

A KINETIC STUDY OF HKUST-1 FOR DESULFURIZATION APPLICATIONS

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In this study, HKUST-1 prepared under solvothermal conditions and tested in desulphurization of model gasoline. The prepared HKUST-1 samples were characterized using surface area and pore volume analysis (BET), powder X-ray diffraction (XRD), and Fourier transforms infrared spectroscopy (FTIR). The prepared HKUST-1 was used for desulphurization of model gasoline (thiophene with iso-octane), and the influence of the thiophene concentration, HKUST-1 dose, temperature, and contact time. The experimental results revealed that the sulfur content in model fuel was reduced from 1500-148.2 ppm (90.12% removal efficiency) for four hours contact time at 30 °C. In addition, an isotherm adsorption and kinetics study were performed for a batch process to understand the system equilibrium (i. e., the best fitting Langmuir isotherm or Freundlich isotherm). The kinetics study proved that the contained sulfur removal was best fitted by pseudo-second-order kinetics. Regeneration results show that the HKUST-1 has a reversible nature as an adsorbent. Therefore, HKUST-1 might be used as a promising adsorbent for removing thiophene compounds from gasoline.

Key words: HKUST-1, desulphurization, thiophene, adsorbent

Introduction

Sulfur contained in fuel oil has considered as a significant source in the pollution of the environment and one of the reasons for the acid rain. The organosulphur compounds in car fuel reduced the catalyst life by poisoning the auto-exhaust catalyst active sites, which led to increases of pollutants gases discharged into the environment. Thus, reducing the content of sulfur compounds in fuel oil has a great significance [1].

One of the main organosulfur form in gasoline is thiophenes. Thiophenes could be present in different chemical compounds such as: 2-methylbenzothiophene, benzothiophene 3-methylthiophene, 2-methylthiophene, and 2,4-dimethylthiophene). In addition, organosulfur compounds are causing significant corrosion problems in the pipe-lines, pumps, and the refining equipment, plus the deactivation of the catalyst in oil processing. Therefore, organosulfur compounds removal is crucial in reducing their influence on air pollution, human health, and the environment. There are many traditional methods for desulphurization process. However, each method has advantages and disadvantages [2].

Hydrodesulfurization (HDS) work on the elimination of non-aromatic organosulphur compounds and thiophene at high pressure, high temperature, and hydrogen environment,

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however, it is challenging to eliminate aromatic organosulfur compounds. Therefore, the main drawbacks of HDS are the high operations cost and lower octane number due to olefins saturation [2].

The oxidative desulfurization (ODS) dependent on the electron density of sulfur atoms, since, the higher electron density means that the atoms are more favorable for oxidation so it can easily remove alcohol organosulphur compounds. However, the ODS process cannot eliminate the thiophene compounds, also the despatching of disulfide and liquid wastes [3].

Nowadays, adsorption desulphurization (ADS) considered as a significant solution for the organosulfur removal due to its efficiency and being an economical way of sulfides removal. The ADS process can be operated at ambient temperature, atmospheric pressure, and does not have any effect on octane number, also easy to catalyst regeneration. The ADS depend on the adsorbent selective for organosulfur compounds [4]. Different type of adsorbents has been used in ADS process such as zeolites, activated carbon, and recently, metal-organic frameworks (MOF).

The MOF were investigated for desulphurization due to their tunable pore size, high porosity, high surface area, and easy regeneration. The MOF are a crystalline porous material made by binding the metal ions with organic ligands [5].

The MOF have drawn attention as a new adsorbent for desulphurization process. Researchers have investigated a different type of MOF in ADS processes such as MOF-5, MOF-177, HKUST-1, and MOF-505 to eliminate 4,6-Dimethyldibenzothiophene (4,6-DMDBT), Dibenzothiophene (DBT), and Benzothiophene (BT). The MOF revealed a significant selectivity for removing organosulphur compounds [6].

In 1999, HKUST-1 was prepared for the first time. It was reported that MOF have an equilibrium adsorption capacity higher than NaY for thiophene [7]. Kareem [8] studied the effect of changing the synthesis operation conditions on the equilibrium adsorption capacity of HKUST-1.

