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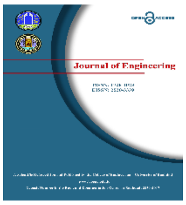

Chemical, Petroleum and Environmental Engineering

Adsorption Desulfurization of Iraqi Light Naphtha Using Metals Modified Activated Carbon

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ABSTRACT

The study aims to evaluate the removal of sulfur content from Iraqi light naphtha produced in Al-Dora refinery by adsorption desulfurization DS technique using modified activated carbon MAC loaded with nickel Ni and copper Cu as single binary metals. The experiments were carried in a batch unit with various operating parameters; MAC dosage, agitation speed, and a contact time of 300 min at constant initial sulfur concentration 155 ppm and temperature. The results showed higher DS% by AC/Ni-Cu (66.45)% at 500 rpm and 1 g dosage than DS (29.03)% by activated carbon AC, increasing MAC dosage, agitation speed, and contact time led to increasing DS% values. The adsorption capacity of MAC results was recorded (16, 15, and 20) mg sulfur/g MAC for AC/Ni, AC/Cu and, AC/Ni-Cu, respectively. Equilibrium isotherm study results show good fitting with Freundlich isotherm model with R^2 value (0.95) for AC/Ni-Cu. The kinetic study results showed R^2 value (0.974, 0.981, and 0.95) by pseudo first order and (0.96, 0.916 and, 0.909) by pseudo second order for AC/Ni, AC/Cu, and AC/Ni-Cu, respectively. The calculated $q_{e(cal)}$ (4.337-4.79) mg/g by first order model was the nearest to the obtained $q_{e(exp)}$ (5.125) mg/g by the experiments where no interparticle diffusion referring to more than one process is controlling the adsorption process of sulfur compounds by MAC.

Keywords: light naphtha, adsorption, desulfurization, modified activated carbon.

أزالة الكبريت من النافثا الخفيفة بطريقة الامتزاز باستخدام فحم منشط معدل

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الخلاصة

تهدف الدراسة الى تقييم أزالة الكبريت من النافثا الخفيفة المنتجة في مصفى الدورة بتقنيات ازالة الكبريت بالامتزاز باستخدام فحم منشط محمل بعناصر ثقيلة النيكل و النحاس بشكل مفرد و ثنائي. تم أجراء التجارب بشكل وجبات مع متغيرات نوع الفحم

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المنشط المعدل محمل مع (النيكل ، النحاس والنيكل – النحاس و) ، جرعة الفحم المعدل ، سرعة التحريك و زمن تلامس اقصى 300 دقيقة بثبوت التركيز الأولي للكبريت الكلي 155 ملغم/لتر ودرجة حرارة الغرفة علما . حيث اظهرت التنائج ان افضل ازالة للكبريت باستخدام فحم منشط محمل (نيكل - نحاس)هي (66.45)% على التوالي عند جرعة 1 غرام و سرعة 500 دورة بالدقيقةمقارنة مع الفحم الغير محمل كانت الازالة (29.03)%، حيث ،أما نتائج سعة الامتزاز للفحم المعدل اظهرت القيم (16 و 15 و 20) ملغم كبريت /غرام فحم معدل لكل من (فحم منشط محمل بالنيكل ، النحاس والنيكل – النحاس) على التوالي . اظهرت نتائج موديلات التوازن تطابق جيد مع موديل فرندلش و باعلى قيمة مربع معامل الانحدار (0.95) الفحم المعدل ب نيكل – نحاس ،بينما نتائج الدراسة الحركية لأمتزاز الكبريت بواسطة الفحم المعدل اظهرت قيم مربع معامل الانحدار (0.974 و 0.981 و0.95) من خلال موديل سيدو-الدرجة الاول و (0.96 و0.916 و0.982) من خلال موديل سيدو- الدرجة الثانية لكل من الفحم المنشط المعدل محمل مع (النيكل ، النحاس و النيكل – النحاس) على التوالي حيث كانت قيم سعة الامتزاز المستخرجة من موديل سيدو –الدرجة الاولى هي اقرب لقيم سعة الامتزاز التي تم الحصول عليها عمليا في التجارب ،حيث وضح موديل الانتشار داخل الجزيئات عدم مرور المنحني في نقطة الاصل وهذا يشير الى ان هناك اكثر من ميكانيكة تسيطر على عملية امتزاز الكبريت بواسطة الفحم المعدل بالعناصر الثقيلة.

الكلمات الرئيسية: النافثا الخفيفة ، الامتزاز ،أزالة الكبريت ،الفحم المنشط المعدل

1. INTRODUCTION

Full-range naphtha is the production of crude oil thermal distillation at a boiling range between 30-200ºC, and represent about 15–30% by w/w of the crude oil. It includes light naphtha with boiling range from 30-90ºC, containing the C5 - C6 hydrocarbons while heavy naphtha is the fraction boiling from 90- 200ºC, naphtha of different origin contain small amounts of additional compounds containing elements such as sulfur **(Goarge and Abdullah, 1995).** Light naphtha is used for producing of gasoline in the petroleum refinery (**Yahya and Hussein, 2019)** Sulfur content in fuel oil, such as mercaptans, thiophenes (T), benzothiophenes (BT), and dibenzothiophenes (DBT), produce sulfur oxide (SO_x) upon combustion, which are the main sources of acid rain and air pollution, **(Muhammad, et al., 2019)**,**(Ibrahim, et al., 2016).** The US Environmental Protection Agency (EPA) has set the primary National Ambient Air Quality Standards (NAAQS) for SO_2 exposure at 78 g/m^3. The annual average ambient concentration of SO^2 in the US is 15 g/$m^{3.}$ These compounds also cause corrosion in refinery equipment and deactivate ("poison") the catalysts that promote desired chemical reactions in certain refining processes, **(González-García, et al., 2018).**

Therefore, removal of such sulfur-containing compounds is imperative for the production of green fuel oils and to meet the new standards of sulfur content (10–15 ppm) as per the recommendations of the United State Protection Agency (USEPA), given the environmental concerns surrounding sulfur, **(Subhan, et al., 2019).** The removal of sulfur from transportation fuel and petrochemicals is gaining more attention due to the increased awareness of the adverse effects of burning sulfur-containing oils on human health, which is undesirable and may be subject to stringent regulatory controls and the environment. Desulfurization can be classified according to its techniques to Hydrodesulfurization HDS and Non- Hydro desulfurization Non-HDS, (**Betiha, et al., 2018)**.

