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Adsorption Kinetic and Isotherms Studies of Thiophene Removal from Model Fuel on Activated Carbon Supported Copper Oxide

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Abstract

In the present study, activated carbon supported metal oxides was prepared for thiophene removal from model fuel (Thiophene in n-hexane) using adsorptive desulfurization technique. Commercial activated carbon was loaded individually with copper oxide in the form of Cu_2O/AC. A comparison of the kinetic and isotherm models of the sorption of thiophene from model fuel was made at different operating conditions including adsorbent dose, initial thiophene concentration and contact time. Various adsorption rate constants and isotherm parameters were calculated. Results indicated that the desulfurization was enhanced when copper was loaded onto activated carbon surface. The highest desulfurization percent for Cu_2O/AC and origin AC at initial thiophene concentration of 500 ppm, adsorbent dose of 0.01 g/ml and equilibrium time of 5 hr were 87.4% and 53.4% respectively, for outlet concentration of 63 mg/L for copper oxide and 236 mg/L for original AC. Generally, the percent removal of thiophene increases with the increase in adsorbent dose and decrease with increase in initial thiophene concentration. The present study was mainly focusing on the kinetics and adsorption isotherms aspect; adsorption kinetics of thiophene onto activated carbon supported Cu_2O adsorbent was closely represented by the second order kinetic model and Freundlich isotherms well represented the equilibrium adsorption of thiophene from model fuel.

Key words: Adsorptive desulfurization; activated carbon; copper; thiophene, kinetics, isotherms.

Introduction

Since most crude oils from different origins contains large amounts of sulfur and nitrogen compounds, many desulfurization techniques have been considered for sulfur-nitrogen removal; they are required for the purpose of protecting the environment against pollution by sulfur- and nitrogen-oxide emanations (SO*x* and NO*x*). Also, these contents cause catalyst poisoning as well as effecting vehicle engines [1] [2]. The removal of sulfur compounds from crude oil is basically carried out via catalytic hydrodesulfurization (HDS) process. The hydrodesulfurization process considered being highly-costing process for the expensive conditions it requires, i.e., high temperature and pressure, and the high-cost catalysts it required. Moreover, it does not fulfill the need to reach ultra-low sulfur content; thereby, other processes have been considered for such aim [3] [4]. Oxidative desulfurization considered being an alternative process for sulfur removal aspect, in addition to many other processes such as extractive desulfurization, photochemical desulfurization, biodesulfuriation and the most important process which this study is considered to subject the light on is adsorptive desulfurization. The main advantages of adsorptive desulfurization process are the availability of the adsorbents used and it's low cost, and it does not require expensive conditions as in (HDS) [5] [6]. Many adsorbents are used for this purpose such as activated carbon, modified composite oxides, zeolites and many other porous material; Moreover, metal oxides considered as good type of adsorbents used. The adsorbents used have a major effect for sulfur removal and to reach ultra-low sulfur content [7].

The present work employes three prepared adsorbents for thiophene removal from model fuel (Thiophene in n-hexane) are tested. The adsorption kinetics to study the behavior of this process as well as to employs adsorption isotherms for the same concept.

Experimental

1. Model Fuel

Simulated model fuel consists of n-hexane (C_6H_{14}, purity ≥ 99%, supplied from Sigma-Aldrich company, molecular weight, 86.18 g/mol; density, 0.871 gm/cm^3 at 16 ^{o}C; and boiling point, 74.1 ^{o}C) is mixed with different amounts of thiophene (C_4H_4S of 99.9% purity, supplied from Fluka Chemie AG, Company, molecular weight, 84; density, 1.071 gm/cm^3 at 16 ^{o}C; and boiling point, 84.1 ^{o}C) as a sulfur source.

2. Adsorbents

Activated carbon pellets (AC) (supplied from Research Products International Corp. USA) of purity 99.9% was used as support without any heat or chemical pretreatment. The surface area (BET) and pore volume were tested using sorption of N_2 and their values were 1066 (m^2/g) and 0.65 cm^3/g respectively. The AC pellets were milled and sieved to size range of (0.3-0.6) mm before impregnation. Copper nitrate, $Cu(NO_3)_2.3H_2O$, 97% purity supplied by Fluka Chemie AG company was used as copper precursor.