The main objective of this work is to use inhouse HKUST-1 as an adsorbent to eliminate organosulphur compounds in model gasoline using. The HKUST-1 was synthesized and characterized prior to the desulfurization test. The ADS test was achieved in a batch reactor using different operation conditions. Finally, the regeneration for HKUST-1 was examined at optimum conditions.

The Material and method

Material and preparation of HKUST-1

In this work, HKUST-1 was prepared based on the solvothermal method reported by Kareem and Al-Rubaye. [9]. A 0.42 g trimesic acids dissolved in 24 ml ethanol solution (de-ionized water and ethanol 1:1 vol.%). The prepared solution was mixed for 10 minutes. Then, a 0.875 g $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (copper nitrate trihydrate) was added to the prepared solution and stirred until a clear blue solution obtained. The blue solution was poured into a 150 ml autoclave in teflon-lined stainless steel and heated to 100 °C for 24 hours in a furnace for the crystallization occur. A blue crystalline powder was formed.

Then, the reactor was left to cool to ambient temperature. The blue powder was isolated from the mother solution by filtration and washed with a mixture of de-ionized water and ethanol (a 60 ml 1:1 vol.%) and left to dry at 100 °C. Finally, the HKUST-1 powder was activated under vacuum at 100 °C for 16 hours by using rotary dryer evaporator and then kept in a closed desiccator.

Desulfurization process by HKUST-1

The desulfurization was accomplished by dissolving the aromatic sulfur compounds (thiophene 1000-2500 ppm) in 10 ml iso-octane with accurately measured amount of activated HKUST-1 (0.05-0.25 g) in a vial (125 ml), then the vial placed in the shaker at 250 rpm for calculated time (1-6 hours) at temperature (25-55 °C). After adsorption equilibrium, the adsorbent separated from the mixture by centrifugal for 30 minutes at 3000 rpm. The sulfur concentration in the clear supernatant was analyzed by X-ray fluorescence (XRF). The amount of adsorbent, time of the ADS, amount of thiophene, and effect were monitored to understand their effect on the desulfurization efficiency.

The equilibrium adsorption amount, q_e [mgg⁻¹] is the amount of sulfur loading per unit mass of HKUST-1, was obtained:

$$q_e = (C_o - C_e) \frac{V}{m} \quad (1)$$

Moreover, the removal efficiency percent of sulfur contained was obtained:

$$\text{Removal efficiency} = \frac{C_o - C_e}{C_o} \times 100\% \quad (2)$$

where C_o and C_e [mgL⁻¹] are initial and equilibrium concentration in, m [g] – the mass of adsorbent, and V [L] – the volume of solution.

Characterization of HKUST-1

The prepared HKUST-1 was characterized using the surface area and pore volume based on Brunauer Emmett, and Teller (BET, ASTM ISO-9277-2010). The XRD analysis for the samples was investigated by using X-ray diffract meter (Shimadzu SRD 6000) with 40 kV tube voltage, 30 mA tube current and 5-70° scan range. The chemical bonds between molecules were investigated using Shimadzu FTIR 8400S (600-4000 1/cm wavenumber). Finally, the sulfur content of model fuel and ADS product were determined by XRF in the Petroleum Research and Development Center / Ministry of Oil by using SINDIE (OTG-ASTM D7039) sulfur-in-oil analyzer EDX3000.

Results and discussions

Characterization analysis of HKUST-1

The HKUST-1 samples have been analyzed using XRD and FTIR. The XRD analysis reveals the pure phase domination of the HKUST-1 at 100 °C for 24 hours synthesis time with high crystallinity up to 104%. The prepared HKUST-1 samples have higher crystallinity compared to the MOF prepared under the same condition by Kareem with crystallinity 100 [8].

The HKUST-1 pore volume and surface area were measured using the BET method by calculation of the amount of N₂ adsorption at 77 K on the HKUST-1 (adsorbent). The HKUST-1 was degassed prior physical adsorption process to remove any moisture or gases that might cause decreasing in surface area of HKUST-1. Surface area and pore volume of adsorbent play a significant role in physical adsorption process since increasing in the surface area reflect positively on the adsorbent activity due to the increase of activity site [10].