(Marc, et al., 2005) showed application of modified Hydro desulfurization HDS as a new approach to the ultra-deep desulfurization of liquid fuel, with high selectivity towards the refractory substituted dibenzothiophenes that are very difficult to remove by standard hydro desulfurization techniques. The new method is based on the selective adsorption of dibenzothiophenes by the formation of charge-transfer complexes with immobilized p-acceptor molecules. The application of very mild process conditions (low pressure, ambient temperature, no hydrogen consumption) is an additional advantage of this new approach in comparison to traditional HDS.

(Kazumasa et al., 2010) examined Oxidative desulfurization ODS of naphtha with H_2O_2 and AcOH as a polar solvent in the presence of H_2SO_4 . The effectively reduction of the sulfur content of naphtha and adsorption with silica gel further reduced the sulfur content to below 0.5 mass ppm where the oxidation proceeded in the AcOH phase, and most of the oxidized sulfur compounds resided in this phase, resulting in the successive removal of the sulfur compounds from the octane phase.

(Mohammed and AbdulWahhab, 2014) showed desulfurization of sulfur by ion-exchange using NaY zeolite from kaolin clay origin the results were shown as promoted adsorbent gives a higher percentage of sulfur removal percentage (82.15%) after 10 minutes while removing records 40.15% after 2 hrs.

(Ibrahim and Jabbar, 2015) examined the effects of the operating conditions (contact time, temperature, mixing speed, and sorbent dose) on the desulfurization efficiency, where they examined two different oxidative desulfurization strategies based on oxidation/adsorption or oxidation /extraction were evaluated for the desulfurization of AL-Ahdab (AHD) sour crude oil(3.9wt% sulfur content).

(Mohammed, et al., 2015) showed that desulfurization by oxidation process using hydrogen peroxide as an oxidant and acetic acid as a homogeneous catalyst. The solvent extraction process used acetonitrile (ACN) and N-methyl–2-pyrrolidone (NMP) as extractants. These best conditions were applied upon real diesel fuel (produced from Al-Dora refinery) with 1000 ppm sulfur content. It was found that sulfur removal was 64.4% using ACN solvent and 75% using NMP solvent.

Desulfurization by adsorption using Activated carbon and modified activated carbon by metals as oxides or salts to enforce the process of removal of sulfur compounds from petroleum products as an alternative and low-cost method in order to enhance the adsorbent surface to increase the ability of adheres the adsorbate in fluid at the surface of activated carbon,

(Sarahm, 2017) examined different metal zinc , cobalt and nickel for loading at activated carbon AC and the samples of experiment includes ZnO/AC, ZnO/NiO/AC and ZnO/NiO/CoO/AC where, the loading was kept constant at 10%. Characterization revealed that the three types are highly crystalline with distinct peaks, of nanoparticle size below 100nm, and have high surface area.,

(Suryawanshi, et al., 2018) studied desulfurization under batch experiment conditions temperature 28 ^oC, initial sulfur concentration (25-600 ppm S), and equilibrating with a known weight of the adsorbent (0.05-0.75 g per 10mL of the model fuel) for single and double metal modifications were studied using zinc, cobalt, nickel, and copper.

(Abbas and Ibrahim, 2020) studied modified desulfurization of light naphtha LN to remove the best removal of sulfur content from light naphtha in batch mode using Activated carbon and white eggshells WES. The operating conditions studied were hydrogen peroxide to LN ratio, pH of the solution, agitation speed, temperature, contact time, and the catalyst weight.

The aim of this study is the evaluation of sulfur removal using modified activated carbon at different conditions. Equilibrium and kinetic studies are done for explaining the nature of the adsorption of sulfur.

2. EXPERIMENTAL WORK

2.1 Materials

Light naphtha was supplied from Al-Dora refinery in Baghdad with specific gravity 0.64-69, initial boiling point(30-40)C^o and sulfur content 155 ppm(mg/l) which are shown in **Table 1**, granular activated carbon AC from coconut shell origin is produced by Unicrbo Co., Italy with particle size (1.18)mm, surface are (1100)m^2/gm and particle density (1100-1200) kg/m^3 which are shown in

Table 2. as base for modification and loaded metals are Nickel nitrate $Ni(NO_3)_2.6H_2O$ with copper nitrate $Cu(NO_3)_2.3H_2O$, produced by Himedia, India.

Table 1. Properties of light naphtha.

Property	Value
Sp.gr	0.64 -0.69
IBP C^o	30-40
FBP C^o	80-85
Sulfur content (wt%, ppm)	0.0155 ; 155
RON	60 -65

Table 2. Properties of activated carbon.

Item of analysis	Specification	Results	Method
Dimensions (granular)	-	12X40 mesh (0.4-1.6)mm	-
Bulk density(kg/m3)	460-520	460-480	ASTM D 2854-96
Particledensity (kg/m^3)	-	1100-1200	
Void fraction	-	0.45	
Surface area (m^2/gm)	1000 (min)	1100-1130	ASTM D4607-94
Hardness (%)	97 (min)	98 (min)	ASTM D3802-94
Ash (%)	5 (Max)	5(Max)	ASTM D4607-94
Micropore	-	High	

2.2 Modification of Activated Carbon

All adsorbents of MAC (AC/Ni, AC/Cu, and AC/Ni-Cu) were prepared for modification of original activated carbon using adsorption method which involves mixing of 50 gram activated carbon with 100 ml of known metal solution contain 1% w/w of metal concentration (1000) ppm individually for exact time 4 hours and agitation speed 500 rpm speed of mixing using a magnetic stirrer to reach equilibrium and saturation of activated carbon to adsorb the metal ions on the available adsorption sites where the results show loaded concentrations of Ni and Cu were 12.4 and 11.6 mg/g respectively.

2.3 Experiments Condition

2.3.1 Type of adsorbent

Four samples of 50 ml light naphtha were prepared with initial sulfur content 155 ppm where 1 gram of origin activated carbon AC – non modified- and modified activated carbon AC/Ni , AC/Cu and AC/Ni-Cu (MAC) were added to these samples respectively at normal atmospheric condition room temperature 25$_-^+$ 2 °C, agitation speed 500 rpm for 300 min (6 hrs). At the end of adsorption desulfurization the mixture is filtered by filter paper for sulfur content analysis.

