in ***Figure S7*** indicated that reaction time was not significant factors affect leaching process of vanadium whether other factor changes.

In summary, the leaching efficiency of chromium was affected significant by mass ratio of NaOH and volume ratio of $H_2O_2$ to mass of vanadium-chromium residue.

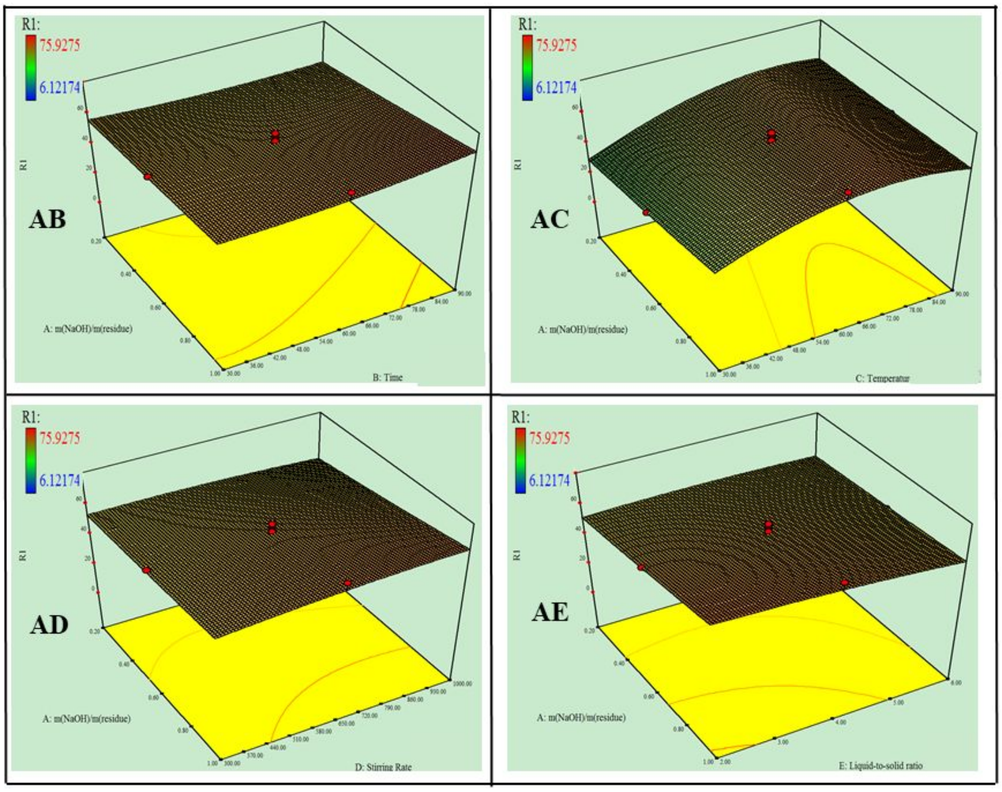


***Figure S5*** Response surface plots for factors (A to B, C, D and E)

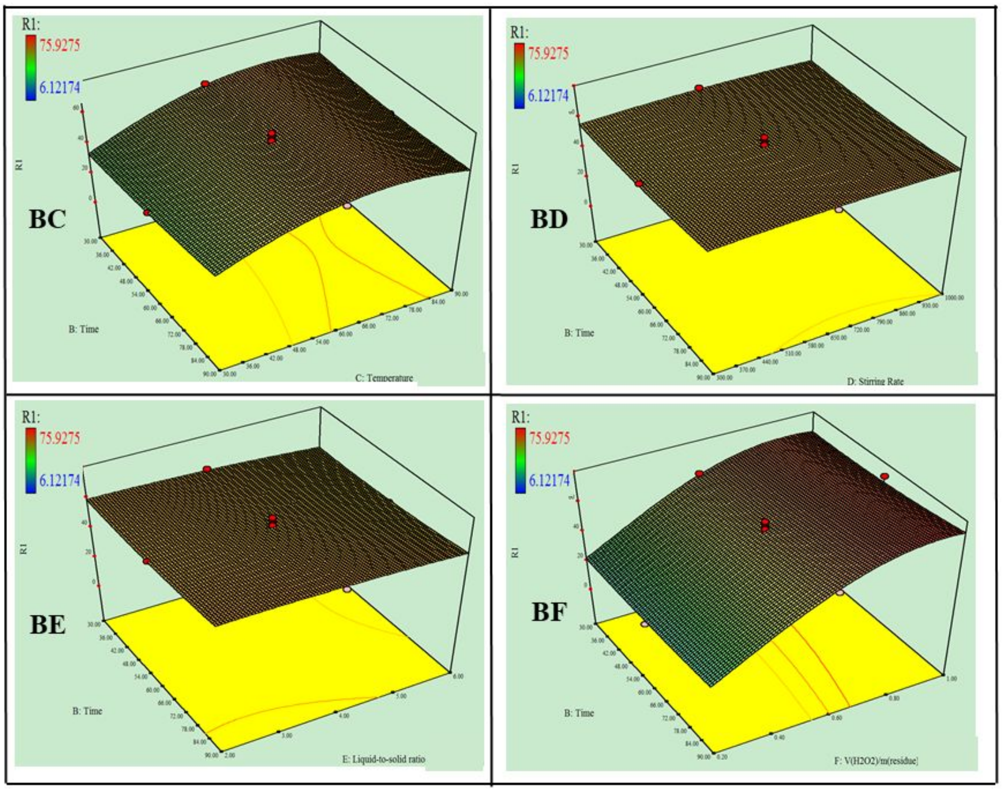


***Figure S6*** Response surface plots for factors (B to C, D, E and F)

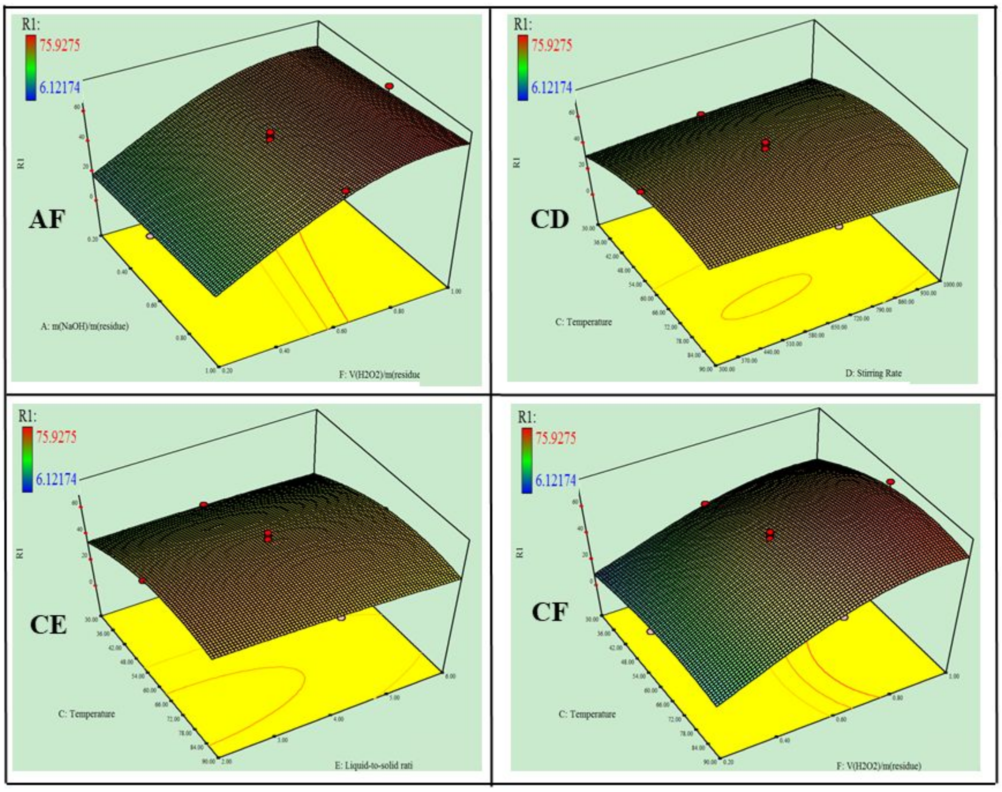


