Removal of Pyrene from Aqueous Solution Using Fe-based Metal-organic Frameworks

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Abstract. Metal-organic frameworks (MOFs), MIL-88(Fe) and NH2-MIL-88(Fe) were synthesized using microwave-assisted solvothermal technique. BET analysis has shown the porous nature of the MOFs, possessing surface areas with corresponding pore volumes of 1240 m² g⁻¹ and 0.7 m³ g⁻¹, 941 m² g⁻¹ and 0.6 m³ g⁻¹ for MIL-88(Fe) and NH2-MIL-88(Fe), respectively. Other characterizations were also conducted using scanning electron microscopy (SEM), powdered X-ray diffraction (XRD) and Fourier transformed infrared (FTIR) spectroscopy. The MOFs were evaluated for application as adsorbents for the removal of pyrene (PYR) in aqueous solution. The removal efficiency achieved by MIL-88(Fe) was 99.7% while for NH2-MIL-88(Fe) was 96.0% within 40 minutes. Both MOFs has shown good removal of the PYR even after 5 consecutive uses. The adsorption isotherm was studied and favoured more by the Langmuir model, while the kinetics was found to follow pseudo-second-order model. The process was thermodynamically exothermic and spontaneous. Thus, the MOFs studied exhibited favourable features as potential adsorbents for the removal of PYR in wastewater.

1.0 Introduction

Water pollution as a result of the presence of various contaminants from natural and anthropogenic sources have been a major environmental problem for many decades. Organic pollutants are usually discharged from industrial, mining and agricultural areas and are usually run off into the water bodies where they reside in the ground and surface water. Most of these contaminants are highly toxic and exert various adverse health effects to human as well as destroy aquatic life and plants [1][2].

Polycyclic aromatic hydrocarbons (PAHs) are groups of hydrophobic organic compounds with two or more benzene rings. PAHs are known to originate extensively from anthropogenic sources, particularly from crude oil exploration, discharge of petrochemical effluents, oil spillage etc. [3]. They are usually persistent in the environment, and when present in the wastewater, they do not easily undergo environmental degradation due to their lipophilic nature, hence possessed potentialities to accumulate in the fatty tissues of living organisms, causing adverse health effects. Pyrene are four-membered benzene rings PAH with highly environmental impact. They are frequently detected in air, sediment and water. Their lipophilic nature when present in water renders them recalcitrant to photo
and biodegradations. It has a half-life of around 30 to 300 days [4]. Thus, their frequent discharge into the environment is associated with various toxicities of carcinogenic, mutagenic and teratogenic effects. Human long term exposure causes eye irritations, liver and kidney failure, lung cancer, nausea and vomiting [5]. Thus, the growing interest from health and environmental protection bodies, such as EU, USEPA and other internationals and national regulatory agencies have result in categorizing some PAHs as priority emerging contaminants in the environments [6].

Techniques of wastewater treatments such bioremediation [7][8], ultrafiltration membrane [9], coagulations [10][11], activated sludge techniques[12], enzymatic degradation [13], heterogeneous catalytic process [14][15] and adsorption [16][17] have been reported for PAH elimination. Among them adsorption has been regarded as promising, simple, low-cost and friendly for environmental applications. The use of various adsorbents materials such as biomass [18], clay and modified clay minerals [19], mesoporous carbon nanoparticles and activated carbons [20], polymer materials [21], zeolite and alumina [22][23] has been reported. However, porous materials of natural and synthetic origins for more efficient removal of these toxic contaminants have been proposed.

Metal-organic frameworks (MOFs) are class of advanced crystalline porous materials containing large number of pores within the framework. They are made of metal ion as the central building block with organic linkers serving as ligands. MOFs has been an active area of research due to their promising features and broad applications. MOFs possessed unique properties, uncommon to other synthetic materials such as ultrahigh surface area, uniform pore sizes and volumes and structural tunability [24]. Their BET surface area and pore volumes surpass all other synthetic materials, reaching up to 9000 m$^2$g$^{-1}$ and 2 cm$^3$g$^{-1}$ respectively. The applications of MOFs in CO$_2$ capture and conversions, chemical separations, drug delivery, nerve agents, sensing, energy conversion, pre-concentrators of explosive vapours, catalysis etc, has been reported [25]. The high porosity of the materials also qualified them to be used as potential adsorbents for wastewater remediations.