3. Adsorbents Preparation

The adsorbent was prepared by incipient wetness impregnation technique where 40 gm activated carbon was impregnated under vacuum and room temperature with aqueous solution of $Cu(NO_3)_2.3H_2O$. This was prepared previously by dissolving 12.3 g copper nitrate in 26 ml of distilled water to get 10 wt% metal loaded. The sample was left over 24 hr at the ambient conditions to load the largest amount of metal precursor. Then the impregnated activated carbon sample was dried at 90 ^{o}C for 6 hr and calcined at 500 ^{o}C under vacuum for 3 hr.

4. Desulfurization Procedure

The model oil used consisted of thiophene dissolved in n-hexane at different initial thiophene concentration. A series of experiments were carried out in batch operation in order to evaluate the influence of process parameters: initial thiophene concentration (250-2000 mg/L) and adsorbent dose (0.01-0.08 g/ml). All adsorption experiments were performed at room temperature and using 10 ml of liquid model fuel.

In the first set of adsorption experiments, the contact time was varied from 15-360 min while fixing the other parameters initial thiophene concentration (C_{in}) of 500 mg/L, and adsorbent dose of 0.01 g/ml. In the second set of experiments the effect of initial thiophene concentration was investigated by varying the initial concentration of sulfur as 250, 500, 1000 and 2000 mg/L and fixing the adsorbent dose at 0.01 g/ml and the contact time was equilibrium time (estimated from the first set results). Finally, in the third set of experiments the effect of adsorbent dose (varied as 0.01, 0.02, 0.04 and 0.08 g/ml) was studied at constant contact time of equilibrium time and initial sulfur concentration of 500 mg/L.

The desulfurization percentages were calculated as the ratio of the thiophene concentration that was adsorbed by the adsorbent to the thiophene concentration present initially in the model fuel according to equation bellow:

$$\text{Desulfurization\%} = \frac{C_{in} - C_{out}}{C_{in}} * 100 \quad \ldots(1)$$

The sulfur adsorption capacity (q) was calculated by using the following equation:

$$q = \frac{V_{sol}(C_{in} - C_e)}{m} \quad \ldots (2)$$

Where q is the amount of sulfur adsorbed (mg /g cat.), V_{sol} is the volume of solution (L), C_{in}, C_{out} and C_e are initial, outlet and equilibrium concentrations (mg /l), and m is the mass of adsorbent (g).

The sulfur content in model fuel and real gasoil was determined by X-ray fluorescence in the Petroleum Research and Development Center/Ministry of Oil/Baghdad by using Horiba sulfur-in-oil analyzer type (SLFA-2100).

Results and Discussion

1. Adsorbent Characterization

X-ray powder diffraction (XRD) was used to analyze the crystallinity and also to determine the oxidation phase of copper loaded onto activated carbon, using an XRD-6000 (Bruker D2 PHASER). According to thermal decomposition data of $Cu(NO_3)_2.3H_2O$ under vacuum [8] firstly, $Cu(NO_3)_2.3H_2O$ is melted at 115-155 °C, then converted to phase β-$Cu_2(OH)_3NO_3$ at 200-217 °C. By increasing the calcination temperature it is converted to CuO at 260–310 °C, finally CuO decomposes to Cu_2O at calcination temperature > 450 °C. Figure 1 shows the XRD analysis of copper-impregnated AC sample. As shown in this figure, the diffraction peaks are at 2θ = 36°, 42.5°, 61° and 74° which indicate presence of Cu_2O crystals in AC.

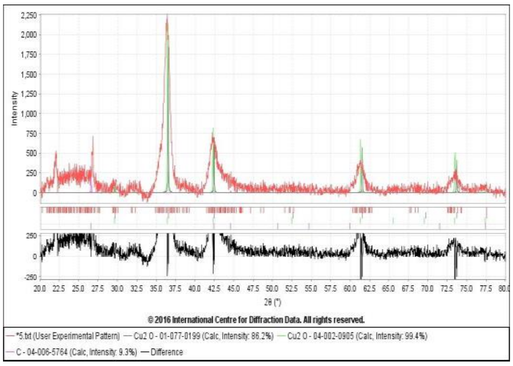


Fig. 1: XRD analysis of Cu_2O-impregnated AC sample

Atomic absorption spectroscopy model (Varian AA240 FS) was used for determination the total content of copper loaded onto activated carbon. The measured total content of copper was about 9.25 wt%.