2.3.2 Agitation speed experiment.

Three sets each involve three samples of 50 ml light naphtha were prepared for each (MAC) with initial sulfur content of 155 ppm where 1 gram of modified activated carbon (MAC) AC/Ni, AC/Cu, and AC/Ni-Cu were added to these samples respectively at three agitation speed (200, 300 and 500) rpm, normal atmospheric condition at room temperature 25± 2 °C, for 300 min (6 hrs). At the end of adsorption desulfurization the mixture is been filtered for sulfur content analyses.

2.3.3 MAC dosage experiment.

Three sets involve samples of 50 ml light naphtha with 155 ppm initial concentration were prepared, and different dosage of each MAC (0.1, 0.3, 0.5, 0.7, and 1 gm) were added to the light naphtha samples respectively at room temperature with agitation speed 500 rpm until equilibrium at 300 min, separation of filtrate is done for sulfur content analysis.

2.3.4 Contact time experiment.

Five samples of 250 ml light naphtha were prepared with initial sulfur content 155 ppm where 2 grams of MAC AC/Ni , AC/Cu and AC/Ni-Cu and were added to these samples respectively at normal atmospheric condition room temperature 25$_-^+$ 2 °C, agitation speed 500 rpm for 0-300 min (0-6 hrs).at the end of adsorption desulfurization the mixture is filtered for sulfur content analyses.

2.4 Analytical Procedure.

- Amount of loaded metal on AC by Atomic absorption spectrophotometer.
- Xrd analyses by X-Ray Diffraction.
- Sulfur content by using ANTEK 9000N/S analyzer A according to ASTM D-5453.

2.5 Data Analyses

Removal of sulfur content was shown as Desulfurization efficiency (DS) Eq.(1), which is calculated as the ratio of sulfur removed to that initially present in light naphtha.

$$DS\% = \frac{Co-Ce}{Co} x\ 100 \qquad (1)$$

Where: C_o: the initial sulfur content in light naphtha and Ce the measured sulfur content in light naphtha at equilibrium ppm.

Determination of the MAC adsorption capacity Eq.(2) and (3)

$$qe = \frac{Co-Ce}{m} x\ V \quad at\ constant\ mixing\ time \qquad (2)$$

$$qt = \frac{Co-Ct}{m} x\, V \quad at\ different\ \ mixing\ time \tag{3}$$

Where qe adsorption capacity at equilibrium mg/g , qt adsorption capacity at sampling time mg/g, and Ct are sulfur content at intervals sampling time respectively ppm.

3. RESULTS and DISCUSSION

Loading of metals on AC was in order to modify the surface of the adsorbent to be more acceptable to adsorb sulfur compounds, after preparation of MAC by loading Ni and Cu by adsorption method to prepare MAC for adsorption desulfurization, where the amount of adsorbed Ni and Cu were 12.2 mg Ni/g MAC and 11.6 mg Cu/g MAC. In **Fig.1, Fig.2, and Fig.3** XRD analyses for AC/Ni, AC/Cu, and AC/Ni-Cu, respectively. Recorded 2θ values were (26.2, 36.5, 43.5 and 48) for AC/Ni, (26, 34.5, 38.5, 48.4 and 53) for AC/Cu and(26.5, 34.6, 36.6, 38.4,43.5, 50 and 58) for AC/Ni-Cu where these result approximately in agreement with previous works standard values for Ni 2θ =43.295 refers to crystalline NiO and Cu 2θ values of 35.7° and 38.5° are characteristic of CuO **(Al-Karkhi, 2017) and (Suryawanshi, et al., 2018), w**here one previous work show XRD for activated carbon before loading, as shown in **Fig.4.**

