Response surface methodology optimization and kinetics study for anthracene adsorption onto MIL-88(Fe) and NH2-MIL-88(Fe) metal-organic frameworks

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Abstract. The experimental adsorption of Anthracene (ANT), a model polycyclic aromatic hydrocarbon (PAHs) was optimized using central composite design (CCD) of response surface methodology (RSM). MIL-88(Fe) and NH2-MIL-88(Fe) Metal-organic frameworks (MOFs) were employed as the potential adsorbents. The model was described as the significant according to the analysis of variance (ANOVA) for the statistical fittings of R² (0.991 and 0.992), and adequate precision (43.55 and 47.82) with the lack of fit F-values (2.15 and 1.59) for the MIL-88(Fe) and NH2-MIL-88(Fe) respectively. The highest adsorption efficiency achieved were 99.55 and 95.67 % for the MIL-88(Fe) and NH2-MIL-88(Fe) respectively based on the RSM optimized conditions. The pseudo-second-order kinetic model has been described as the best mechanism for the adsorption process.

Keywords: Adsorption, anthracene, kinetics, response surface methodology.

1. Introduction

Adsorption process has been a powerful technique for wastewater remediation and is receiving much attention among the researchers for the last three decades [1]. However, the batch adsorption experiment has been mostly conducted using the conventional trial and error method, where the process parameters are optimized individually through a series of experiments to obtain the optimum conditions [2]. This is tedious and one could not predict the number of experiments required to obtain the best condition and thus, large amount of reagents are consumed [3]. To alleviate these difficulties, advanced methods of design of experiments (DOE) was introduced. Several techniques of experimental design and optimization of the experimental conditions have been developed. Among the DOE techniques available, the most widely employed are the RSM and Taguchi designs [4]. Depending on the application, the methods can be applied individually or in combination when comparison studies are aimed. These techniques are applicable to various branches of knowledge and technology. In short, they are extensively employed by engineers and scientists to design different experiments.

RSM is a powerful tool used for DOE to perform process optimizations using modeling techniques. It is a collection of statistical and mathematical techniques used to set series of experimental designs for determining the optimum conditions based on the model input variables to predict the output variables [5][6]. Thus, the RSM method is valuable to describe the adsorptive studies of pollutants from wastewater and for evaluating the effects of primary parameters involved.

An empirical model is chosen for the design based on the minimum and maximum predefined control parameters of interest. This generates a set of experiments for the defined conditions and the hypothetical statistical analysis is conducted to determine the experimental responses for the respective sets of experiments [7]. The most widely employed DOE technique for adsorption studies is central
composite design (CCD) and Box-Behnken design (BBD). The set of experimental runs is dictated by the factorial design according to the levels and factors [8]. Along the RSM design using the CCD and BBD techniques, analysis of variance (ANOVA) in a quadratic polynomial model and other hypothetical tests such as Fischer (t-test), probability (probability > F), and lack of fit tests, etc., are carried out to determine the significance of the model [9].