The HKUST-1 was 0.7 cm³/g pore volume and 3400 m²/g and surface area that was far from Kareem's results (2902 m²/g) under the same operating conditions [9].

For FTIR analysis, HKUST-1 functional groups (BTC ligand) that formed when the copper ion is co-ordinating with a BTC ligand. The FTIR spectrum identified the changes in BTC ligand due to absorption of carboxyl groups. The FTIR analysis of the HKUST-1 shows

at 1612.38 1/cm an energetic stretching vibration of carboxylate anions which confirm the presences of -COOH groups in the BTC acid with copper ion. At 3600-2800 1/cm, broadband appeared that indicated the existing -OH groups in d structure of HKUST-1. The HKUST-1 prepared was free of the Cu₂O and CuO (410, 500, 610, and 615 cm⁻¹). At 3100-3600, there was the loss of bond to water molecules in HKUST-1 was shifting and expanding due to H₂O loss by the carboxyl uptake [11]. The bands of FTIR spectra for HKUST-1 were in good agreement with the published data on HKUST-1 [12].

The ADS of model fuel (Gasoline) by prepared HKUST-1

The HKUST-1 dose influence on ADS

The adsorbent dose influence investigated by changing the dose (0.05, 0.1, 0.15, 0.2, and 0.25 g) and fixed the other conditions at 25 °C temperature, six hour contact time, 1000

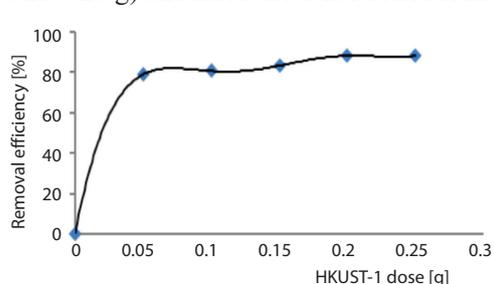


Figure 1. The HKUST-1 dose influence on ADS at 25 °C, 6 hours, 1000 ppm thiophene

ppm thiophene concentration. Figure 1 reveals that by increasing the adsorbent dose, the sulfur removal increased. The significant increasing appeared after increasing HKUST-1 dose to 0.2 g with maximum removal of thiophene 88.33% sulfur removal. Further addition of HKUST-1 had not shown any significant increase in sulfur removal. The sulfur removal of model gasoline was increased from 42.5% at dose 0.05 g HKUST-1 dose to 88.33% at 0.2 g dose under the same operating conditions.

The sulfur removal increasing can be explained due to the increase in adsorbent surface area as a result of HKUST-1 dose increasing. This increase in the dose of HKUST-1 resulted in adsorption of more sulfur compound until reached a 0.25 g where there was no significant change in sulfur removal because of the over-crowding of HKUST-1 particles that causing adsorption sites overlapping [13]. While decreasing the HKUST-1 dose leads to the opposite [14].

Contact time influence on ADS

Depending on the analysis of HKUST-1 dose, a 0.2 g HKUST-1 dose was chosen to presume the rest of the experiments. The contact time on ADS process using 0.2 g HKUST-1 dose, 25 °C temperature, 1000 ppm thiophene Concentration investigated in fig. 2. The HKUST-1 samples were collected every one hour for six hours.

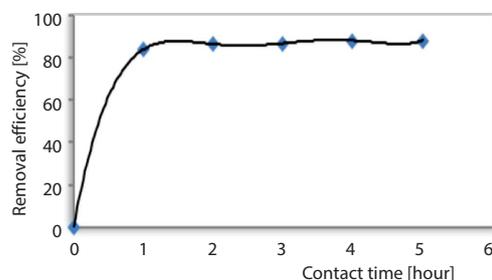


Figure 2. Contact time influence on ADS at 25 °C, 0.2 g HKUST-1, 1000 ppm thiophene

After one hour of ADS, 84% sulfur removal was obtained, fig. 2. It was clear that there was a fast increasing sulfur removal efficiency due to the adsorption sites available at the beginning of the reaction [14]. The equilibrium time was reached after four hours, with 88.33% sulfur removal efficiency. This was revealed by observing the influence of increasing time on the sulfur removal efficiency. In other words, contact time increasing led increases the efficiency of removal slightly due to increasing the contact period between HKUST-1 and sulfur compounds.