Therefore, this worked is aimed at evaluating the removal capacity of highly porous and water stable MOFs, MIL-88(Fe) and NH$_2$-MIL-88(Fe) towards PYR removal in aqueous medium. The kinetics for the adsorptions, isotherms and thermodynamics was also studied. Also, the reusability of the MOFs will be considered for practical applications.

2.0 Materials and Methods
The standard of pyrene, iron (III) chloride, terephthalic acid and amino terephthalic acid were purchased from Sigma Aldrich, USA. The solvents; N, N-dimethylformamide (DMF), acetone and ethanol were supplied by Avantis Laboratory, Malaysia. All the materials were of analytical grad and were used as received with no further purifications.

2.1 Synthesis of the MIL-88(Fe) and NH$_2$-MIL-88(Fe)
The procedure for the synthesis of MIL-88(Fe) and NH$_2$-MIL-88(Fe) were reported in our previous paper [26] as described originally by Xu et al., (2016) [27].

2.2 Characterizations
The as-synthesized MOFs were characterized using Field-emission scanning microscope (FESEM, Zeiss Supra 55 VP) operated at 200 kV, with the samples sputter-coated with gold metal, and surface area and porosimeter (ASAP Micrometrics 2020) conducted at 77 K with the samples degassed at 150 °C. The full characterizations was reported in our previous work [28].

2.3 Batch adsorption experiment
To prepare the stock solution (20 mg L$^{-1}$) of PYR, 2 mg of the analyte was dissolved in 100 mL of acetone and refrigerated at 4 °C prior to any usage. Working solution of the analyte is then prepared from the stock solution for any usage.

Removal of PYR from the aqueous solution was conducted in 100 mL flask in an incubator shaker (Incubator ES 20/60, bioSan). The procedure involved transferring 30 mL of 4 mg/L PYR solution
into the flask. About 5 mg of the MOF was added to the solution and the mixture was agitated at 200 rpm at room temperature. 2 mL aliquots of the analyte were collected at regular time interval, filtered with syringe membrane (0.45 µm) and analysed with UV-visible spectrophotometer (GENESYS 30). The absorbance was measured at 377 nm and the analysis was conducted in triplicate.

The quantity adsorbed at a given time \( q_t \) is calculated from the Equation 1.

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

And the equilibrium quantity adsorbed \( q_e \) is calculated as in Equation 2:

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

Whereas, the percentage Removal (%R) is calculated from Equation 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).

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

3.0 Results and Discussions

3.1 Characterizations of MIL-88(Fe) and NH\(_2\)-MIL-88(Fe)

Figure 1 depicted the surfaces of the MOFs morphology, which consisted of spindle shape crystals with uniform dispersibility, having particle size of 3.1 to 4.5 µm and 3.5 to 4.1 µm for MIL-88(Fe) and NH\(_2\)-MIL-88(Fe), respectively. The formation of the spindle crystalline particles suggested that the MOFs were successfully synthesized as previously reported [29][30].

EDX results were presented in Figure 2. It depicted the presence of carbon, oxygen and iron inside the MOFs. The disappearance of nitrogen peak of the amine functional group in NH\(_2\)-MIL-88(Fe) MOF was probably due to the shielding effect of carbon from the organic linker at the surface of the MOF. Chlorine was also observed in trace amount which may be attributed to the incomplete precipitation of the element from the metal-salt during synthesis.

![Figure 1](image_url)  

**Figure 1.** FESEM images of (a) MIL-88(Fe) and (b) NH\(_2\)-MIL-88(Fe)
Figure 2. EDX spectrum of (a) MIL-88(Fe) and (b) NH$_2$-MIL-88(Fe)

Table 1. Surface area, pore volume and pore size of MIL-88(Fe) and NH$_2$-MIL-88(Fe) MOFs

| Properties                      | MIL-88(Fe) | NH$_2$-MIL-88(Fe) |
|---------------------------------|------------|-------------------|
| BET surface area (m$^2$ g$^{-1}$)| 1242       | 941               |
| Micropores surface area (m$^2$ g$^{-1}$) | 761        | 749               |
| Pore volume (m$^3$ g$^{-1}$)    | 0.7        | 0.6               |
| Particle sizes (nm)             | 12.5       | 8.8               |