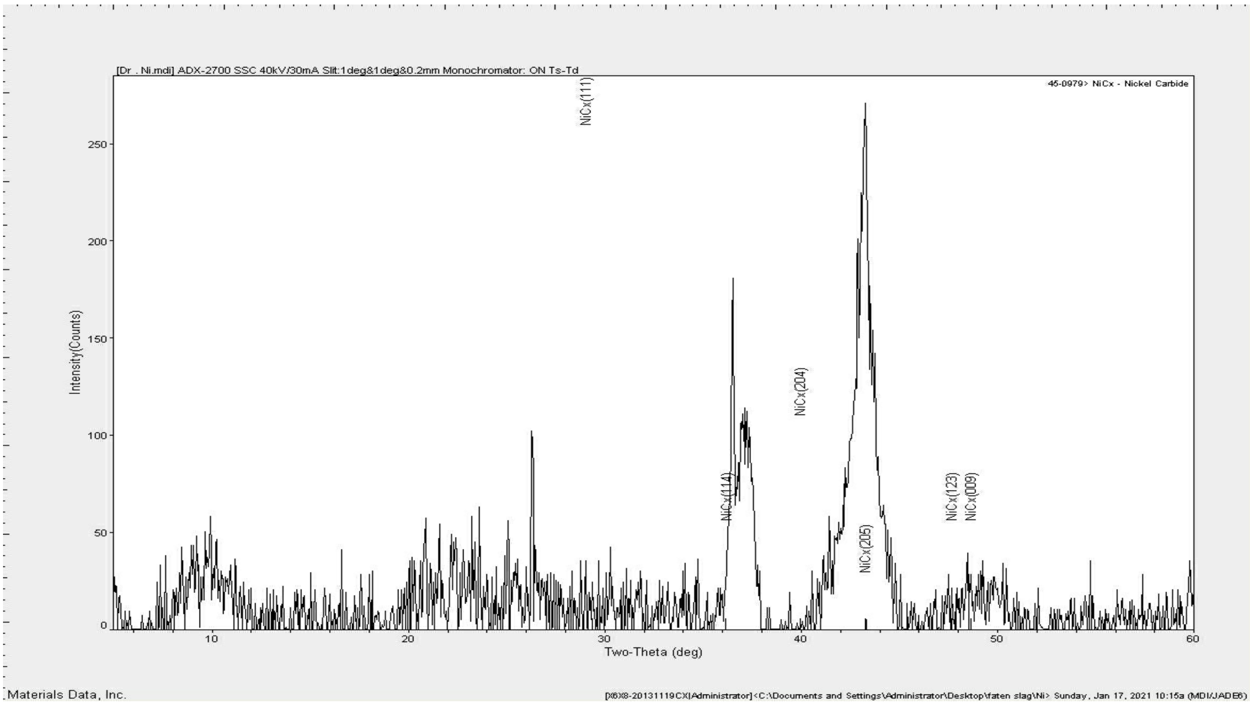

Figure 1. Xrd analyses of MAC AC/Ni**.**

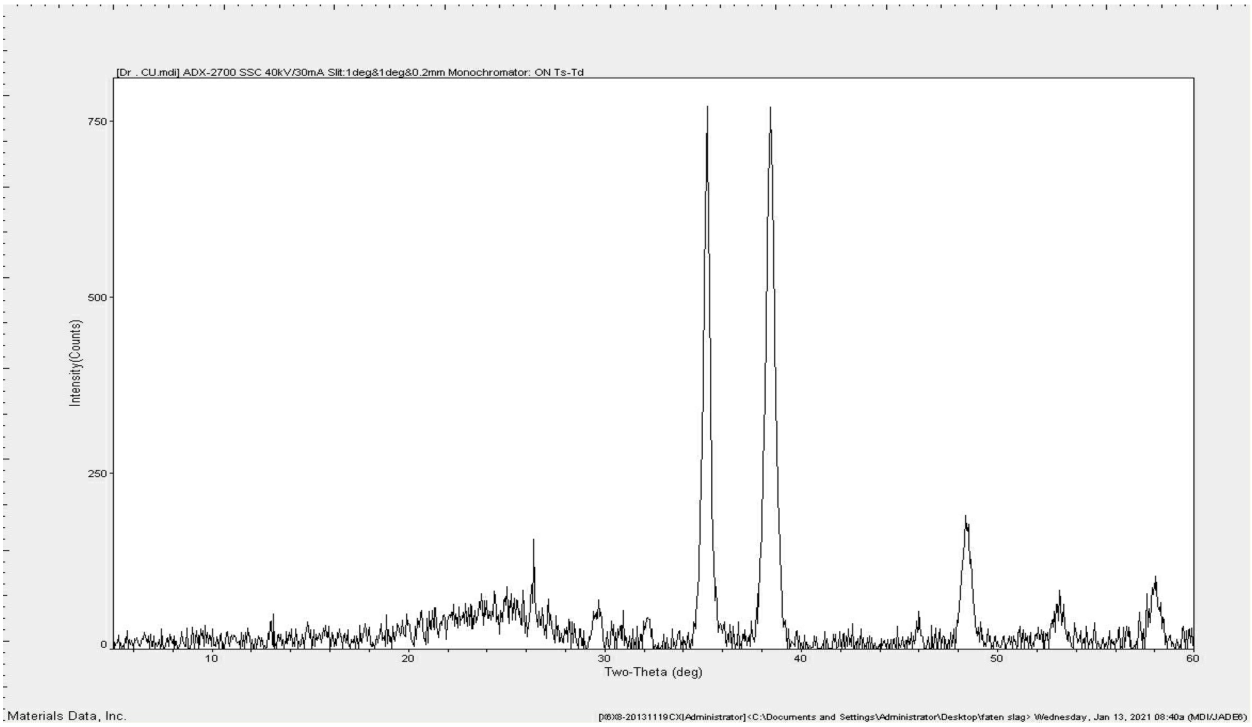

Figure 2. Xrd analyses of MAC AC/Cu.

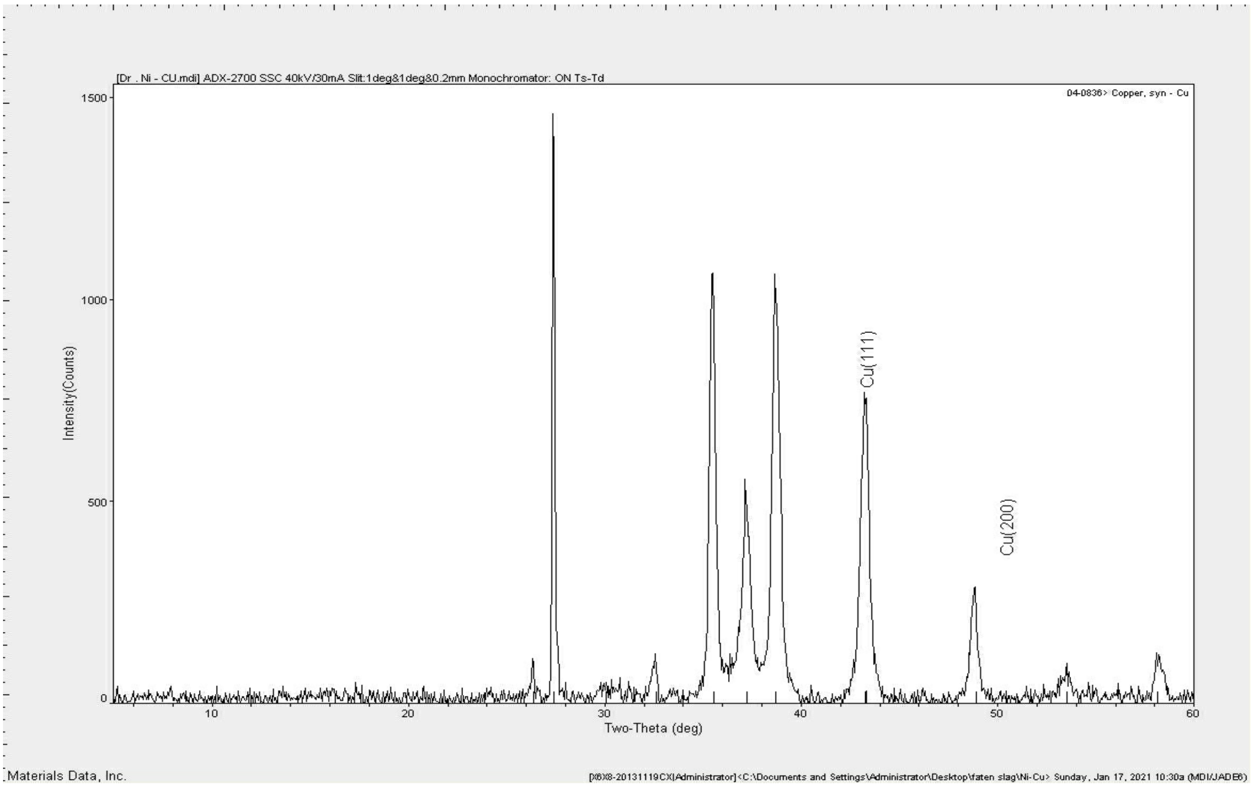

Figure 3. Xrd analyses of MAC AC/Ni-Cu.