Several researchers have reported the application of RSM for wastewater remediations. Nair et al., (2014), reviewed the systematic application of RSM for the wastewater remediations of coagulation-flocculation, advanced oxidation, electrochemical remediations, and adsorption [10]. RSM studies on the adsorptive removal of dissolved solids in wastewater were conducted by Ani et al., (2019) using activated coal as an adsorbent using CCD. The response was expressed in terms of adsorption efficiency (%R) for the minimum number of 21 runs [11]. Adsorption of the azo dye sunset yellow (SY), malachite green (MG), and methylene blue (MB) from tannery wastewater onto copper nanostructured composites were reported by Dastkhoom et al., (2017) with the experimental parameters optimized by the CCD. The input variables studied were pH, adsorbent mass, sonication time, and the adsorbents concentration within 33 experimental points [12]. Brahmi et al., (2019) explored the adsorption of acid dye onto AC obtained from wild date stones. The number of experiments was restricted at 30 runs as designed by the CCD and the prediction was made for the percentage removals and compared with the corresponding experimental values [13]. Zhang et al., (2017) described the CCD optimized adsorption of antibiotics onto desiccated rice husk-derived AC. Four factorial design was employed with 30 number of experiments and the adsorption capacity was obtained as the response variables [14]. RSM for heavy metals removal was reported by Thuan et al., (2017) with a minimum number of 20 runs for the Cu^{2+}, Ni^{2+}, and Pb^{2+} adsorption onto AC obtained from banana peel. The significance of the model was described by a lack of fit of 0.22 [15]. Polycyclic aromatic hydrocarbons (PAHs) are among the most widely detected organic pollutants from wastewater. They are organic compounds consisted of fused benzene-rings with hydrophobic properties [16]. They usually resulted from industrial production such as fuel exploration and refining, petrochemical processing, textile dyeing and to a small extent, burning of biomass [17,16]. When released in form of effluents into the environment usually exert various toxic effects to living organisms. They are listed as priority pollutants by USEPA due to their endocrine disrupting properties [18], acute toxicities even at low concentrations [19,20]. Anthracene has been a frequently detected PAHs in environmental wastewater [21,22]. It is known to have carcinogenic potency associated with hazardous effect such as respiratory complication, eye irritation, diarrhoea, defect in reproduction system, cardiovascular disorder [23,24]. They have low solubility in water, hence resistance to various forms of remediation such as biodegradation and photolysis [25,26]. Thus, it is important to explore other techniques for the effective remediation of these pollutants from the environment. Adsorption has been considered as efficient, cheap and greener remediation technique for their elimination from environmental waters.

Metal-organic frameworks (MOFs) have been recently recognized as highly porous and efficient materials for wastewater remediation process such as adsorption and photocatalytic degradation [27][28]. The tunability of the MOFs frameworks, selectivity, water stability and reusability of some MOFs have been emphasized as their characteristic superiority for adsorption application over the conventional adsorbents used for the removal of organic and inorganic pollutants from wastewater [29][30]. Thus, this work is aimed at exploring RSM optimization for the adsorption of Anthracene (ANT) as a model PAHs from aqueous medium using MIL-88(Fe) and NH2-MIL-88(Fe) MOFs. The mechanism for the adsorption will also be studied using the well-established models of pseudo-first-order, pseudo-second-order and intra-particles diffusion.

2. Materials and Methods

Anthracene standard, iron (III) chloride, benzene-1,4-dicarboxylic acid and 2-aminobenzene-1,4-dicarboxylic acid was purchased from Sigma Aldrich, USA. N,N-dimethylformamide (DMF), acetone and ethanol were supplied by Avantis Laboratory, Malaysia. All the materials were analytically graded and are used as received with no further purifications.
2.1 Synthesis of MIL-88(Fe) and NH2-MIL-88(Fe) MOFs
The synthesis of MIL-88(Fe) and MIL-88(Fe) was described by Xu et al., (2016) [31], with some modifications reported in our previous article [32].

2.2 RSM for batch adsorption study
For the batch study of ANT adsorption, the experiment was designed using CCD comprising of five parameters as the input variables: contact time (5 - 45 min), adsorbent dosage (2 - 6 mg), initial concentration (1 - 5 mg/L), pH (2 - 10) and temperature (25 - 45 °C) according to the Table 1. Thus, 47 sets of experimental runs were generated under different conditions described in Table 2.

Table 1. CCD for the adsorption of ANT, CRY and PYR onto the Zr-based and Fe-based MOFs

| Factors                        | Levels          |
|--------------------------------|-----------------|
| Contact time (min)             | 5, 15, 25, 35, 45 |
| Adsorbent dosage (mg)          | 2, 3, 4, 5, 6   |
| Initial concentration (mg/L)   | 1, 2, 3, 4, 5   |
| pH                             | 2, 4, 6, 8, 10  |
| Temperature (°C)               | 25, 30, 35, 40, 45 |

The adsorption was carried out in 100 mL flask containing 30 mL of the ANT solution in an incubator shaker (Incubator ES 20/60, bioSan) at 200 rpm at under room temperature. The sample aliquot was withdrawn at regular time interval and filtered with syringe membrane (0.45µm) prior to UV-visible spectrophotometer (GENESYS 30) analysis at 377 nm. All the analysis were conducted in triplicates for reproducibility.

