Separation Sulfur Components by Adsorption Technique

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الملخص:

على مدى العقود القليلة الماضية، كانت تقنيات الامتزاز إحدى الطرق المستخدمة بنجاح في إزالة مكونات الكبريت. في العمل الحالي، تمت دراسة فروع شجرة الأوكالبتوس (Eu-GAC)
باستخدام وعاء الامتزاز الدفعي لقياس قدرتها على الامتزاز. تمت دراسة تأثير زمن التلامس والتركيز في تعزيز عملية الامتزاز. أظهرت النتائج أن الفحم المنشط كممتز يبدو أكثر كفاءة للتخلص من Dibenzothiophene (DBT 98%) مقارنة بـ 4-6 di methyl dibenzothiophene (4-6-DMDBT 97%)

Abstract

For the past few decades, adsorption techniques are one of the methods used successfully in removing sulfur components. In the present work, Eucalyptus tree branches (Eu-GAC) have been studied by using a Batch Adsorption vessel to measure their capability for adsorption. The effect of contact time and concentration in enhancing adsorption has been investigated. The results showed that the Eu-GAC agent as adsorbent appears more efficient in eliminating Dibenzothiophene (DBT,98%) compared to 4, 6-di methyl dibenzothiophene (4, 6-DMDBT,97%).

Keywords*:* Sulfur components; Eucalyptus tree branches (Eu-GAC); contact time; concentration.

1. Introduction.

Many fuels, such as crude oil and natural gas are used in industry these days. As it is well known, the main components of this fuel are hydrocarbons, which reach 96% percentage, in addition to some other compounds such as sulfur compounds. Although the proportions of these compounds are simple, they cause significant problems that require their removal. These problems are corrosion in equipment such as heat exchangers and pumps and catalyst poisoning in reactors. [1]. In addition, the presence of sulfur in fuels is considered a significant source of atmospheric pollution because sulfur atmospheric discharge from combustion is a precursor of acid rain due to the formation of sulfur oxides, [2].

In recent years, we notice the increasing demands for environmental preservation, whether from governmental organizations or environmental protection societies, which are calling for a pollution reduction. Among these organizations is the US Environmental Protection Agency. It is known that sulfur compounds have a direct impact, whether on the environment or on corrosion problems. Several regulations and laws emphasize the reduction of sulfur levels in many types of fuels such as kerosene or jet fuels. [3].

Many scientific journals explain the extent of the damage caused by pollution caused by sulfur compounds, which is directly reflected in human health due to the many diseases it causes. Among these diseases are heart and respiratory diseases and cancer. [4].

Sulfur compounds, like SO2 , are short-lived species in the atmosphere that are subject to chemical transformation, washout, and dry deposition and lead to acid precipitation problems. We know of sulfur dioxide as a pollutant because it reacts with water (H2O) to form sulfuric acid (H2SO4). [5]. Among the problems

caused by the sulfur present in the fuel is its combustion and its transformation into sulfur dioxide, and this compound has a direct effect on the efficiency of the fuel in addition to its effect on the engine itself. [6,7].

Reducing sulfur levels in fuels of all kinds has recently become a basic requirement for many manufacturers, whether they are companies that manufacture vehicles of all kinds or oil refineries and refining companies.[8].

The investigation of the adsorption capacity of activated carbon and determining its ability to remove sulfur content (Dibenzothiophene (DBT,98%) and 4, 6-di methyl dibenzothiophene (4, 6-DMDBT,97%)) in diesel fuel oil was carried out in a fixed bed column.

2. Materials and methods.

2.1Materials.

In this research, activated carbon was used as adsorbent material. Two types of model sulfur compounds are selected which are (Dibenzothiophene (DBT,98%), and 4, 6-di methyldibenzothiophene (4, 6-DMDBT,97%)).

2.2. Method.

Desulfurization by adsorption of the model and industrial diesel fuel over the adsorbent was performed in a fixed bed column consisting of a glass tube (2.9 cm i.d., 10 cm long) as shown in Figure 1. The activated carbon was packed in this tube and the feed was introduced into the tube by a liquid pump. The adsorption was carried out at atmospheric pressure and temperature 313 K.