The BET surface area and the pore volume of the original activated carbon and impregnated activated carbon was determined using Quanta chrome

Autosorb gas sorption system estimated from nitrogen adsorption and desorption. The surface area and pore volume of Cu_2O/AC were 995 m^2/gm and 0.592 cm^3/gm respectively compared with the origin AC which were 1066 m^2/g and 0.65 cm^3/g respectively. This indicates that the impregnating of 9.25 % copper oxide on AC did not have a big effect on the porosity of produced adsorbent. Therefore, there are few carbon pores plugged due to metal impregnation compared with the original AC.

2. Adsorption and Kinetics Studies

The purpose of these studies is to determine the equilibrium time, mechanism of adsorption and to determine the rate-controlling step. The effect of contact time (0-6 hr) on thiophene adsorption from n-hexane as a model fuel onto Cu_2O/AC is shown in Figure 2. It is clear that the rate of thiophene adsorption from model fuel was fast during the first 1 hr, this is clear due to the fact that a large number of unoccupied active sites are initially available for the adsorption and therefore higher driving force and fast mass transfer of thiophene take place. With the passage of adsorption time, the remaining unoccupied active sites are difficult to be taken due to repulsive forces between thiophene molecules on the adsorbent surface and in the liquid solution. In late stages, the adsorption of thiophene remains approximately constant and the difference between the uptake at 5 hr and 6 hr and was less than 0.5%. Therefore, the approximation of steady state was specified and an equilibrium condition was considered to be 5 hr. Maximum thiophene capacities were reported as 43.7 and 26.4 mg/g for Cu_2O/AC and AC respectively at initial thiophene concentration of 500 mg/l and adsorbent dose of 0.01 g/mg as shown in Figure 2. Based on the above results, the kinetic studies including. pseudo 1st order (Lagergren), pseudo 2nd order, Weber-Morris (Intra-particle diffusion) and Elovich kinetics models were performed on all thiophene adsorbent systems.

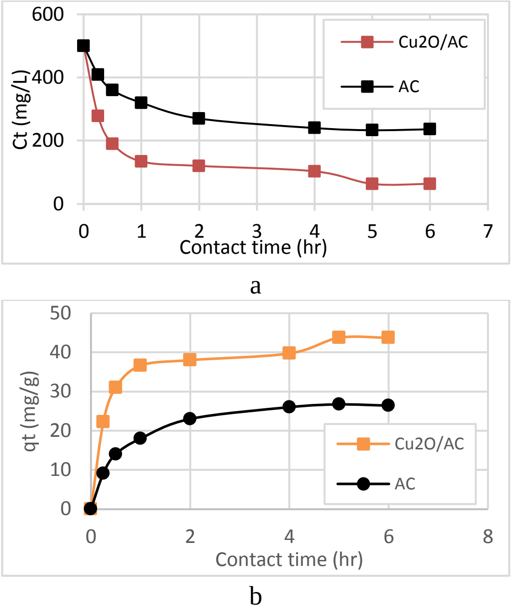


Fig. 2: Outlet thiophene concentration (C_t) (a) and uptake (qt) (b) vs. contact time of model fuel for Cu2O/AC and original AC (initial thiophene concentration of 500 mg/l and adsorbent dose of 0.01 g/ml)

A comparison of thiophene adsorption onto Cu_2O/AC and the original AC shows that the copper impregnation increases the thiophene uptake. The experimental results indicated that the thiophene removal was enhanced when copper was loaded onto AC surface about 65 % (at initial thiophene concentration of 500 mg/l and adsorbent dose of 0.01 g/ml). These results are in agreement with several previous studies such as [9] [10]. As suggested by Seredych and Bandosz [11], the enhancement in thiophenic compounds may take place due to the specific interactions between the supported metal species and thiophenic compounds molecules involving πcomplexation and acid-base interactions in addition to the original dispersion interactions in AC micro and meso pores.