3.2 Removal Studies

The removal efficiency of the PYR adsorbate was evaluated using MIL-88(Fe) and NH$_2$-MIL-88(Fe) MOFs. Both MOFs have shown effective removal of the pollutant with rapid uptake at the start of the adsorption processes. Within 40 minutes of the batch adsorption process an equilibrium was attained for both of the MOFs with MIL-88(Fe) and NH$_2$-MIL-88(Fe) having adsorption capacities of 24.1±1 and 23.0±1 mg g$^{-1}$ respectively (Figure 3). The percentage removal achieved by both MOFs were 99.8±1 and 96.1±2% for MIL-88(Fe) and NH$_2$-MIL-88(Fe) MOFs respectively. The rapid and effective removals was attributed to the highly porous nature of the MOFs. MIL-88(Fe) achieved higher adsorptions compared NH$_2$-MIL-88(Fe) which is due to its relatively higher surface area, hence more vacant adsorption sites. To ascertain the efficiency of the MOFs towards PYR adsorption, a comparison study was conducted with other absorbent materials previously reported. As presented in Table 2, the MOFs reported in this work possessed higher removal capacity and shorter equilibrium time than most of the absorbents reported in the literature.
Table 2. Comparisons of various adsorbents materials used for the removals of CRY and PYR with the present study

| Adsorbent materials            | Analyte | Equilibrium time (mins) | $Q_{\text{max}}$ (mg g$^{-1}$) | R (%) | Ref.     |
|--------------------------------|---------|-------------------------|-------------------------------|-------|----------|
| Non-imprinted silica aerogel   | PYR     | 240                     | N/A                           | 29    | [31]     |
| Imprinted silica aerogel       | PYR     | 240                     | N/A                           | 30    | [31]     |
| Mesoporous organosilica        | PYR     | 24 hours                | 1.32                          | 70    | [32]     |
| Microwave radiated Activated carbon | PYR   | 180                     | 61.96                         | N/A   | [33]     |
| Mesoporous silica              | PYR     | 80                      | 3.28                          | N/A   | [34]     |
| Nanofiber                      | PYR     | 30                      | 1.480                         | 95    | [35]     |
| MIL-88(Fe)                     | PYR     | 40                      | 23.95                         | 99.8  | This work|
| NH$_2$-MIL-88(Fe)              | PYR     | 40                      | 23.03                         | 96    | This work|

Figure 3. Effect of contact time for the removal of PYR by MIL-88(Fe) and MIL-88(Fe)

3.3 Effect of initial concentrations

The effect of changing the concentration of the adsorbate was also investigated. At the concentration of 4 mg L$^{-1}$, optimum removal was achieved, the percentage removals were 99.7 and 95.9% for MIL-88(Fe) and NH$_2$-MIL-88(Fe) respectively as depicted in Figure 4. Similarly, the equilibrium adsorption capacities were 23.9 and 23.0 mg/g for the MIL-88(Fe) and NH$_2$-MIL-88(Fe) respectively. Thus, this concentration was maintained for the subsequent studies.

Figure 4. Effect of initial concentration on the removal of PYR by MIL-88(Fe) and MIL-88(Fe).

3.4 Kinetics of the adsorptions
Kinetic models were established to propose the probable mechanisms as well as the rates for the adsorptions. It explained the major factors for the affinity of the adsorbent to the adsorbate as the main objective of adsorption process. The factors upon which the controlled adsorption process mechanism depends include the adsorption capacity, mass transfer, diffusion control and chemical reaction. Adsorption data generated are subjected to various models and the one which fits most is regarded as the best to describe the process based on which the kinetic parameters provide the information for modelling as well as designing the adsorption processes. In this work, the most pronounced models of pseudo-first-order, pseudo-second-order, and intra-particle kinetic models were employed.

3.4.1 Pseudo-first-order model
This model was proposed by Lagergren [36] for the dye adsorption kinetics. It is based on the adsorption capacity. Mathematically, it is linear form is given as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

(4)

The value $k_1$ (min$^{-1}$) represents the equilibrium rate constant for the pseudo-first order model. To obtain the values of the parameters in the equation, kinetics graph of $ln (q_e - qt)$ against $t$ is plotted.

3.4.2 The pseudo-second-order model
This kinetic model was first used by Ho’s to examine the kinetic data [37]. It is based on the availability of the adsorption sites which is considered as the process driving force. It can also be used to find the sorption rate. It is expressed mathematically as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

(5)

The pseudo-second-order equilibrium rate constant is given as $k_2$ (gmg$^{-1}$min$^{-1}$). To determine the kinetics parameters, graph of $t/qt$ against $t$ is plotted.

3.4.3 Intra-particle diffusion model
This model is employed to determine the rate controlling step in the adsorption process and how the adsorbate molecules diffuse into the adsorbents. It is mathematically given as:

$$q_t = K_p t^{1/2} + C$$

(6)

Where $K_p$ is the intra-particle diffusion rate constant.