***Figure S7*** Response surface plots for factors (A to F and C to D, E and F)

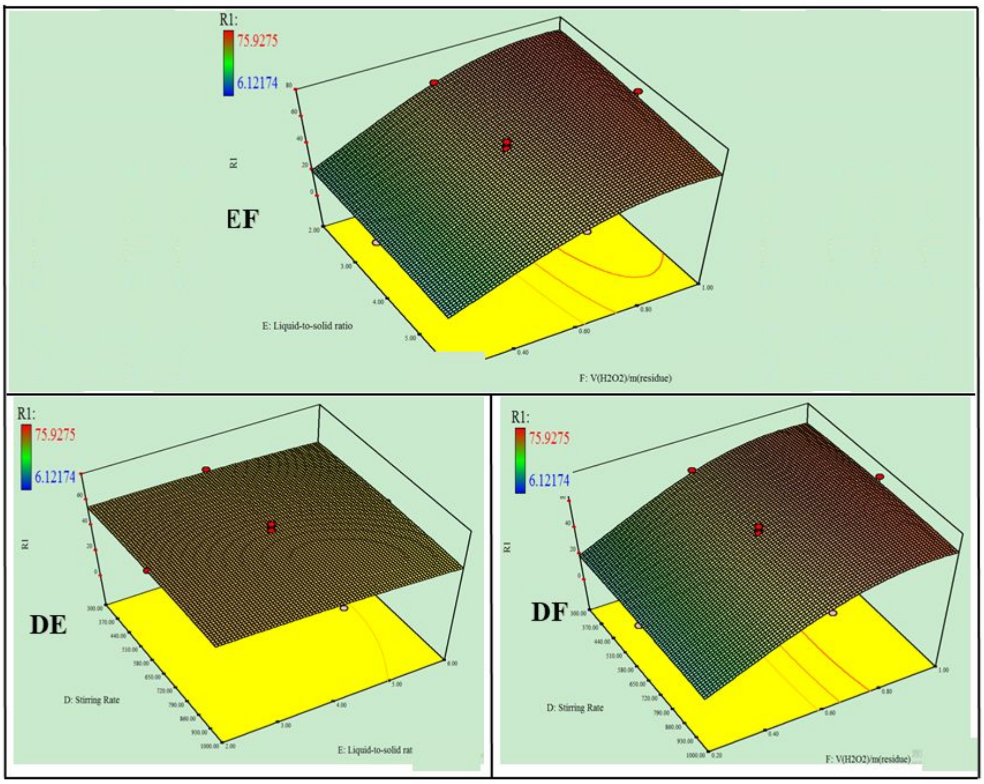


***Figure S8*** Response surface plots for factors (D to E, F and E to F)

## References

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[2] U. Rashid, F. Anwar, M. Arif, Optimization of Base Catalytic Methanolysis of Sunflower (Helianthus annuus) Seed Oil for Biodiesel Production by Using Response Surface Methodology, *Industrial & Engineering Chemistry Research* **2009**, *48*, 1719-1726.

[3] R.L. Mason, R.F. Gunst, J.L. Hess, Statistical Design and Analysis of Experiment: with Applications to Engineering and Science, John Wiley& Sons Incorporation, New York, 2003.