The adsorption capacity at a given time \( q_t \) was calculated from the formula:

\[
q_t = \frac{(C_0 - C_t)V}{w}
\]

(1)

While the adsorption capacity at equilibrium \( q_e \) was calculated from the formula:

\[
q_e = \frac{(C_0 - C_e)V}{w}
\]

(2)

And the adsorption efficiency (%R) was calculated from the formula:

\[
%R = \frac{C_0 - C_e}{C_0} \times 100
\]

(3)

Where \( C_0, C_t, \) and \( C_e \) are the initial, time and equilibrium concentrations (mg/L), respectively and \( w \) is the weight of the adsorbent (g), and \( V \) is the volume of the solution (L).

3. Results and discussion
Optimization studies for the adsorption of the ANT onto the MIL-88(Fe) and NH2-MIL-88(Fe) was conducted according to full factorial design of CCD with five central points based on the five input variables described in section 2.2. The adsorption efficiency with respect to the different experimental conditions were presented in the tables 2. The highest adsorption efficiency recorded by MIL-88(Fe) was 99.55, 95.67% for the MIL-88(Fe) and NH2-MIL-88(Fe) respectively at run 23 under the described experimental conditions (contact time 35 minutes; MOF dosage 4 mg; initial concentrations 2mg/L; pH 2; and temperature 30 °C). The 3D graphs for the removal efficiency based on the RSM optimized conditions was depicted in Figure 1a and 1b for the MIL-88(Fe) and NH2-MIL-88(Fe) respectively.
Table 2. CCD optimization for ANT adsorption onto Fe-based MOFs

| Run | Time | Dosage | Conc | pH | Temp | MIL-88(Fe) ANT removal (%) | NH₂-MIL-88(Fe) ANT removal (%) |
|-----|------|--------|------|----|------|----------------------------|------------------------------|
| 1   | 15   | 4      | 2    | 4  | 30   | 87.65                      | 81.22                        |
| 2   | 5    | 3      | 6    | 25 | 25   | 67.22                      | 63.15                        |
| 3   | 25   | 5      | 1    | 2  | 25   | 98.75                      | 92.11                        |
| 4   | 15   | 6      | 2    | 4  | 30   | 87.12                      | 83.75                        |
| 5   | 15   | 4      | 2    | 4  | 30   | 86.35                      | 82.14                        |
| 6   | 25   | 5      | 1    | 6  | 25   | 97.46                      | 93.62                        |
| 7   | 25   | 3      | 1    | 6  | 35   | 92.33                      | 89.25                        |
| 8   | 15   | 2      | 2    | 4  | 30   | 81.12                      | 77.25                        |
| 9   | 15   | 4      | 2    | 4  | 45   | 86.62                      | 82.17                        |
| 10  | 15   | 4      | 4    | 4  | 30   | 83.19                      | 79.45                        |
| 11  | 45   | 4      | 2    | 4  | 30   | 98.36                      | 94.11                        |
| 12  | 25   | 5      | 3    | 6  | 35   | 98.15                      | 93.65                        |
| 13  | 15   | 4      | 2    | 8  | 30   | 88.34                      | 82.55                        |
| 14  | 5    | 5      | 1    | 6  | 35   | 69.22                      | 65.16                        |
| 15  | 15   | 4      | 5    | 4  | 30   | 83.92                      | 76.22                        |
| 16  | 15   | 4      | 2    | 10 | 30   | 85.52                      | 77.75                        |