The adsorption desulfurization of DBT and 4,6-DMDBT were conducted with the same technique. Details for adsorption desulfurization of

DBT may be described as follows. A stock solution of DBT was prepared (989.8, 456.4, 307.5 ppm) and the column was packed with 12gm of activated carbon. For the 4,6-DMDBT the adsorbtion described was conducted in the same technique of DBT. The choice of adsorbent (activated carbon (A.C)) is because it has a high surface area (pore size) and may be regenerated without loss of its efficiency.

Figure 1: photograph of assembled apparatus used for adsorption.

3. Results and discussions.

3.1 Adsorption of model sulfur compounds:

3.1.1 influence of primary concentration on the adsorption ability of model sulfur compounds:

a. Dibenzothiophene compound:

For the three samples that we studied, we note that the capacity of adsorption increases with increasing contact time until reaches about 13 hours, then the capacity adsorption decreases up to reach equilibrium. Also, we note that the rate of adsorption is very high when the initial concentrations of DBT are high in the solution because the concentration gradients of the compound is high between the bulk and the surface area of the adsorbent; that refers to the external diffusion being predominant.

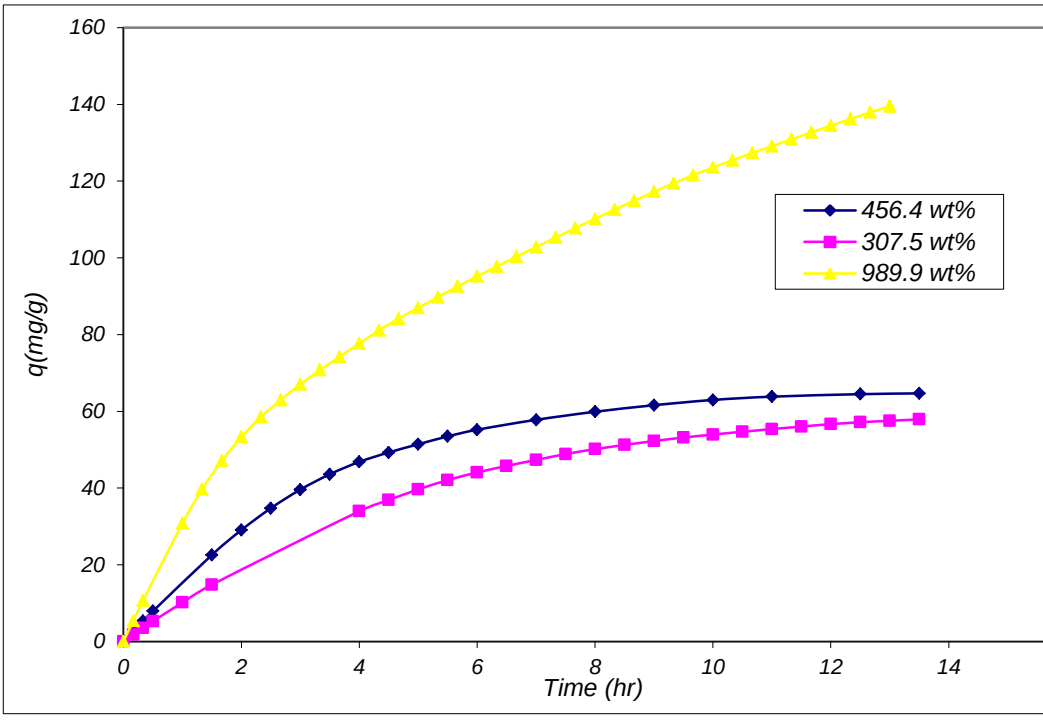

Figure 2: Adsorption capacity of DBT on 12 gm activated carbon at different initial concentration, 40 C° and flow rate 0.8833 gm/min.

b . 4,6 –dimethyldibenzothiophene compound:

The influence of concentration on the adsorption ability of 4,6DMDBT is offered in Figure 3. The same trend may be noted in this Figure , the rate of adsorption increases with increasing contact time. The time required to reach equilibrium is about 13 hrs.