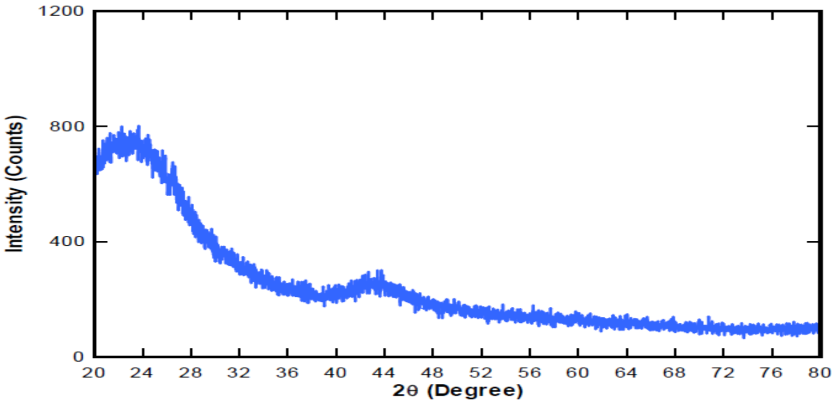

Figure 4. Xrd analyses of AC by (**AlKarkhi, 2017**).

3.1 Effect of Adsorbent Type

Fig.5 represents the efficiency of desulfurization DS % for activated carbon before and after modification by loaded metals where the DS% at initial sulfur content 155 ppm, adsorbent dosage 1 g, and agitation speed 500 rpm (29, 58, 59.3, and 66.45)% for AC, AC/Ni, AC/Cu, and AC/Ni-Cu, respectively which was explained by past works due to that modification play a major role in enhancing adsorption of the sulfur compound by improving their surface, where the chemistry of activated carbon surface is the main factor for the removal of sulfur content. **(Gaddafi, et al., 2017).** Furthermore, the results show increasing % removal of sulfur for modified activated carbon with multi-metals. It is concluded that the addition of di metal exhibited more efficiency than mono, where these metals act as active sites for interaction with cycle sulfur compounds **(Al-Karkhi, 2017).** Previous work showed a slightly decrease in surface area are reported for modified activated carbon.

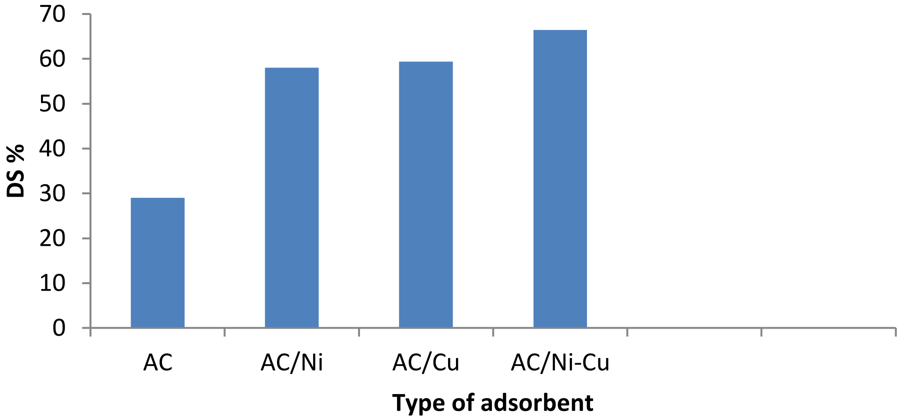

Figure 5. DS% for AC and MAC at an initial sulfur concentration of 155 ppm, agitation speed 500rpm, and adsorbent dosage 1 gm.

3.2 Effect of agitation speed on DS% for MAC

Fig.6 shows the effect of the agitation parameter on the DS process where three different mixing speed (200, 300, and 500) rpm and constant other variables 1 gm MAC dosage and agitation speed

which show positive relation of increasing of agitation with increasing DS% value with all different types of MAC.
The results of Fig.5 show increasing in DS % with the best result at 500 rpm were recorded (58, 59.3, and 66.45)% for AC/Ni ,AC/Cu and AC/Ni-Cu, respectively may be due to enhance mass transfer of sulfur compounds from fluid phase to solid phase to be adsorbed on sites of adsorbent surface (MAC) where high agitation will give the sulfur molecules high energy to contact with solid surface at same time high agitation will reduce the thickness of layer between the fluid and the adsorbent surface **(AlKarkhi, 2017)**.

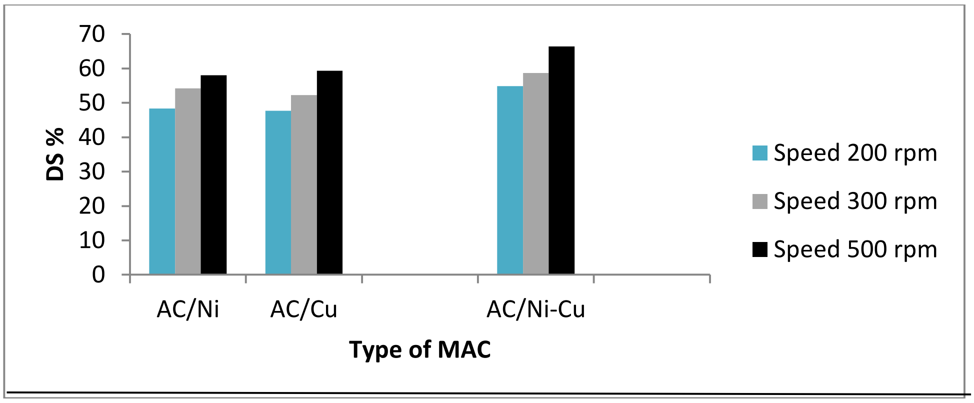

Figure 6. Effect of agitation speed on DS% for MAC at an initial sulfur concentration of 155 ppm and adsorbent dosage 1 gm.