| 17  | 25   | 3      | 1    | 2  | 35   | 96.46                      | 91.17                        |
| 18  | 5    | 3      | 1    | 6  | 25   | 67.82                      | 63.32                        |
| 19  | 5    | 5      | 1    | 6  | 25   | 70.16                      | 65.27                        |
| 20  | 25   | 3      | 3    | 2  | 25   | 94.55                      | 88.35                        |
| 21  | 5    | 5      | 3    | 2  | 25   | 66.85                      | 63.22                        |
| 22  | 25   | 3      | 1    | 6  | 25   | 97.18                      | 89.77                        |
| 23  | 35   | 4      | 2    | 4  | 30   | 99.55                      | 93.75                        |
| 24  | 5    | 3      | 1    | 2  | 25   | 67.25                      | 62.15                        |
| 25  | 15   | 4      | 2    | 4  | 30   | 88.64                      | 82.11                        |
| 26  | 5    | 3      | 3    | 6  | 25   | 66.22                      | 62.26                        |
| 27  | 5    | 3      | 3    | 2  | 35   | 65.75                      | 62.05                        |
| 28  | 5    | 3      | 3    | 2  | 25   | 66.17                      | 62.22                        |
| 29  | 25   | 5      | 3    | 6  | 25   | 98.77                      | 91.85                        |
| 30  | 25   | 3      | 3    | 6  | 35   | 90.25                      | 89.14                        |
| 31  | 15   | 4      | 2    | 4  | 30   | 86.77                      | 82.11                        |
| 32  | 25   | 5      | 3    | 2  | 25   | 97.17                      | 90.45                        |
| 33  | 5    | 3      | 1    | 6  | 35   | 64.55                      | 64.23                        |
| 34  | 5    | 5      | 3    | 2  | 35   | 67.16                      | 63.53                        |
| 35  | 25   | 3      | 1    | 2  | 25   | 97.64                      | 89.33                        |
| 36  | 15   | 4      | 2    | 4  | 40   | 87.22                      | 82.11                        |
| 37  | 5    | 5      | 1    | 2  | 35   | 67.11                      | 64.13                        |
| 38  | 25   | 5      | 1    | 6  | 35   | 98.33                      | 92.25                        |
| 39  | 25   | 3      | 3    | 2  | 35   | 93.52                      | 86.61                        |
| 40  | 15   | 4      | 2    | 4  | 30   | 87.22                      | 83.65                        |
| 41  | 5    | 5      | 1    | 2  | 35   | 67.86                      | 64.11                        |
| 42  | 5    | 3      | 3    | 6  | 35   | 66.45                      | 62.52                        |
| 43  | 25   | 3      | 3    | 6  | 25   | 95.12                      | 89.95                        |
| 44  | 25   | 5      | 3    | 2  | 35   | 97.53                      | 90.08                        |
| 45  | 5    | 5      | 3    | 6  | 35   | 67.83                      | 63.84                        |
| 46  | 25   | 5      | 1    | 2  | 35   | 98.22                      | 93.22                        |
| 47  | 5    | 5      | 1    | 2  | 25   | 67.45                      | 64.25                        |
Figure 1. RSM 3D graph for ANT adsorption onto (a) MIL-88(Fe) and (b) NH$_2$-MIL-88(Fe)MOFs