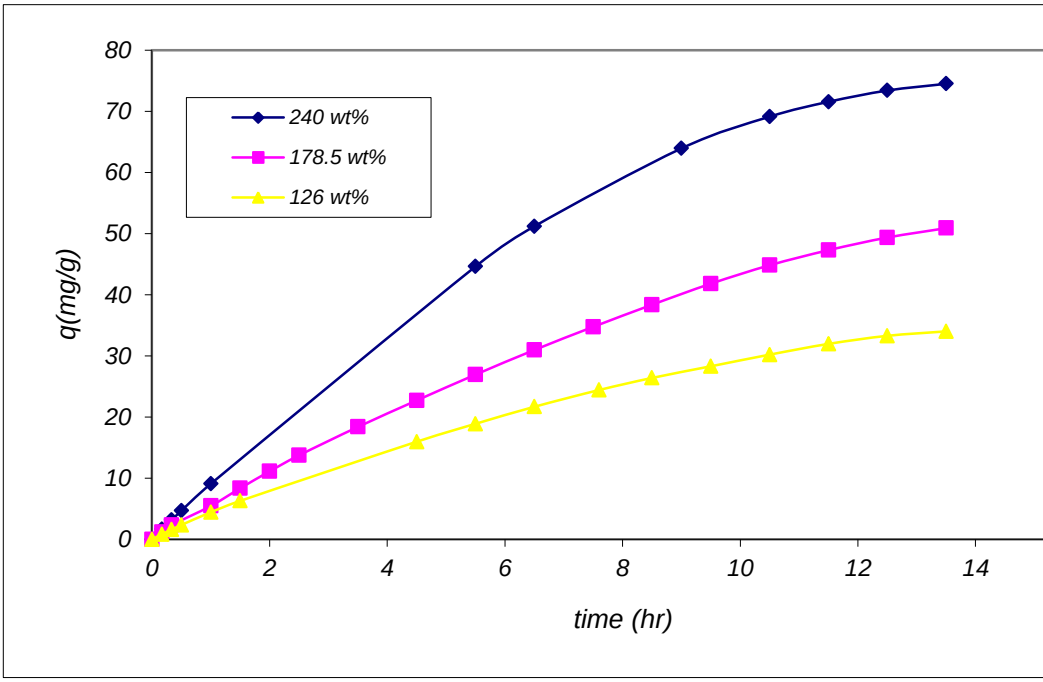

Figure 3: Adsorption Capacity of 4,6DMDBT on 12 gm activated carbon at different initial concentration, 40 C° and flow rate 0.8833 gm/min.

3.2 Adsorption Isotherms:

To check the connection between adsorbed (sulfur model compound q) and sulfur concentration C in solution, adsorption isotherm models are closely used for appropriate data, of which the Langmuir and Freundlich equations have been used .

3.2.1. Langmiur isotherm:

The Langmiur model is expressed as follow:

$$Q_e = \frac{K_L C_e}{1 + a_L C_e}$$

…….. (1)

$$\frac{1}{Q_e} = \frac{1}{K_L C_e} + \frac{a_L}{K_L}$$

…….. (2)

a. Adsorption of dibenzothiophene:

Figure 4 displays the Langmuir isotherm for the adsorption of model sulfur compound DBT on activated carbon.

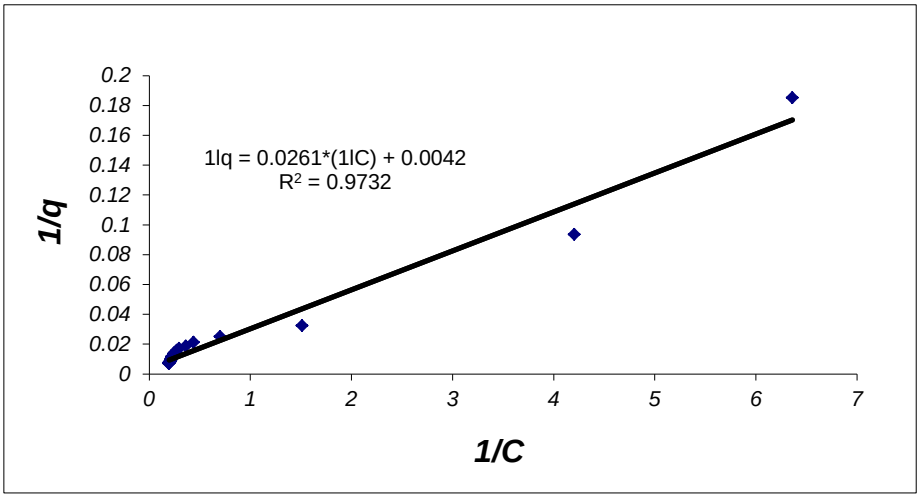

Figure 4: langmuire isotherm of the DBT, 12 gm adsorbent at different initial concentration, 40 C° and flow rate 0.8833 gm/min.