3.3 Effect of MAC dosage on DS%

Fig.7 shows the effect of MAC dosage on removal of sulfur content in the batch system of 50 ml of light naphtha with initial sulfur concentration 155 ppm, agitation speed 500 rpm, and room temperature. The results show increasing of DS% with increasing of MAC dosage where the best removal order can be arranged as shown below
AC/Ni-Cu>AC/Ni>AC/Cu
Adsorbent dosage was increased, the DS % was increased too due to excess availability of adsorption site at the adsorbent surface (**Ahmed and Ahmaruzzaman, 2015),** resulting in increasing the available surface area that proportional with the amount of used MAC **(Abood, 2012).** These metals act as active sites for interaction with cycle sulfur compounds **(Al-Karkhi, 2017).**

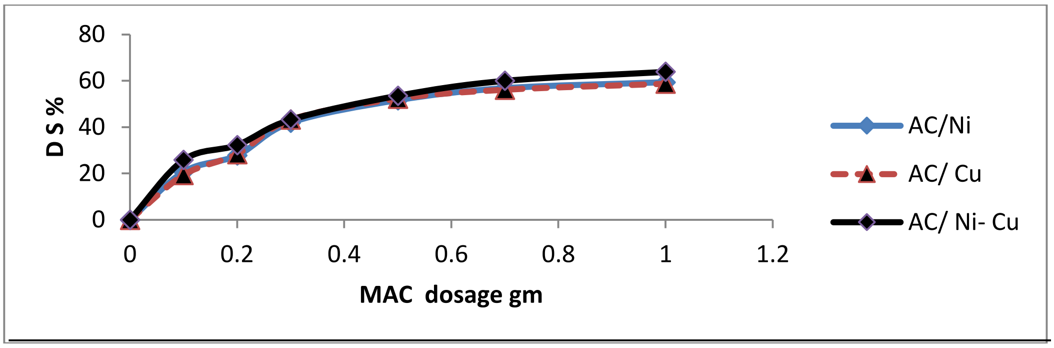

Figure 7. Effect of MAC dosage on DS% for MAC at an initial sulfur concentration of 155 ppm and agitation speed 500 rpm.

3.4 Equilibrium isotherm models

Fig.8 shows the equilibrium isotherm curve as a relation between sulfur concentration Ce and adsorption capacity qe by Eq.(2) at equilibrium for a different type of MAC according to the effect of MAC dosage.

Eq.(4) and Eq.(5) represent the nonlinear and linear formula of the Langmuir isotherm model, and Eq.(6) and Eq.(7) represent a nonlinear and linear form of the Freundlich isotherm model.

$$qe = \frac{q_m \; Kl \, Ce}{1 + Kl \, Ce} \tag{4}$$

$$\frac{Ce}{qe} = \frac{1}{qm \, Kl} + \frac{1}{qm} Ce \tag{5}$$

$$qe = Kf \; C_e^{1/n} \tag{6}$$

$$log \, log \, qe \; = Kf + \frac{1}{n} C_e \tag{7}$$

By plotting Ce/qe vs. Ce and log qe vs. log Ce, the results show invalid fitting with Langmuir model due to negative slope while acceptable for Freundlich isotherm model as shown in **Fig.9,** and the obtained constants are shown in **Table 3**.

The listed results which are shown in **Table 3.** best R^2 is (0.95) for AC/Ni-Cu even though the other value are accepted, which refers to good fitting with the Freundlich model for desulfurization of light naphtha by all type of MAC which agreement with the previous works (**Gaddafi and Tawfik, 2017)** but It doesn't indicate a finite uptake capacity of the adsorbent. It can thus only be reasonably for low and intermediate concentration range (**Ahmed and Ahmaruzzaman, 2015)** where the Freundlich model doesn't show maximum adsorption capacity as by the Langmuir model.

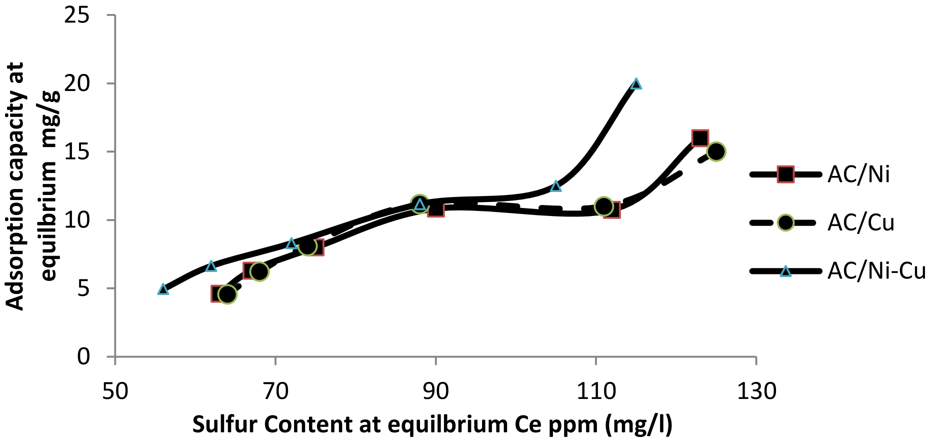

Figure 8. Equilibrium isotherm curves for all MAC.

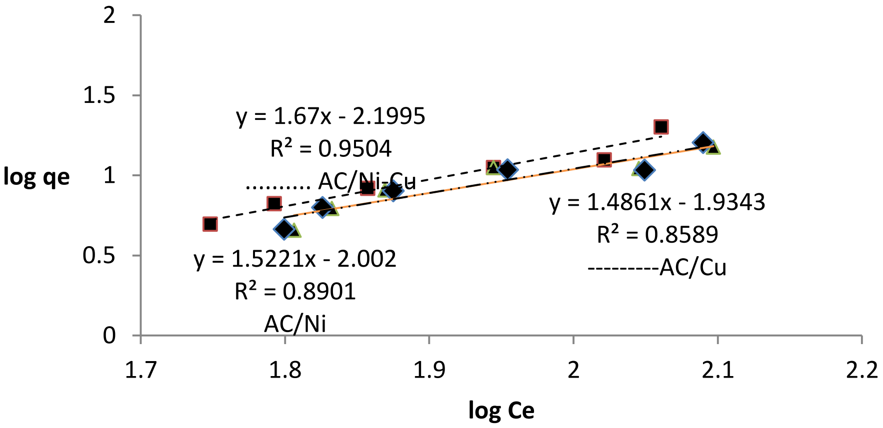

Figure 9. Freundlich isotherm linear model.