For the kinetic study of model fuel desulfurization, various kinetic models had been proposed and used to determine the mechanism by which solute (thiophene) may be adsorbed. Therefore, three kinetic models were used as follows:

Pseudo 1st - Order Model (Lagergren Model)

The nonlinear and linear forms of Lagergren model are [12].

$$q_t = q_e(1-\exp(-k_1 t)) \quad \ldots(3)$$

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad \ldots(4)$$

Where q_t is the amount of sulfur adsorbed (mg sulfur/g cat.) at time *t* (min), q_e the amount of sulfur adsorbed at equilibrium (mg sulfur/g cat.) and K_1 is the equilibrium rate constant of pseudo first-order adsorption (min^{-1}).

Pseudo2nd -Order Model

The pseudo second order model can be represented in the following forms [13]:

$$q_t = \frac{tk_2 q_e^2}{1+tk_2 q_e^2} \quad \ldots(5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 qe^2} + \frac{t}{qe} \quad \ldots(6)$$

Where k_2 is the pseudo second order rate constant of adsorption (mg/g min).

Intra-Particle Diffusion Model

Based on the theory of Weber and Morris [14], the adsorption kinetics was described according to the following model:

$$q_t = k_3\sqrt{t} \quad \ldots(7)$$

Where k_3 is the intra particle diffusion rate constant (mg/g $min^{1/2}$).

Elovich Model

The Elovich model is mainly applied for chemical adsorption kinetics (chemisorption), it is predominately suitable for heterogeneous systems. This model can be expressed as follows [15]:

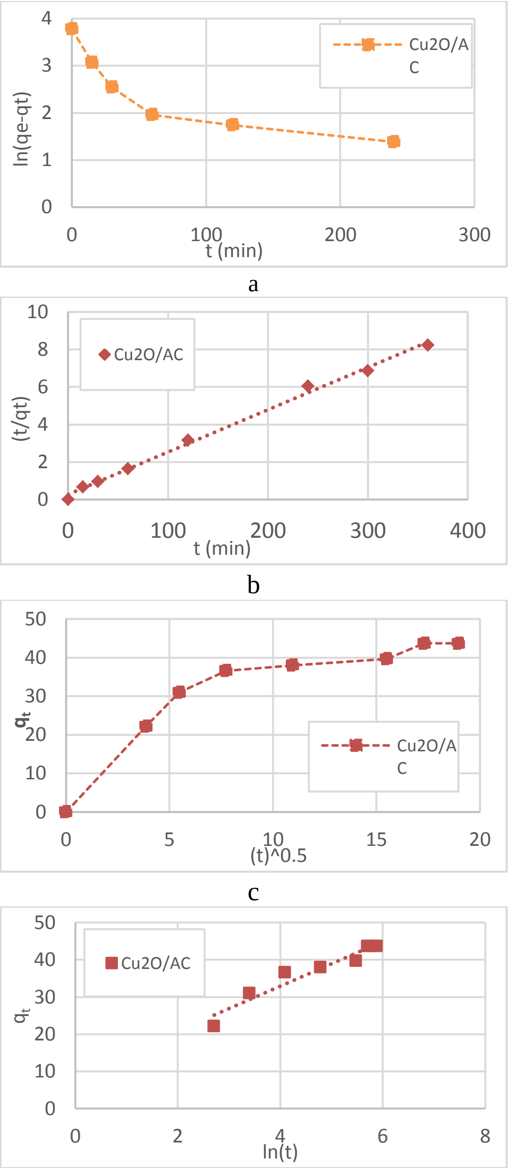
$$\frac{dq_t}{dt} = \alpha e^{(-\beta q_t)} \quad \ldots(8)$$

Where α = initial adsorption rate (mg/g min) and β is constant related to the surface coverage and the activation energy for chemical adsorption (g/mg). By assuming αβt >>> 1 the integration form of this model is: [16]

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \quad \ldots(9)$$

Equation 9 can be used to examine the validity of the Elovich model to the kinetics of thiophene adsorption onto prepared catalysts by plotting q_t vs. ln(t).