Temperature influence on ADS

The temperature influence on ADS was studied at 0.2 g HKUST-1 dose, 4 hours, and 1000 ppm thiophene concentration by varying temperature between 25-55 °C, see fig. 3.

Figure 3 reveals fast increasing in the sulfur removal efficiency (88.33 %) at ambient temperature (25°C) and then decline in efficiency when increasing the temperature more than 30 °C. At 30 °C, the removal efficiency reached to the maximum value of 89.12%. Figure 3 illustrates that by increasing the heating to 55 °C the sulfur removal efficiency reduced to 87.01%. At higher temperatures, the drop sulfur removal efficiency near thiophene boiling point temperature could be a result of the loss of the thiophene amount and the occurrence of desorption. Temperature influence analysis on ADS process in this work has a significant similarity to that reported by Demir *et al.* at 25 °C [15]. The slight difference in temperature might be because of the difference in the model fuel solvent in this work (iso-octane) instead of Demir reported *n*-octane.

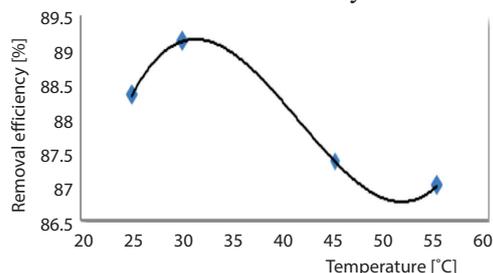


Figure 3. Temperature influence on ADS at 0.2 g HKUST-1, 4 hours, 1000 ppm thiophene

Initial concentration of thiophene influence on ADS

Figure 4 shows the initial thiophene concentration influence on ADS process by changing (thiophene) from 1000-2500 ppm at 0.2 g HKUST-1 dose, four hours contact time, and 30 °C temperature.

From fig. 4 it was found that by increasing the initial thiophene concentration above 1500 ppm reflect negatively on the sulfur removal efficiency, and that means the lower amount of the sulfur-containing was eliminated in ADS process. At 1000 ppm, the sulfur removal was 89.12%, and this percentage was increased to 90.12% at 1500 ppm initial thiophene concentration, before it dropped to 80.2 % at 2500 ppm, alternatively, it could only mean that the proportion between the high concentration and surface area available, however, by raising the thiophene concentration above 1500 ppm will reduce adsorbent efficiency as a result of the active sites plugged [16]. Therefore, a 1500 ppm has chosen as an optimum initial thiophene concentration for maximum sulfur removal efficiency (90.12%) with a 0.2 g HKUST-1 dose, four hours contact time, and 30 °C temperature.

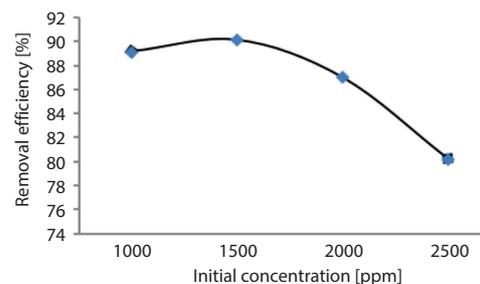


Figure 4. Initial concentration of thiophene influence on ADS at 0.2 g HKUST-1, 4 hours, 30 °C temperature

Adsorption isotherms

Adsorption isotherm occurs at a constant temperature when the the solute adsorbed on adsorbent is related to the equilibrium concentration of the adsorbent in contact with the adsorbate. Two models of adsorption isotherm are applied (Langmuir and Freundlich isotherms).