This model was further fitted using statistical regression analysis to determine the coefficient of determination ($R^2$), adjusted coefficient of determination ($R^2$ adj), root means square error (RMSE) and Akaike information criterion (AIC) [38]:

$$R^2 = \left( \sum_{i=1}^{n} (q_{i \text{exp}} - q_{i \text{model}})^2 / \sum_{i=1}^{n} (q_{i \text{exp}} - q_{i \text{exp}}^\text{exp})^2 \right)$$

(7)

$$R^2 \text{adj} = 1 - (1 - R^2) \left( \frac{n-1}{n-p} \right).$$

(8)

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^{n} (q_{i \text{exp}} - q_{i \text{model}})^2}{n}}$$

(9)

$$\text{AIC} = n \ln \left( \frac{\text{SSE}}{n} \right) + 2np + \frac{2np(n_p+1)}{n(n_p+1)}$$

(10)

The $q_e \text{exp}$ is the adsorption capacity that is determined experimentally, while the $q_e \text{exp}$ is the average experimental $q_e$. The $q_e$ model is the calculated adsorption capacity generated from the model,
n represents the number of experimental points, whereas p is the number of parameters of the fitted model.

The values of the parameter involved in the various kinetics models studied were presented in Table 3. Among the models evaluated, pseudo-second-order was found to describe the adsorption data in terms of higher $R^2$, as well as lower RMSE and AIC values than the other remaining models. Also, its calculated $q_e$ (mg g$^{-1}$) values are closer to the experimental results.

The rate at which the adsorption takes place can also be considered from the intra-particle model. As observed, (figure not shown), it comprises of two basic steps. The faster uptake of the analyte was recorded at the initial step of the process, signifying the rapid adsorption capacity due to the external diffusion of the PYR molecules from the aqueous solution to the active external pores of the MOFs. The second step is relatively slower, and subsequently became linear, signifying the adsorption of the analyte onto the external pores of the MOFs and thus the equilibrium was established.

Table 3. Kinetics parameters for the adsorption of PYR onto the MOFs

| Kinetic Models                      | MIL-88(Fe) | NH$_2$-MIL-88(Fe) |
|------------------------------------|------------|------------------|
| Pseudo-first-order model           |            |                  |
| $q_e$, exp (mg g$^{-1}$)           | 24.1±1     | 23.0±1           |
| $q_e$, cal (mg g$^{-1}$)           | 34.550     | 26.33            |
| $K_1$ (min$^{-1}$)                 | 0.135      | 0.090            |
| $R^2$                              | 0.827      | 0.54             |
| RMSE                               | 2.734      | 3.15             |
| AIC                                | 9.743      | 20.04            |
| Pseudo-second-order model          |            |                  |
| $q_e$, cal (mg g$^{-1}$)           | 30.30      | 26.66            |
| $K_2$ (g mg$^{-1}$ min$^{-1}$)     | 0.003      | 0.004            |
| $R^2$                              | 0.925      | 0.999            |
| RMSE                               | 0.098      | 0.014            |
| AIC                                | -35.42     | -66.69           |
| Intra-particle diffusion model     |            |                  |
| $K_p$ (mg$^{-1}$g$^{-1}$ min$^{-1/2}$) | 1.169     | 1.048            |
| $C$                                | 5.216      | 5.015            |
| $R^2$                              | 0.798      | 0.932            |
| RMSE                               | 3.148      | 1.486            |
| AIC                                | 20.05      | 8.035            |

3.5 Isotherms of the adsorption

Isotherms study explains the affinity of the adsorbent to the adsorbate and the nature of the interactions between the adsorbent MOFs with the PYR molecules for equilibrium to be established. Isotherms studies also help to explain the surface properties of the adsorbents, as such is use to set-up the equilibrium adsorption system based on which method could be designed and the discrete relationship between various concentrations of the adsorbates molecules with the adsorbent surfaces at a function of constant temperature could be easily interpreted. In this study, Langmuir, Freundlich and Temkin models were employed.

3.5.1 Langmuir isotherm

This model takes into consideration the effects of monolayer adsorption for adsorbent with finite number of identical sites. As such, it explains only adsorptions onto specific homogenous adsorbent surfaces as they interact with the adsorbate molecules [39]. The model is mathematically expressed as in Equation 11 and 12:
\[
\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m C_e} 
\]

(11)

\[
R_L = \frac{1}{1 + C_e K_L} 
\]

(12)

where \(q_m\) and \(K_L\) are constants representing the adsorption capacity and adsorption energy respectively. \(R_L\) is a dimensionless parameter, representing the favorability of the adsorption process. Thus; \(R_L > 1\), unfavorable; \(0 < R_L < 1\), favorable; and \(R_L = 1\), linear.