Figures 3a, 3b, 3c and 3d. show the application of the above kinetic models by plotting log (q_e-q_t) vs. *t*, (t/q_t) vs. *t*, q_t vs. $\sqrt{t}$ and q_t vs. ln(t) respectively for Cu_2O/AC adsorbent. To determine the extent of approval of each kinetic model, the coefficient correlation (R^2) was calculated from these plots. The greatest R^2 value indicates the applicability of the model. Different adsorption rate constants including experimental and calculated q_e values are summarized in Table 1. It can be concluded from this table and also from Figures 3a., 3c. and 3d. that the results did not obeys the 1st order, diffusion kinetic or Elovich models due to relatively low values of R^2. For 1st order model, a large variation was noticed between the experimental (q_e exp.) and calculated (q_e cal.) equilibrium uptake values. In case of 2nd order model, a linear relationship was noted between (t/q_t) and t over all the entire adsorption period as shown in Figure 3b. The experimental and calculated q_e values from the pseudo 2nd order kinetic model are close to each other and the calculated correlation-coefficients (R^2) are closer to unity for pseudo 2nd order kinetics than that for other models. Based on these results, the thiophene adsorption over Cu_2O/AC can be represented more suitably by the pseudo 2nd order kinetic model.



a

b

c

d

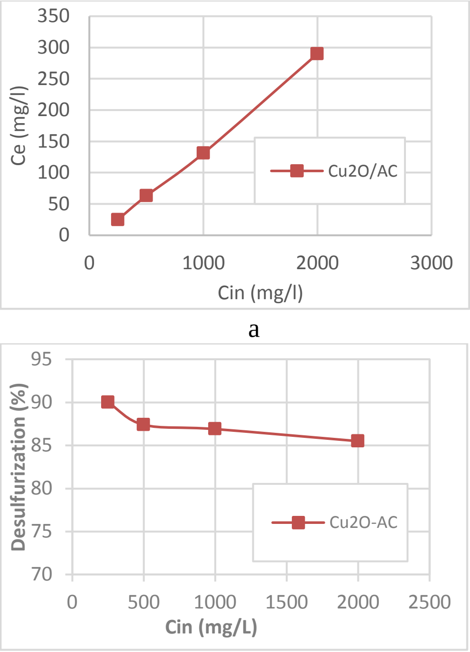
Fig. 3: Plot of pseudo 1st order (a), pseudo 2nd order (b), Intra particle diffusion (c) and Elovich (d) kinetic models for thiophene adsorption from model fuel at initial thiophene concentration of 500 mg/l and adsorbent dose of 0.01 g/ml

Table 1: Adsorption kinetic parameters for the desulfurization of model fuel (C_{in}=500 mg/l, catalyst concentration = 0.01 g/ml, $V_{sol.}$ = 10 ml, m_{cat} = 0.1 g)

Adsorption model	**Parameters**	**Value Cu2O/AC**
Pseudo 1st order model $q_t = q_e(1 - \exp(-k_1 t))$	K_1 (min^{-1})	0.008
	q_e (mg/g) *exp*	43.7
	q_e (mg/g) *cal*	21.327
	R^2	0.708
Pseudo2nd order model $q_t = \frac{tk_2q_e^2}{1 + tk_2q_e^2}$	k_2 (mg/g min)	0.001735
	q_e (mg/g) *exp*	43.7
	q_e (mg/g) *cal*	45.45
	R^2	0.995
Diffusion model $q_t = k_3\sqrt{t}$	k_3 (min^{-1})	1.866
	I_1 (mg/g)	0
	I_2 (mg/g)	13.23
	R^2	0.757
Elovich model $q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t)$	α (mg/g min)	26.17
	β (g/mg)	0.166
	R^2	0.9246

3. Effect of Initial Thiophene Concentration

Figures 4a and 4b show the effect of initial thiophene concentration, C_{in} (from 250 to 2000 mg/l) on the equilibrium thiophene concentration (C_e), and desulfurization percentage. Figure 5 shows the adsorption isotherms (equilibrium uptake vs. equilibrium thiophene concentration) of thiophene onto Cu_2O/AC of model fuel at constant adsorbent dose of 0.01 g/ml and equilibrium time of 5 hr. The results represented in Figures 4a and4b, show that the desulfurization percentage decreases (and the equilibrium thiophene concentration increases) with increasing initial thiophene concentration. This can be attributable to that all the adsorbent have a limited number of active sites on its surface, which becomes saturated at a certain concentration.