Table3. Equilibrium isotherm models parameters**.**

Type of MAC	Freundlich model			Langmuir model		
	K_f	1/n	R^2	K_l	q_m	R^2
AC/Ni	0.01	1.522	0.88	- 0.00377 (invalid)	-17.63 (invalid)	0.428
AC/Cu	0.0116	1.486	0.859	-0.0036 (invalid)	-18.7 (invalid)	0.345
AC/Ni-Cu	0.00632	1.67	0.95	-0.0048 (invalid)	-14.53 (invalid)	0.76

3.5 Effect of Contact Time on DS% and Adsorption Capacity.

Fig.10 and **Fig.11** show the effect of contact time on desulfurization process where clear increasing of DS% and adsorption capacity with increasing contact time qt applying Eq.(3) at constant other variables until equilibrium time (300 min), and initial sulfur concentration 155 ppm in a batch process to give sufficient time for adsorbate to transfer from fluid bulk to solid bulk where many factors are in a role like available active site and surface are, (**Mohammmed and Suha, 2020**).

The amount of adsorbed sulfur content per amount of MAC adsorbents is (5.625, 5.125, and 6.625) for MAC types AC/Ni, AC/Cu, and AC/Ni-Cu, respectively, and these results agreement fairly with previous work where the amount of adsorbed sulfur was 7.0 mg of S/g of the adsorbent and 6.7 mg of S/g of the adsorbent (**Gaddafi and Tawfik, 2017**).

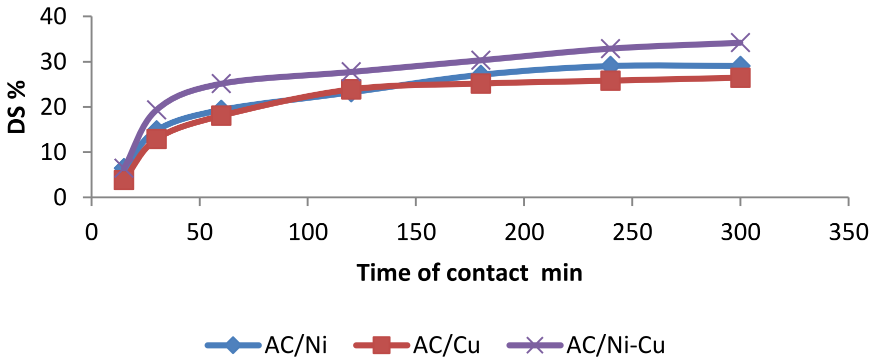

Figure10. Effect of contact time on Desulfurization efficiency for initial Sulfur concentration 155 ppm, MAC dosage 2 gm.

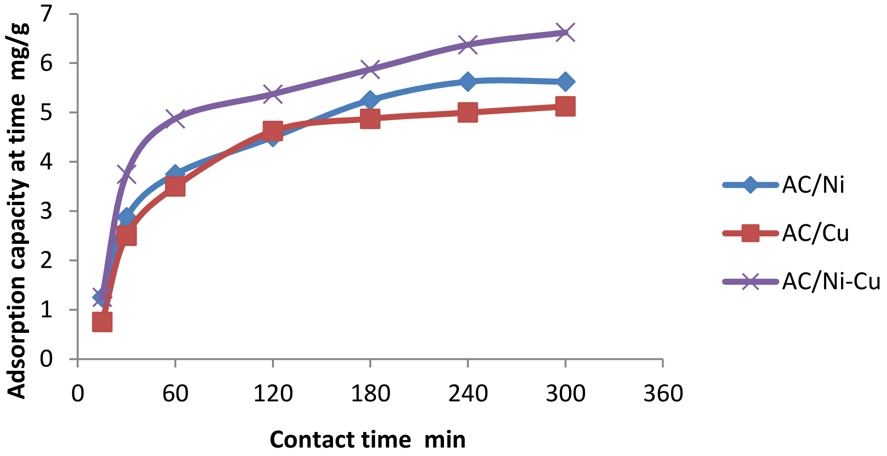

Figure11. Effect of contact time on adsorption capacity for initial Sulfur concentration 155 ppm, MAC dosage 2 gm.

3.6 Kinetic adsorption models.

The fitting of kinetic adsorption models pseudo-first-order, pseudo-second-order, and interparticle diffusion Eq.(8), Eq.(9), and Eq.(10) is applied to determine the equilibrium time, mechanism of adsorption and to determine the rate-controlling step linear form of the kinetic model were log (qe-qt) vs. t for pseudo-first-order, (1/qt) vs. t for pseudo-second-order **(Junxiong and Lan, 2009)** and qt vs. $t^{0.5}$ for interparticle diffusion **Fig.12**, **Fig.13** and **Fig.14** respectively.

$$log\, log\,(qe-qt)\ = log\, log\,(qe)\ -\frac{K_1}{2.303}t \quad (8)$$

$$\frac{1}{qt}=\frac{1}{K_2qe^2}\frac{1}{t}+\frac{1}{qe} \quad (9)$$

$$qt=K_p\,t^{0.5}+C \quad (10)$$

Where: q_e *and* q_t are adsorption capacity at equilibrium and at time t, respectively (mg.g-^{1}), K_1 is the rate constant of pseudo-first-order adsorption (min^{-1}), K_2 is the rate constant of the pseudo-second-order adsorption (g.mg^{-1}.min^{-1}), K_p is the intra-particle diffusion rate constant (mgg^{-1} s$^{-1/2}$), and C (mg/g) is the boundary layer thickness for intra-particle diffusion

Table 4. showes parameters and R^2 values for kinetic models from slope and intercept of the linear form of models.

For AC/Ni R^2 values are (0.974 and 0.96) and value of $q_{e(cal)}$ (4.752 and 5.625) mg/g for pseudo-first and second-order respectively, whereby pseudo-first-order more nearest to the actual value $q_{e(exp)}$ (5.625) mg/ g, for AC/Cu R^2 values are (0.981 and 0.916) and value of $q_{e(cal)}$ (4.337 and 14.86) mg/g for pseudo-first and second-order respectively which show that pseudo-first-order more nearest to the actual value $q_{e(exp)}$ (5.125) mg/ g than one that calculated by second-order, while AC/Ni-Cu R^2 values are (0.95 and 0.909) and value of $q_{e(cal)}$ (4.79 and 11.84) mg/g for pseudo-first and second-order respectively where pseudo-first-order more nearest to the actual value $q_{e(exp)}$ (6.625) mg/ g than one that calculated by second-order

The results in **Table 4.** show more fitting with pseudo-first-order even though there is an acceptable value of R^2 for pseudo-second-order, which disagreement with previous works **(Ammar and Jaafar, 2017)** due to the process of loading metal on activated carbon by this study follow the adsorption method which shows agreement with **(Hua, et al., 2014)**. The intraparticle regression diffusion is not linear, and it did not pass through the origin (**Ibrahim and Jabbar, 2015)**, suggesting that the intraparticle diffusion does not influence the adsorption and that it was not the rate controlling step, implying that more than one process is controlling the adsorption process **(Hua, et al., 2014)**. The initial rapid phase may also be due to the increased number of vacant sites available at the initial stage, an increase in the driving force of the concentration gradient between fluid phase (adsorbate) and solid phase (adsorbent) (**Ong,et al., 2010)**.