The two isotherms models are related to the equilibrium adsorption amount (*i. e.*, sulfur adsorbed per unit mass of solution C_e). The linearized forms of both models for Freundlich and Langmuir isotherm [17]

Freundlich:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (3)$$

Langmuir:

$$\frac{1}{q_e} = \left(\frac{1}{K_L \times q_m} \right) \frac{1}{C_e} + \frac{1}{q_m} \quad (4)$$

where q_e [mgg⁻¹] is the quantity of solute uptake on adsorbent at equilibrium, C_e [mgL⁻¹] – the equilibrium concentration of the solute in the solution, q_m (mgg⁻¹) – the adsorption capacity constant (the equilibrium adsorption amount for a full monolayer), K_f – the adsorption Freundlich equilibrium constant, and K_L [Lmg⁻¹] – the adsorption Langmuir equilibrium constant.

Langmuir isotherm

The Langmuir equation isotherm was applied to the equilibrium data for sulfur ADS on the HKUST-1 and fitted to the linearized Langmuir equation, eq. (4). Figure 5 demonstrates a linear plot of specific adsorption ($1/q_e$) vs. equilibrium concentration ($1/C_e$). The intercept ($1/q_m$) and slope ($1/q_m K_L$) of the plot represented the q_m and Langmuir constants, K_L , respectively. All calculated values are listed in tab. 1. As shown from fig. 5 that the isotherm data fit the Langmuir equation well ($R^2 = 0.95972$). The values of q_m and K_L were identified from fig. 5 (42.01 mg/g and 0.079 L/mg, respectively). The Langmuir equation is well fitted to data, is favorable for describing the equilibrium ADS. A similar conclusion was reached by Nkosi [17] who reported similar negative Langmuir constants using activated carbon in the study of the adsorption of sulfur compounds from diesel.

Table 1. Langmuir and Freundlich isotherm constants and correlation coefficients

Freundlich isotherm		
K_f ([mgg ⁻¹][mg ⁻¹] ^{1/n})	n	R^2
5.92	2.26	0.9604
Langmuir isotherm		
q_m [mgg ⁻¹]	K_L [mg ⁻¹]	R^2
42.01	0.079	0.95972

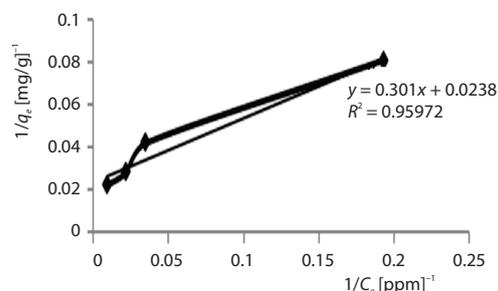


Figure 5. Langmuir isotherm for ADS at C_0 of 1500 ppm

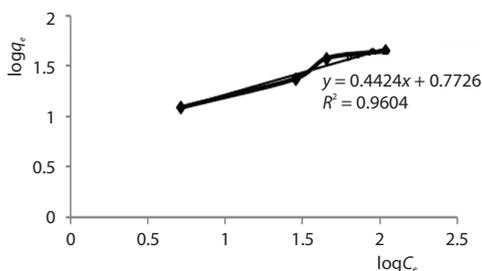


Figure 6. Freundlich isotherm for ADS at C_0 of 1500 ppm

Freundlich isotherm

The Freundlich isotherm was used to analyze the equilibrium information for sulfur adsorption uptake on the HKUST-1. Freundlich equation was linearized, eq. (3) and the equilibrium data was applied, as shown in fig. 6. This figure illustrates the linear log plot of q_e vs. C_e with the value of intercept, K_f , and $1/n$ slope. Figure 6 analysis demonstrates a well-fitting of the Freundlich equation the isotherm data ($R^2 = 0.96$).

All calculated values are listed in tab 1. The K_f and n values were found from fig. 6 (5.92 and 2.26, respectively). The $1/n$ calculation represents the adsorption intensity, the intercept K_f value can be identified for the adsorbent capacity of adsorption. The value of n showed that adsorption conditions were preferred $n < 1$ [17]. The results show that adsorption is close to Langmuir and Freundlich, but when we return to the value of the, R^2 , note that the value of the ($R^2 = 0.96$) for Freundlich model is higher than the value of the Langmuir model ($R^2 = 0.95$).