a

b

Fig. 4: Effect of initial thiophene concentration on thiophene equilibrium concentration (a), and desulfurization (b) at adsorbent dose of 0.01 g/ml and equilibrium time of 5 hr

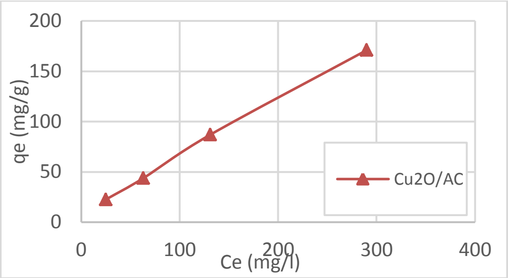
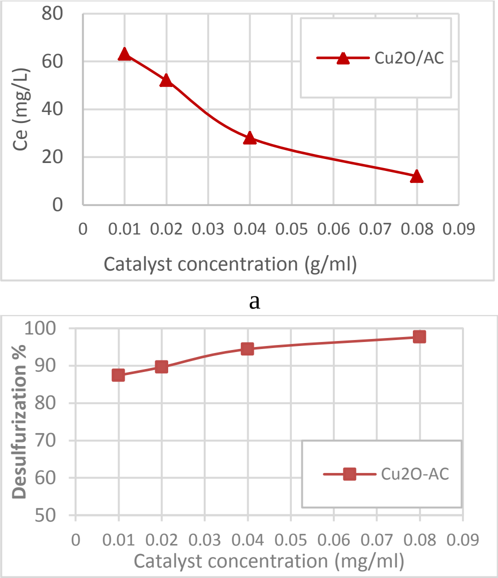


Fig. 5: Equilibrium uptake of thiophene adsorption from model fuel onto Cu_2O/AC at different initial thiophene concentration (adsorbent dose of 0.01 g/ml and equilibrium time of 5 hr)

4. Effect of Adsorbent Dose

Figure 6 shows the effect of adsorbent dose (g/ml) on the desulfurization percentage of thiophene onto Cu_2O/AC at constant initial thiophene concentration of 500 mg/l and equilibrium time of 5 hr. The increase in adsorption percentage with adsorbent dose can be attributed to the availability of greater surface area and therefore a larger number of adsorption active sites. When using low sorbent dose (i.e. available surface area is less than optimum or required), the sorbent surface becomes saturated with thiophene and therefore the large concentration of residual thiophene is remained in the solution. On continuous increasing in sorbent dose, more surface area, and active sitesleads to increase in thiophene removal because the thiophene uptake is increased by a more available sorbent. When using adsorbent dose greater than required, the percent removal of thiophene becomes nearly constant. Figure 7 shows the equilibrium uptake vs. equilibrium thiophene concentration of thiophene onto Cu_2O/AC at different adsorbent dose.



a

b

Fig. 6: Effect of adsorbent dose (g/ml) on thiophene equilibrium concentration, C_e (a) and desulfurization% (b) at initial thiophene concentration of 500 mg/l and equilibrium time of 5 hr

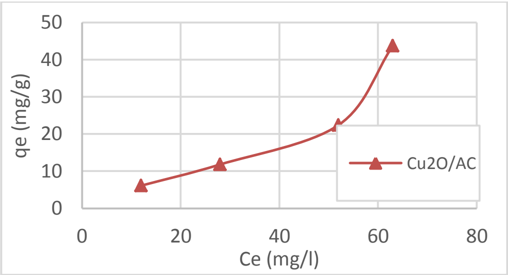


Fig. 7: Equilibrium uptake of thiophene adsorption from model fuel Cu2O/AC at different adsorbent dose at initial thiophene concentration of 500 mg/l and equilibrium time of 5 hr

Adsorption Isotherms

The experimental equilibrium adsorption data of thiophene adsorption onto Cu_2O/AC have been analyzed by using Freundlich and Langmuir isotherms at different initial thiophene concentration and adsorbent dose as shown in Figures 8 and 9.