The ANOVA fitting for the RSM optimization of the ANT adsorption onto the MIL-88(Fe) and NH$_2$-MIL-88(Fe) was presented in Table 3. The linear regression analysis and the statistical values for the Fisher-test (F), degree of freedom (df), sum of the square and mean square error and the p-values of the main variables interactions with 95% confidence level were highlighted. According to the table, the p-
values <0.0001 were described as significant for the adsorption study. Thus, the significant interactions for the input variables of the ANT adsorption onto the Fe-based MOFs were A, B, C, AB, BD, BE, A², B² and A, B, C, D, AB, A², B², D² for the MIL-88(Fe) and NH₂-MIL-88(Fe) respectively. Similarly, the lack of fit test for the model was non-significant with F-values of 2.15 and 1.59 with the respective p-values of 23.97% and 35.29% attributed to the pure error that could occur due to noise for the MIL-88(Fe) and NH₂-MIL-88(Fe) respectively. The non-significant lack of fit has been desirable for the fitting of the model.

According to the values presented in the table, good agreement has been seen between the adjusted and predicted R², likewise, the values of the adequate precision were greater than 4, implying the significance of the model to navigate the design space.

**Table 3** ANOVA for the adsorption of ANT onto Fe-based MOFs

| Source               | Sum of square | df | Mean square | F-value | p-value | Sum of square | df | Mean square | F-value | p-value |
|----------------------|---------------|----|-------------|---------|---------|---------------|----|-------------|---------|---------|
| Model                | 7596.00       | 20 | 379.80      | 248.20  | <0.0001 | 6657.63       | 20 | 332.88      | 248.20  | <0.0001 |
| A-Contact time       | 7134.71       | 1  | 7134.71     | 4662.51 | <0.0001 | 6181.60       | 1  | 6181.60     | 4662.51 | <0.0001 |
| B-Adsorbent dosage   | 63.15         | 1  | 63.15       | 41.27   | <0.0001 | 53.71         | 1  | 53.71       | 41.27   | <0.0001 |
| C-Initial Concentration | 10.77       | 1  | 10.77       | 7.04    | <0.0134 | 12.12         | 1  | 12.12       | 7.04    | <0.0134 |
| D-pH                 | 0.0209        | 1  | 0.0209      | 0.0137  | <0.9078 | 0.0205        | 1  | 0.0205      | 0.0137  | <0.9078 |
| E-Temperature        | 5.21          | 1  | 5.21        | 3.40    | 0.0765  | 6.962         | 1  | 6.962       | 3.40    | 0.0765  |
| AB                   | 8.40          | 1  | 8.40        | 5.49    | <0.0270 | 6.10          | 1  | 6.10        | 5.49    | <0.0270 |
| AC                   | 0.3916        | 1  | 0.3916      | 0.2559  | 0.6172  | 0.0205        | 1  | 0.0205      | 0.2559  | 0.6172  |
| AD                   | 3.20          | 1  | 3.20        | 2.09    | 0.1601  | 0.5177        | 1  | 0.5177      | 2.09    | 0.1601  |
| AE                   | 2.33          | 1  | 2.33        | 1.52    | 0.2280  | 0.4489        | 1  | 0.4489      | 1.52    | 0.2280  |
| BC                   | 1.55          | 1  | 1.55        | 1.01    | 0.3237  | 3.125E-06     | 1  | 3.125E-06   | 1.01    | 0.3237  |
| BD                   | 8.18          | 1  | 8.18        | 5.35    | <0.0289 | 0.3507        | 1  | 0.3507      | 5.35    | <0.0289 |
| BE                   | 6.57          | 1  | 6.57        | 4.29    | <0.0483 | 0.0014        | 1  | 0.0014      | 4.29    | <0.0483 |
| CD                   | 0.7813        | 1  | 0.7813      | 0.5105  | 0.4813  | 1.73          | 1  | 1.73        | 0.5105  | 0.4813  |
| CE                   | 0.5512        | 1  | 0.5512      | 0.3602  | 0.5536  | 0.4348        | 1  | 0.4348      | 0.3602  | 0.5536  |
| DE                   | 3.52          | 1  | 3.52        | 2.30    | 0.1412  | 0.1213        | 1  | 0.1213      | 2.30    | 0.1412  |
| A²                   | 852.20        | 1  | 852.20      | 556.91  | <0.0001 | 675.49        | 1  | 675.49      | 556.91  | <0.0001 |
| B²                   | 20.57         | 1  | 20.57       | 13.44   | <0.0011 | 6.19          | 1  | 6.19        | 13.44   | <0.0011 |
| C²                   | 5.07          | 1  | 5.07        | 3.31    | 0.0803  | 13.13         | 1  | 13.13       | 3.31    | 0.0803  |
| D²                   | 1.22          | 1  | 1.22        | 0.7983  | 0.3798  | 20.07         | 1  | 20.07       | 0.7983  | 0.3798  |
| E²                   | 0.2590        | 1  | 0.2590      | 0.1693  | 0.6841  | 0.3195        | 1  | 0.3195      | 0.1693  | 0.6841  |
| Residual             | 39.79         | 26 | 1.53        | 29.94   | 26      | 1.53          | 29.94 | 26          | 1.53    | 29.94   |
| Lack of Fit          | 36.68         | 22 | 1.67        | 26.87   | 22      | 1.67          | 26.87 | 22          | 1.67    | 26.87   |
| Pure Error           | 3.10          | 4  | 0.7761      | 3.07    | 4       | 0.7761        | 3.07 | 4           | 0.7761  | 3.07    |
| Cor Total            | 7635.78       | 46 |             | 6687.57 | 46      |              |      |             |         |         |
| Adjusted R²          | 0.9908        |     |             | 0.9921  |         |              |      |             |         |         |
| Predicted R²         | 0.9762        |     |             | 0.9821  |         |              |      |             |         |         |
| Adequate precision   | 43.5539       |     |             | 47.8242 |         |              |      |             |         |         |
Thus, the derived quadratic equations for the model representing the removal efficiency of the MIL-88(Fe) and NH\textsubscript{2}-MIL-88(Fe) for the ANT adsorption were given by the equations (4) and (5) respectively.