Kinetic study

In general, the experimental data for the adsorption capacity of adsorbent at equilibrium, and about the kinetics of adsorption can be described using different empirical formulas or models. Two models have been typically applied to describe the adsorption kinetics. The pseudo-first-order is the first known model, which is related to the intraparticle diffusion (*i. e.*, diffusion-controlled process). The pseudo-second-order is the second model, which assumes that the adsorption is controlled by the reaction at the adsorbent interface.

The mechanism that was controlling the pseudo-first-order and the pseudo-second-order based on the assumption that the rate-limiting step is either the mass transfer process or the chemisorption. The rate of adsorption was calculated by the two models for the pseudo-first-order and pseudo-second-order [17]:

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_1}{2.303} \right) t \quad (5)$$

Pseudo-first-order kinetics

The pseudo-first-order linearized model given by eq. (5) was applied to present the thiophene adsorption kinetics. The equilibrium concentration, q_e , rate constant, K_1 , and correlation coefficient obtained are shown in fig. 7, demonstrates a linearized data of time *vs.* $\log(q_e - q_t)$ for the HKUST-1. The slope and intercept of the plot, $K_1/2.303$ and $\log q_e$, respectively, used to find the rate constant, K_1 , the sulfur adsorbed at the equilibrium, q_e , and q_t represents the amount of sulfur adsorbed at any time. A 0.897 correlation coefficient was obtained from the linearized pseudo-first-order model, and that means the need to find other models that fit better to the equilibrium data. Further, the equilibrium concentration calculation does not well agree with the experimental value. Therefore, depending on this result, it can be concluded that the sulfur adsorption on HKUST-1 under these conditions does not follow the pseudo-first-order kinetics.

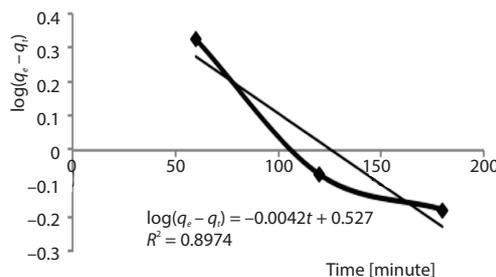


Figure 7. Pseudo-first-order kinetic model for ADS at C_0 of 1500 ppm

Pseudo-second-order kinetics

The pseudo-second-order linearized model, eq. (6) present the thiophene adsorption kinetics on HKUST-1. The rate constant, K_2 , equilibrium concentration, q_e , and correlation coefficient, R^2 , obtained are shown in tab. 2. Figure 8 described a linearized equilibrium data of time *vs.* t/q_t . The amount of sulfur adsorbed at equilibrium, q_e , and the rate constant, K_2 , was calculated from the slope and intercept ($1/q_e$, and $1/K_2 q_e^2$, respectively) of the plot.

Table 2. Kinetics models correlation coefficients and constants

Pseudo-first order			
K_1 [min^{-1}]	q_e , cal [mgg^{-1}]	R^2	
0.0096	3.36	0.897	
Pseudo-second order			
q_e exp [mgg^{-1}]	K_2 [$\text{gmg}^{-1}\text{min}^{-1}$]	exp [mgg^{-1}]	R^2
44.165	0.0076	44.165	1

The pseudo-second-order correlation coefficient was found to be 1, that means this model is the best fitting to the experimental results compared to the pseudo-first-order model. Furthermore, the estimated equilibrium amount, q_e , for the pseudo-second-order equation is closer to the experimental values. The pseudo-second-order adsorption kinetics is best to describe the adsorption of sulfur on HKUST-1, which means the overall thiophene adsorption process is controlled by chemisorption [4].