The non-linear form of Langmuir isotherm model is given by the following equation:

$$q_e = \frac{Q_o K_L C_e}{1+K_L C_e} \qquad \ldots(10)$$

where C_e is the equilibrium concentration of thiophene (mg/l), q_e is equilibrium adsorption capacity of thiophene adsorbed per unit mass of the adsorbent (mg/g), Q_o is the maximum monolayer-coverage amount of thiophene adsorbed per unit mass of the adsorbent given in (mg/g), and K_L is the Langmuir isotherm constant (L/mg). Langmuir adsorption isotherm assumes formation and attachment of a monolayer of adsorbate molecules on a specific number of sites on the surface of the solid adsorbents [17].

Freundlich adsorption isotherm is used to characterize the multilayer adsorption for the heterogeneous surfaces. The Freundlich model in an exponential form is given by the following relation [18]:

$$q_e = K_f C_e^{\frac{1}{n}} \qquad \ldots(11)$$

Where K_f is the Freundlich isotherm constant (mg/g) and n is the adsorption intensity.

The Langmuir isotherm parameters Q_o and K_L, the correlation coefficient (R^2), the Freundlich isotherm constants K_f, n and coefficient-correlation (R^2) were determined by linearized-form regression are shown in Tables 2 and 3. The experimental data fitting to the Langmuir and Freundlich isotherms are shown in Figures 8 and 9. Results indicated that the adsorption situation for thiophene adsorption from model fuel is described better by Freundlich isotherm model. The results areconfirmed by the calculated correlation coefficient (R^2) between the experimental and calculated q_e values for the two isotherm models. Therefore, by using Freundlich isotherm model, results showed that the (R^2) were 0.9971 for initial concentration study and 0.9327 for adsorbent dose study. Figure 10 shows the comparison of experimental, Langmuir and Freundlich adsorption isotherms at different initial thiophene and adsorbent dose.

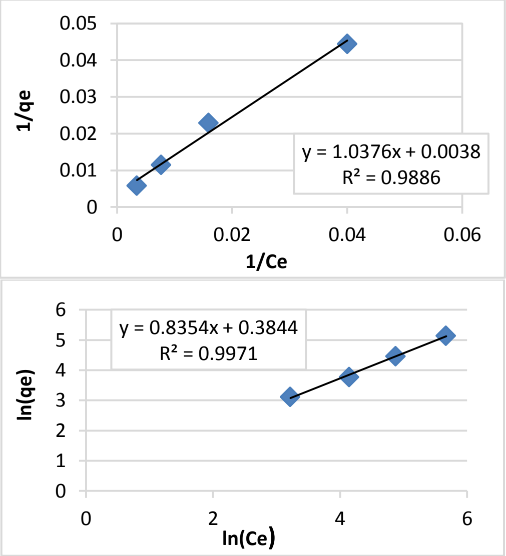


Fig. 8: Fitting of Langmuir (top) and Freundlich (bottom) isotherms at different initial thiophene concentration on Cu_2O/AC adsorbent

Table 2: Langmuir and Freundlich parameters for the desulfurization of model fuel

Isotherm model	**Parameters**	**Value**
		Cu_2O/AC
Langmuir $q_e = \frac{Q_o K_L C_e}{1 + K_L C_e}$	Q_o (mg/g)	263.15
	K_L (l/mg)	0.00366
	R^2	0.9886
Freundlich $q_e = K_f C_e^{\frac{1}{n}}$	K_f (mg/g)	1.468
	N	1.197
	R^2	0.9971

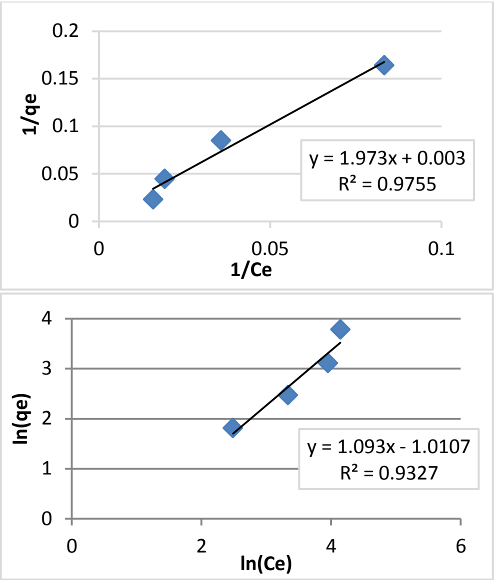


Fig. 9: Fitting of Langmuir (top) and Freundlich (bottom) isotherms at different initial adsorbent dose on ZnO/AC (a), Cu_2O/AC (b) and NiO/AC (c)