3.5.2 **Freundlich isotherm**
This model explains non-identical adsorbent with heterogeneous surfaces. It gives a satisfactory description of the adsorption system with heterogenous surface energy. The model is expressed as:

\[
\log(q_e) = \log K_F + \frac{1}{n_F} \log C_e 
\]

(13)

\(K_F\) is the Freundlich isotherm constant which represents the adsorption capacity. The value \(1/n_F\) represents the adsorption intensity.

3.5.3 **Temkin isotherm**
This model considers indirect interaction between adsorbate molecules and the adsorbent and explains how the heat of adsorption decreases with coverage. It is given by:

\[
q_e = \frac{b_T}{b_T} \ln A_T C_e 
\]

(14)

where, \(b_T\) represents the Temkin heat of adsorption, (kJ mol\(^{-1}\)). \(A\) is the binding constant at equilibrium corresponding to the maximum binding energy (L g\(^{-1}\)). \(T\) is the absolute temperature (K), while \(R\) is the Universal gas constant (8.314 J mol\(^{-1}\)K\(^{-1}\)).

Among the various models studied, the values obtained for all the parameters, \(R^2\), RMSE and AIC were more satisfactorily to the Langmuir. Similarly, the \(R_L\) values obtained for both MOFs were less than unity, indicating the favourable process and the monolayer interactions of the MOFs materials with the PYR molecules. Thus, it was concluded that the MOFs contained homogenous adsorption sites with higher uptake of the analyte studied [40].

**Table 4.** Isotherms parameters for the removal of PYR by MIL-88(Fe) and NH\(_2\)-MIL-88(Fe).

| Isotherm Model         | Parameter      | MIL-88(Fe) | NH\(_2\)-MIL-88(Fe) |
|------------------------|----------------|------------|---------------------|
| Langmuir Isotherm      | \(q_m\) (L mg\(^{-1}\)) | 54.645     | 87.719              |
|                        | \(K_L\) (mg g\(^{-1}\)) | 30.500     | 2.651               |
|                        | \(R_L\)         | 8.314      | 0.086               |
|                        | \(R^2\)         | 0.972      | 0.958               |
|                        | RMSE            | 0.00       | 0.001               |
|                        | AIC             | -60.983    | -59.332             |
|                        | \(K_F\) (L g\(^{-1}\)) | 61.802     | 79.287              |
| Freundlich Model       | \(n_F\)        | 8.518      | 1.654               |
|                        | \(R^2\)         | 0.855      | 0.920               |
|                        | RMSE            | 0.057      | 0.041               |
|                        | AIC             | -21.729    | -24.400             |
|                        | \(B\) (kJmol\(^{-1}\)) | 7.587     | 19.664              |
### Isotherm Model Parameter | MIL-88(Fe) | NH₂-MIL-88(Fe)
--- | --- | ---
Temkin Model | A (L g⁻¹) | 1.653 | 25480
 | R² | 0.838 | 0.920
 | RMSE | 3.918 | 2.552

3.6 Thermodynamics of the adsorptions
Thermodynamics study was conducted based on the effect of temperature changes (298-388K) for the adsorption process as temperature changes under similar condition to batch adsorption experiments. The values of the parameters; Gibbs free energy, enthalpy and entropy changes were deducted from Van’t Hoff’s equations given as:

\[ \Delta G^\circ = -RT \ln K_c \]  
\[ \ln K_c = \frac{\Delta H^\circ}{R} - \frac{\Delta S^\circ}{RT} \]

Where \( \Delta G^\circ \) (KJ mol⁻¹) represents the Gibbs free energy change. \( R \) is the Universal gas constant (J K⁻¹mol⁻¹) and \( T \) is the temperature at which the adsorption experiment was conducted (K). The value \( K_c \) is referred to as distribution coefficient and it represents the ratio of the amount of PYR adsorbed at the surface of the MOFs \( (q_e, \text{mg g}^{-1}) \) to the concentration of the adsorbates \( (C_e, \text{mg L}^{-1}) \) at equilibrium. The \( \Delta H^\circ \) (KJ mol⁻¹) and \( \Delta S^\circ \) (Jmol⁻¹K) represent the enthalpy and entropy changes of the process respectively. From the plots of \( \ln K_c \) against \( 1/T \), the values of the parameters were obtained.