\textbf{ANT adsorption onto MIL-88(Fe) (%R)} = 86.9400 + 14.5998A + 1.2565B - 0.5672C + 0.02501D - 0.3944E + 0.5125AB - 0.1106AC - 0.31625AD - 0.27AE + 0.22BC + 0.505625BD + 0.453125BE + 0.15625CD + 0.13125CE - 0.33187DE - 3.7472A\textsuperscript{2} - 0.8833B\textsuperscript{2} - 0.28901C\textsuperscript{2} - 0.1419D\textsuperscript{2} + 0.06532E\textsuperscript{2}  

(4)

\textbf{ANT adsorption onto NH\textsubscript{2}-MIL-88(Fe) (%R)} = 82.0899 + 13.5897A + 1.15875B - 0.60178C + 0.4506D + 0.14422E + 0.43656AB - 0.02531AC + 0.1272AD - 0.11844AE - 0.0033BC + 0.1047BD + 0.0065BE + 0.2328CD - 0.1166CE - 0.0616DE - 3.3362A\textsuperscript{2} - 0.4847B\textsuperscript{2} - 0.4651C\textsuperscript{2} - 0.5751D\textsuperscript{2} - 0.0726E\textsuperscript{2}  

(5)

From the effect of contact time, rapid adsorption of the ANT has been seen at the initial stage of the adsorption process, which was attributed to the abundant active sites on the surface of the MOFs as previously reported in article [21][33]. An equilibrium has been achieved within 30 minutes with the ANT concentration of 4 mg/L and the MOFs dosage of 5 mg. The removal efficiency was 98.09 and 89.48% with the corresponding adsorption capacity of 23.54 and 21.48 mg/g for the MIL-88(Fe) and NH\textsubscript{2}-MIL-88(Fe) respectively. The adsorption capacity of the MOFs at various contact time was shown in the figure 2. It described the affinity of both MIL-88(Fe) and NH\textsubscript{2}-MIL-88(Fe) for the ANT adsorption from the aqueous medium [34]. Thus, the abundant adsorption sites on the surfaces of the Fe-based MOFs has been the driving force for the adsorption of various pollutants such as heavy metals [35], dye [36] and other organic pollutants [37].

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Effect of contact time for ANT adsorption onto the MIL-88(Fe) and NH\textsubscript{2}-MIL-88(Fe) MOFs}
\end{figure}

The mechanism and the rate controlling steps for the ANT adsorption has been studied according to the kinetics models of pseudo-first-order, pseudo-second order and intra-particle diffusion models conducted at concentration ranges of 1 – 5 mg/L. Table 4 presented the values of the models evaluated. According, the values obtained, the pseudo-second-order model was the best to describe the adsorption according to the linear statistical fittings of R\textsuperscript{2}, R\textsuperscript{2} adjusted, MSE, RMSE and AIC. Similarly, the
calculated adsorption capacities ($Q_{\text{cal}}$, mg/g) of the pseudo-second-order model were in good agreement with the experimental values ($Q_{\text{exp}}$, mg/g) [38]. Intra-particle diffusion also implies that the adsorption proceeds via two steps (data not shown). The first step being the diffusion of the pollutants from the aqueous phase to the surface of the MOFs which took place at faster rate. The second step represent the adsorption of the pollutants to the active pores of the MOFs.
Table 4 Kinetics study values for ANT adsorption onto MIL-88(Fe) and NH₂-MIL-88(Fe) MOFs