Table 3: Langmuir and Freundlich parameters for the desulfurization of model fuel

Isotherm model	**Parameters**	**Value**
		Cu_2O/AC
Langmuir $q_e = \frac{Q_o K_L C_e}{1 + K_L C_e}$	Q_o (mg/g)	333.34
	K_L (l/mg)	0.00152
	R^2	0.9755
Freundlich $q_e = K_f C_e^{\frac{1}{n}}$	K_f (mg/g)	0.364
	N	0.915
	R^2	0.9327

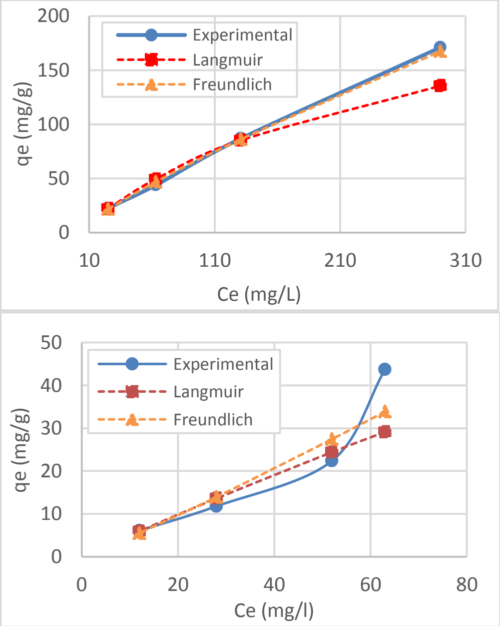


Fig. 10: Experimental, Langmuir and Freundlich adsorption isotherms at different initial thiophene (top) and adsorbent dose (bottom)

Conclusion

Adsorptive desulfurization of the model fuel was performed using Cu_2O/AC prepared by using impregnation method. Thiophene removal capacity, adsorption kinetics and adsorption isotherms were studied in batch operation. The following conclusions can be summarized from the presented study:

- Using activated carbon in adsorptive desulfurization method for sulfur compounds removal from liquid fuels was very efficient especially when loaded with metal oxides. The experimental results indicate that the thiophene uptake was enhanced when copper loaded onto activated carbon surface.
- The equilibrium concentration was established after 5-6 hours, of 63 mg/L for Cu_2O and 236 mg/L for original AC.
- In general, the percent removal of thiophene increases with the increase in adsorbent dose and decrease with increase in initial thiophene concentration.
- The adsorption kinetics of thiophene onto activated carbon supported Cu_2O sorbent could be closely represented by the 2nd order kinetic model.
- Freundlich isotherms in general well represent the equilibrium adsorption of thiophene from model fuel.

Nomenclatures

A= Initial adsorption rate (mg/g.min)
AC= Activated carbon
B= constant related to the surface coverage and the activation energy for chemical adsorption (g/mg)
C_e= Equilibrium concentration (mg/l)
C_{in}= Initial concentration (mg/l)
C_{out}= Final concentration (mg/l)
K1= Equilibrium rate constant of pseudo first-order adsorption (min^{-1})

k_2= Pseudo second order rate constant of adsorption (mg/g.min)

k_3= Intra particle diffusion rate constant (mg/g.min^{-1})

K_f= Freundlich isotherm constant (mg/g)

K_L = Langmuir isotherm constant (L/mg)

$m_{cat.}$= The mass of the catalyst (g)

q =The amount of sulfur adsorbed (mg/g)

q_o=The maximum monolayer-coverage amount of thiophene adsorbed per unit mass of the adsorbent (mg/g)

q_e =The amount of sulfur adsorbed at equilibrium (mg/g)

q_t =The amount of sulfur adsorbed at time (t) (mg/g)

R^2 =the coefficient of correlation

t =Time (min)

V_{sol} =The volume of the solution (L)

α = initial adsorption rate (mg/g.min)

β= constant related to the surface coverage and the activation energy for chemical adsorption (g/mg)

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