For all the MOFs, the adsorption capacity values were found to decreased as the temperature was increased (Figure 5), indicating the exothermic process. Also, the values of all the thermodynamic parameters were negative and decreased as well when the temperature increased. These values also further confirmed the spontaneous and exothermic nature of the process, and it is unfavourable at higher temperature. Meanwhile, the negative values of the \( \Delta H^\circ \) for MIL-88(Fe) is higher (- 49.664 KJ mol⁻¹) compared to NH₂-MIL-88(Fe) (- 17.658 KJ mol⁻¹), implying more spontaneity of the former.

3.7 Regeneration and reuse of the MOFs
Reusability of the MOFs upon regeneration was evaluated to further ascertain the efficiency of the MOFs for the PYR adsorptions. Thus, the MOFs were easily regenerated from the adsorption mixture upon centrifugation. Further fresh adsorption experiments were conducted with the regenerated MOFs up to 5 consecutive cycles (Figure 6), in each case, the efficiency of the MOFs was considerably high. The performance was decreased from 99.5 to 95.5% for MIL-88(Fe) and 95.2 to 90.7 for NH₂-MIL-88 at 1ˢᵗ to 5ʰ cycles respectively. The good reusability of the MOFs has confirmed their water stability and their potential to be applied as adsorbents for the remediations of toxic PAHs in wastewater.
Figure 5. Effect of temperature for the removal of PYR by MIL-88(Fe) and NH$_2$-MIL-88(Fe).

Figure 6. Reusability of MIL-88(Fe) and NH$_2$-MIL-88(Fe) for PYR adsorptions.

Table 5. Thermodynamic parameters for the adsorption of PYR onto the MOFs.

| MIL-88(Fe) | Temp (K) | $\Delta G^\circ$ (KJ mol$^{-1}$) | $\Delta H^\circ$ (KJ mol$^{-1}$) | $\Delta S^\circ$ (J mol$^{-1}$ K$^{-1}$) |
|------------|----------|-------------------------------|-------------------------------|--------------------------------------|
| 298        | 18.856   |                               |                               |                                      |
| 308        | 15.098   |                               |                               |                                      |
| 318        | 14.837   | 49.664                        | 107.309                       |
| 328        | 14.622   |                               |                               |                                      |
| 338        | 14.051   |                               |                               |                                      |

| NH$_2$-MIL-88(Fe) | Temp (K) | $\Delta G^\circ$ (KJ mol$^{-1}$) | $\Delta H^\circ$ (J mol$^{-1}$ K$^{-1}$) | $\Delta S^\circ$ (KJ mol$^{-1}$) |
|-------------------|----------|-------------------------------|--------------------------------------|-------------------------------|
| 298               | 12.437   |                               |                                      |                               |
| 308               | 12.402   |                               |                                      |                               |
| 318               | 11.979   | 17.658                        | 17.469                              |
| 328               | 11.835   |                               |                                      |                               |
| 338               | 11.859   |                               |                                      |                               |

4.0 Conclusions
The metal-organic frameworks, MIL-88(Fe) and NH$_2$-MIL-88(Fe) has been successfully synthesized. Characterizations conducted have shown the high crystallinity of MOFs with BET surface area of 1242 m$^2$ g$^{-1}$ and of 941 m$^2$ g$^{-1}$ for MIL-88(Fe) and NH$_2$-MIL-88(Fe), respectively. Investigation into the removal of PYR as toxic pollutant in wastewater was conducted with the MIL-88(Fe) and NH$_2$-MIL-88(Fe) MOFs, achieving percentage removals of 99.8±1 and 96.1±2 respectively within 40 minutes. Kinetics was found to follow pseudo-second-order model, while the isotherm is best explained by Langmuir model. The thermodynamics study has shown the exothermic and spontaneous nature of all the processes. Thus, the findings of this work suggest applications of these MOFs as potential adsorbents for the removal of PAHs in wastewater.