| Models                  | MIL-88(Fe)          | NH₂-MIL-88(Fe)       |
|-------------------------|---------------------|----------------------|
|                         | 1 mg/L | 2 mg/L | 3 mg/L | 4 mg/L | 5 mg/L | 1 mg/L | 2 mg/L | 3 mg/L | 4 mg/L | 5 mg/L |
| Qₑ (Experimental mg/g) | 23.780  | 23.814 | 23.678 | 23.542 | 22.966 | 22.085 | 22.153 | 21.678 | 21.475 | 20.935 |
| Pseudo-first order      |         |        |        |        |        | 15.740 | 16.276 | 16.440 | 16.490 | 15.004 |
| Qₑ (Calculated mg/g)   | 0.117   | 0.276  | 0.33   | 0.116  | 0.289  | 0.273  | 0.339  | 0.286  | 0.180  |
| K₁ (1/min)              | 0.960   | 0.685  | 0.630  | 0.971  | 0.961  | 0.697  | 0.695  | 0.674  | 0.749  | 0.977  |
| R²                      | 0.950   | 0.622  | 0.556  | 0.963  | 0.952  | 0.637  | 0.634  | 0.609  | 0.699  | 0.973  |
| R² adj                  | 0.099   | 0.904  | 9.124  | 0.057  | 0.091  | 5.082  | 4.570  | 7.783  | 3.848  | 0.104  |
| MSE                     | 0.315   | 2.214  | 3.021  | 0.239  | 0.302  | 2.255  | 2.138  | 2.790  | 1.962  | 0.323  |
| RMSE                    | -12.286 | 12.773 | 17.121 | -15.591 | -12.789 | 13.029 | 12.281 | 16.008 | 11.077 | -14177 |
| AIC                     |         |        |        |        |        | -12.286 | 12.773 | 17.121 | -15.591 | -12.789 |
| Pseudo-second order     |         |        |        |        |        | 24.631  | 24.510 | 24.450 | 24.331 | 23.810 |
| Qₑ (Calculated mg/g)   | 0.024   | 0.023  | 0.022  | 0.022  | 0.029  | 0.029  | 0.030  | 0.028  | 0.030  |
| K₂ (g/mg/min)           | 0.998   | 0.998  | 0.998  | 0.998  | 0.998  | 0.999  | 0.999  | 0.999  | 0.999  |
| R²                      | 0.998   | 0.998  | 0.998  | 0.998  | 0.998  | 0.999  | 0.999  | 0.999  | 0.999  |
| R² adj                  | 0.000   | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  |
| MSE                     | 0.016   | 0.016  | 0.015  | 0.017  | 0.016  | 0.012  | 0.011  | 0.011  | 0.011  |
| RMSE                    | -47.805 | -47.728 | -48.714 | -48.082 | -48.037 | -51.851 | -52.476 | -52.813 | -52.051 | -45.787 |
| AIC                     | -25.203 | 24.875 | 24.618 | 24.350 | 24.028 | 24.562 | 24.501 | 24.326 | 23.962 | 23.688 |

Intra-particle diffusion

| Kₚ | 1.252 | 1.254 | 1.258 | 1.254 | 1.231 | 1.148 | 1.151 | 1.134 | 1.132 | 1.100 |
| C  | 8.750 | 8.369 | 8.354 | 8.208 | 8.009 | 8.323 | 8.230 | 8.190 | 7.972 | 7.871 |
| R² | 0.655 | 0.666 | 0.675 | 0.682 | 0.684 | 0.636 | 0.639 | 0.638 | 0.649 | 0.641 |
| R² adj | 0.586 | 0.599 | 0.611 | 0.619 | 0.621 | 0.563 | 0.567 | 0.566 | 0.579 | 0.570 |
| MSE | 28.948 | 27.620 | 26.626 | 25.625 | 24.474 | 26.414 | 26.186 | 25.539 | 24.244 | 23.676 |
| RMSE | 5.380 | 5.256 | 5.160 | 5.062 | 4.947 | 5.139 | 5.117 | 5.054 | 4.924 | 4.866 |
| AIC | 25.203 | 24.875 | 24.618 | 24.350 | 24.028 | 24.562 | 24.501 | 24.326 | 23.962 | 23.688 |
4. Conclusion

RSM was used to optimize the adsorption of ANT onto MIL-88(Fe) and NH₂-MIL-88(Fe) MOFs based on the CCD. The significant fitting of the model was described by the ANOVA test with R² of 0.991 and 0.992 and adequate precision of 43.55 and 47.82 for the ANT adsorption onto the MIL-88(Fe) and NH₂-MIL-88(Fe) MOFs respectively. The highest optimized adsorption efficiency achieved were 99.55 and 95.67% for the MIL-88(Fe) and NH₂-MIL-88(Fe) respectively. The kinetic data was best described as pseudo-second-order model according to the statistical linear fitting of R², RMSE and AIC for the adsorption process.

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