Regeneration of adsorbent

It is necessary for adsorbent to be reactivable and reused. The MOF can be easily reactivated using rinsing by methanol [18]. The HKUST-1 reactivated for ADS process was evaluated by taking a sample of the HKUST-1 at the end the adsorption process which operated at 30 °C temperature, four hours contact time, 1500 ppm thiophene initial concentration. This HKUST-1 sample was regenerated by putting the used adsorbent in a 125 ml vial containing 60 ml of methanol ultrasonic bath for 12 hours at ambient temperature. Then the adsorbent was separated from the solution using filter paper and washing with methanol. The filtrate solution is examined for the sulfur containment, and the washing process continues until the zero concentration of sulfur is obtained. In this study, three attempts were made with a volume of 60 ml of alcohol per attempt. The sorbent is then dried for 24 hours at 120 °C in a vacuum dryer. After regeneration of the HKUST-1, the adsorption process will be repeated under the same ADS operating conditions mentioned previously.

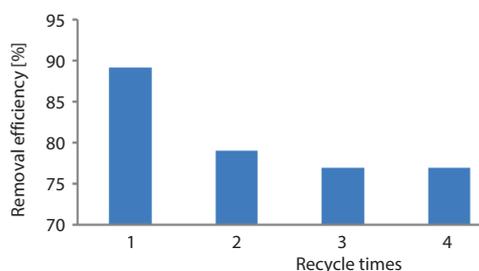


Figure 9. The HKUST-1 regeneration at 0.2 g dose of adsorbent, contact time 4 hours, initial concentration of thiophene 1500 ppm and temperature 30 °C

The influence of the regeneration times on the amount of the sulfur compounds (thiophene) that adsorbed by HKUST-1 are shown in fig. 9. After four cycles of adsorptive desulfurization experiments, it was found that the removal efficiency of regenerated HKUST-1 was reduced by 13.6% compared with fresh HKUST-1. Although the efficiency of HKUST-1 decreased after the fourth cycle, it remains a high value regenerated efficiency was due to that the formation of secondary bonding, such as hydrogen bonding or vander Waals interactions [18]. Therefore, the HKUST-1 can be considered an excellent regenerated and recycled adsorbent.

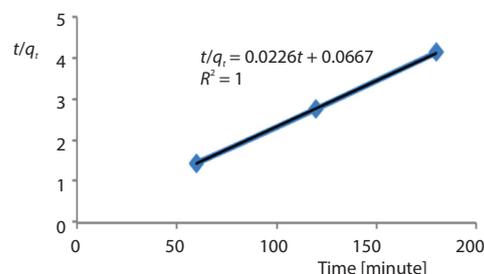


Figure 8. Pseudo-second-order kinetic model for ADS at C_o of 1500 ppm

Conclusion

In this research, The HKUST-1 has been successfully prepared and used as an excellent adsorbent for thiophene elimination in ADS process. The HKUST-1 was in house synthesized using the solvothermal method with high crystallinity up to 104% and 0.7 cm³/g pore volume and 3400 m²/g and surface area. The synthesis HKUST-1 was applied in ADS process to remove sulfur contained in model gasoline. The experiments showed that the highest removal efficiency for thiophene adsorption on HKUST-1 is 0.2 g adsorbent dosage, four hours contact time, 1500 ppm initial thiophene concentration, and 30 °C temperature. The used HKUST-1 was regenerated easily by alcohol washing and reused at least four times. The isotherm adsorption showed that the equilibrium data were best represented by the Freundlich isotherm model ($R^2 = 0.96$). The kinetic study confirmed that the pseudo-second-order model could present the adsorption kinetics, and the chemisorption was the controlled step.

Nomenclature

C_e – equilibrium concentration, [mgL ⁻¹]	q_t – adsorption capacities at time t
C_o – initial concentration, [mgL ⁻¹]	t – time
K_f – Freundlich constant, ([mgg ⁻¹][mg ⁻¹] ^{1/n})	V – volume of solution, [L]
K_L – Langmuir constant, [Lmg ⁻¹]	<i>Subscripts</i>
K_1, K_2 – pseudo-first order, [min ⁻¹]	e – equilibrium
m – mass of adsorbent, [g]	o – initial
q_e – quantity of solute uptake on, [mgg ⁻¹]	
q_m – adsorption capacity, [mgg ⁻¹]	

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