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References

[1] Zhang Y and Tao S 2009 Global atmospheric emission inventory of polycyclic aromatic hydrocarbons (PAHs) for 2004 Atoms. Environ. 43 812–9
[2] Shen H, Huang Y, Wang R, Zhu D, Li W, Shen G, Wang B, Zhang Y, Chen Y, Lu Y, Chen H, Li T, Sun K, Li B, Liu W and Liu J 2013 from 1960 to 2008 and Future Predictions Environ. Sci. Technol. 47 6415–24
[3] Xiao Y, Tong F, Kuang Y and Chen B 2014 Distribution and source apportionment of polycyclic aromatic hydrocarbons (PAHs) in forest soils from urban to rural areas in the Pearl River Delta of southern China Int. J. Environ. Res. Public Health 11 2642–56
[4] Rani M and Shanker U 2018 Enhanced photocatalytic degradation of chrysene by Fe 2 O 3 @ ZnHCF nanocubes Chem. Eng. J. 348 754–64
[5] Lawal A T 2017 Polycyclic aromatic hydrocarbons. A review Cogent Environ. Sci. 3 1–89
[6] Mezzanotte V, Anzano M, Collina E, Marazzi A and Lasagni M 2015 Polycyclic Aromatic Compounds Distribution and Removal of Polycyclic Aromatic Hydrocarbons in Two Italian Municipal Wastewater Treatment Plants in 2011 – 2013
[7] Jie D, Baoliang C and Lizhong Z H U 2013 Biosorption and biodegradation of polycyclic aromatic hydrocarbons by Phanerochaete chrysosporium in aqueous solution 58 613–21
[8] Cea-Barcia G, Carrère H, Steyer J P and Patureau D 2013 Evidence for PAH Removal Coupled to the First Steps of Anaerobic Digestion in Sewage Sludge Int. J. Chem. Eng. 2013 1–6
[9] Gonzalez-perez D and Ruiz L 2012 bioreactor Desalination and Water Treatment Wastewater polycyclic aromatic hydrocarbons removal by membrane bioreactor
[10] Gong C, Huang H, Qian Y, Zhang Z and Wu H 2017 Integrated electrocoagulation and membrane filtration for PAH removal from realistic industrial wastewater e ff ectiveness and mechanisms † 52366–74
[11] Rosi A 2018 Selection of Coagulants for the Removal of Chosen PAH from Drinking Water 2013
[12] Wang Z, Pan F, Hesham A E L, Gao Y, Zhang Y and Yang M 2015 Impacts of produced water origin on bacterial community structures of activated sludge J. Environ. Sci. (China) 37 192–9
[13] Qi Y Bin, Wang C Y, Lv C Y, Lun Z M and Zheng C G 2017 Removal capacities of polycyclic aromatic hydrocarbons (PAHs) by a newly isolated strain from oilfield produced water Int. J. Environ. Res. Public Health 14
[14] Man X, Ning X an, Zou H, Liang J, Sun J, Lu X and Sun J 2018 Removal of polycyclic aromatic hydrocarbons (PAHs) from textile dyeing sludge by ultrasound combined zerovalent iron/EDTA/Air system Chemosphere 191 839–47
[15] Ke Y, Ning X an, Liang J, Zou H, Sun J, Cai H, Lin M, Li R and Zhang Y 2018 Sludge treatment by integrated ultrasound-Fenton process: Characterization of sludge organic matter and its impact on PAHs removal J. Hazard. Mater. 343 191–9
[16] Liu J J, Wang X C and Fan B 2011 Characteristics of PAHs adsorption on inorganic particles and activated sludge in domestic wastewater treatment Bioresour. Technol. 102 5305–11
[17] Guo W, Wang S, Wang Y, Lu S and Gao Y 2018 Sorptive removal of phenanthrene from aqueous solutions using magnetic and non-magnetic rice husk-derived biochars R. Soc. Open Sci. 5
[18] Mangrich A S 2017 Evaluation of waste biomass and their biochars for removal of polycyclic aromatic hydrocarbons J. Environ. Manag. 200 186–95
[19] Meleshyn A and Tunega D 2011 Adsorption of phenanthrene on Na-montmorillonite: A model study Geoderma 169 41–6
[20] Kalantari M, Zhang J, Liu Y and Yu C 2019 Chemosphere Dendritic mesoporous carbon nanoparticles for ultrahigh and fast adsorption of anthracene Chemosphere 215 716–24
[21] Luo Z, Fan S, Id J L, Liu W, Shen X and Wu C 2018 polymers A 3D Stable Metal – Organic
Framework for Highly Efficient Adsorption and Removal of Drug Contaminants from Water

[22] Marcilla A, Gómez-Siurana A, Berenguer D, Martínez-Castellanos I and Beltrán M I 2012 Reduction of tobacco smoke components yields by zeolites and synthesized Al-MCM-41 Microporous Mesoporous Mater. 161 14–24