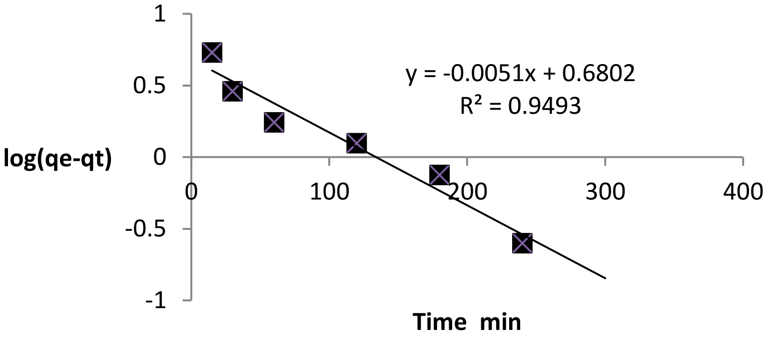

Figure.12 Pseudo-first-order linear form for AC/Ni-Cu.

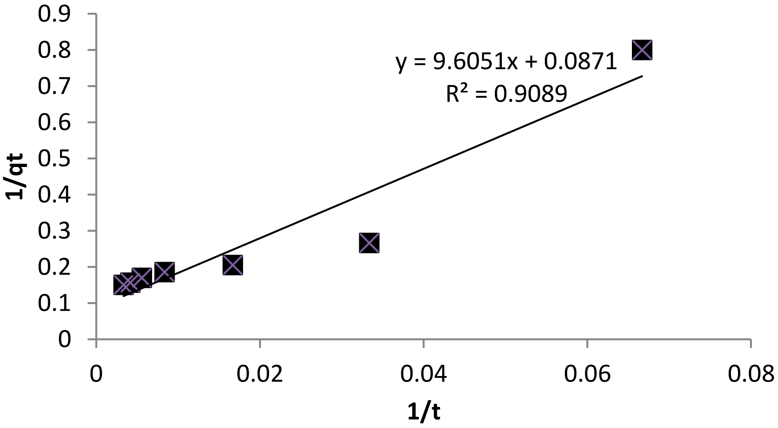

Figure13. Pseudo-second-order linear form for AC/Ni-Cu.

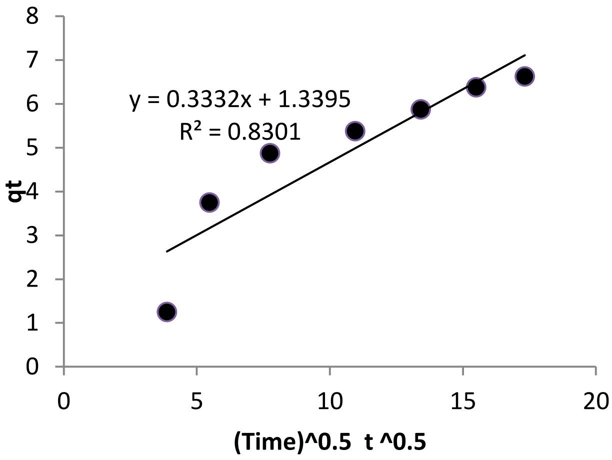

Figure14. Interparticle diffusion linear form for AC/Ni-Cu.

Table 4. Kinetic models parameters.

Kinetic models	Type of MAC		
	AC/Ni	AC/Cu	AC/Ni-Cu
Pseudo first order			
K_1 min^{-1}	0.0136	0.0156	0.0117
qe($_{cal}$)*	4.752	4.337	4.79
R^2	0.974	0.981	0.95
Pseudo second order			
K_2 mg/g min	0.00167	0.00026	0.00079
qe($_{cal}$)	7.955	14.86	11.48
R^2	0.96	0.916	0.909
Interparticle diffusion			
K_p mgg^{-1} min$^{-1/2}$	0.303	0.2942	0.3332
C mg/g	0.908	0.6459	1.34
R^2	0.9077	0.824	0.88

4. CONCLUSIONS

The following conclusions are pointed during this work:

1. The MAC gives higher removal of sulfur than original AC with order AC/Ni-Cu>AC/Ni>AC/Cu>AC.
2. Maximum DS % and adsorption capacities are 66.45% and 20 mg/g, respectively, with AC/Ni-Cu of 1 gm dosage.
3. DS% are increasing with increasing MAC dose, agitation speed, and contact time.
4. Equilibrium isotherm results show a good fitting Freundlich model with a maximum R^2 value of 0.95.
5. Kinetic study results show good fitting with pseudo-first-order model with range R^2 values (0.95-0.981) and suggest that the adsorption is not influenced by the intraparticle diffusion and that it was not the rate controlling step more than one process is controlling the adsorption process.

NOMENCLATURE

Sp .gr= Specific gravity

IBP= Initial boiling point

FBP= Final boiling point

RON= Research octane number

C_o= Initial concentration of Sulfur ppm(mg/l)
C_e= Concentration at equilibrium (mg /l)
C_t= Concentration of dye (mg /l) at time t
K_F= Freundlich constant for adsorbate (l/mg)
K_1= The rate constant of pseudo-first-order adsorption (s^{-1})
K_2= The rate constant of the pseudo-second-order adsorption ($g.mg^{-1}. s^{-1}$)
K_L= Coefficient related to the affinity between the adsorbate and adsorbent for Langmuir model (l/mg)
K_p= The intra-particle diffusion rate constant($mg.g^{-1}\ s^{-1/2}$)
q_{cal}= Predicted adsorption capacity(mg/g)
q_e= Adsorbent (i.e., solid) phase concentration after equilibrium mg adsorbed/g adsorbent
q_m= Maximum adsorption capacity in for complete monolayer on the surface (mg/g)
q_t= adsorption capacity at equilibrium and at time t, ($mg.g^{-1}$)
m= Mass of adsorbent MAC (g)
t= Time (min)
V= Volume of light Naptha ml

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