[23] Verdolotti L, Salerno A, Lamanna R, Nunziata A, Netti P and Iannace S 2012 A novel hybrid PU-alumina flexible foam with superior hydrophilicity and adsorption of carcinogenic compounds from tobacco smoke Microporous Mesoporous Mater. 151 79–87

[24] Jiang D, Chen M, Wang H, Zeng G, Huang D, Cheng M, Liu Y, Xue W and Wang Z W 2019 The application of different typological and structural MOFs-based materials for the dyes adsorption Coord. Chem. Rev. 380 471–83

[25] Corma A, García H and Llabrés i. X F X 2010 Engineering metal organic frameworks for heterogeneous catalysis Chem. Rev. 110 4606–55

[26] Zango Z U, Jumbris K, Sambudi N S, Abu Bakar N H H, Abdullah N A F, Basheer C, and Saad B 2019 Removal of anthracene in water by MIL-88(Fe), NH₂-MIL-88(Fe), and mixed-MIL-88(Fe) metal–organic frameworks RSC Adv. 9 41490–501

[27] Xu B, Yang H, Cai Y, Yang H and Li C 2016 Preparation and photocatalytic property of spindle-like MIL-88(Fe) nanoparticles Inorg. Chem. Commun. 67 29–31

[28] Zango Z U, Abu Bakar, N H H Sambudi N S, Jumbris K, Abdullah N A F, Abdul Kadir E, Saad B 2019 Adsorption of chrysene in aqueous solution onto MIL-88(Fe) and NH₂-MIL-88(Fe) metal-organic frameworks: kinetics, isotherms, thermodynamics and docking simulation studies J. Environ. Chem. Eng. https://doi.org/10.1016/j.jece.2019.103544

[29] Ma M, Noei H, Mienert B, Niesel J, Bill E, Muhler M, Fischer R A, Wang Y, Schatzschneider U and Metzler-Nolte N 2013 Iron metal-organic frameworks MIL-88B and MIL-88B for the loading and delivery of the gasotransmitter carbon monoxide Chem. - A Eur. J. 19 6785–90

[30] Wang L and Zan L 2019 WO 3 in suit embed into MIL-101 for enhancement charge carrier separation of photocatalyst Sci. Rep. 9 1–11

[31] Saad N, Chaaban M, Patra D, Ghanem A and El-rassy H 2020 Molecularly imprinted phenyl-functionalized silica aerogels: Selective adsorbents for methylxanthines and PAHs Microporous Mesoporous Mater. 292 109759

[32] Vidal C B, Barros A L, Moura C P, de Lima A C A, Dias F S, Vasconcellos L C G, Fechine P B A and Nascimento R F 2011 Adsorption of polycyclic aromatic hydrocarbons from aqueous solutions by modified periodic mesoporous organosilica J. Colloid Interface Sci. 357 466–73

[33] Ge X, Wu Z, Wu Z, Yan Y, Cravotto G and Ye B C 2016 Enhanced PAHs adsorption using iron-modified coal-based activated carbon via microwave radiation J. Taiwan Inst. Chem. Eng. 64 235–43

[34] Zhang Z, Hou X, Zhang X and Li H 2017 The synergistic adsorption of pyrene and copper onto Fe(III) functionalized mesoporous silica from aqueous solution Colloids Surfaces A Physicochem. Eng. Asp. 520 39–45

[35] Jadhav A H, Mai X T, Ofir F A and Kim H 2015 Preparation, characterization, and kinetic study of end opened carbon nanotubes incorporated polyacrylonitrile electrosprun nanofibers for the adsorption of pyrene from aqueous solution Chem. Eng. J. 259 348–56

[36] Lagergren & S (1898). 1898 Zur theorie der sogenannten adsorption geloster stoffe. Kungliga Svenska Vetenskapsakademiens, Handl. Band, 24 39–46

[37] Wu, F.-C., Tseng, R.-L., Huang, S.-C., & Huang R-S 2009 Characteristics of pseudo-second-order kinetic model for liquid-phase adsorption: A mini-review. Chem. Eng. J. 151 1-9.

[38] Dotto G L, Costa J A V and Pinto L A A 2013 Kinetic studies on the biosorption of phenol by nanoparticles from Spirulina sp. LEB 18 J. Environ. Chem. Eng. 1 1137–43

[39] Bonilla-Petriciolet A and HildaElizabethReynel-Avila D I M-C 2017 Adsorption processes for
water treatment

[40] Yang D, Kumar S, Li X and Yang Y 2018 *Ecotoxicol. Environ. Saf.* 383–90