Langmuir constants a_L, K_L and q are tabled in Table (1). From this table we note that the monolayer saturation capacity is 139.53 mg/g when the initial concentration is high, the value of the correlation factor is elevated than the second compound.

b. Adsorption of 4,6-dimethyldibenzothiophene:

Figure 5 shows the Langmuir isotherm for the adsorption of model sulfur compound 4,6DMDBT onto the adsorbent substance.

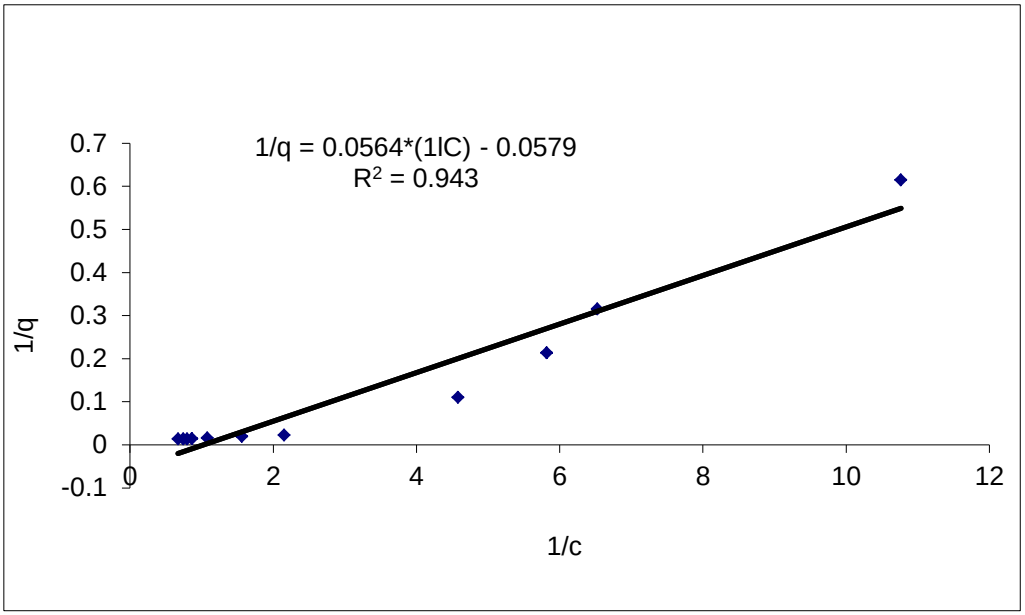

Figure 5: Langmuir isotherm for the adsorption of the 4,6DMDBT, 12 gm adsorbent substance at different initial concentration, 40 C° and flow rate 0.8833 gm/min.

Langmuir coefficient a_L, K_L and q are listed also in Table (1). The correlation factor is lower than that of DBT, that reflex the low capacity of 4,6 DMBT lesser than DBT because the monolayer saturation capacity was 74.499 mg/g.

Table 1: Langmuir adsorption summary for the sulfur compounds onto the adsorbent substance:

Compound	Initial Concentration(wt %)	q(mg/gA.C)	K_l(L/g A.C)	a_l(L/mg)	R(-)
DBT	0.745	139.53	0.03829	1.608*E-4	0.97320
4,6DMDB	0.2276	74.499	0.0177	-1.027*E	0.9430

T			4	-3	

3.2.2 Freundlich isotherm:

Freundlich isotherm equation can be written as

$$q_e = K_F C_e^{1/n} \quad \text{…….. (3)}$$

$$\log q_e = \log K_F + (1/n) \log C_e \quad \text{…….. (4)}$$

Therefore, we can find K_F and n by plotting log q_e versus log C_e.

a. Adsorption of dibenzothiophene:-

Figure 6 explains the Freundlich isotherm for the adsorption of model sulfur compound DBT onto activated carbon.

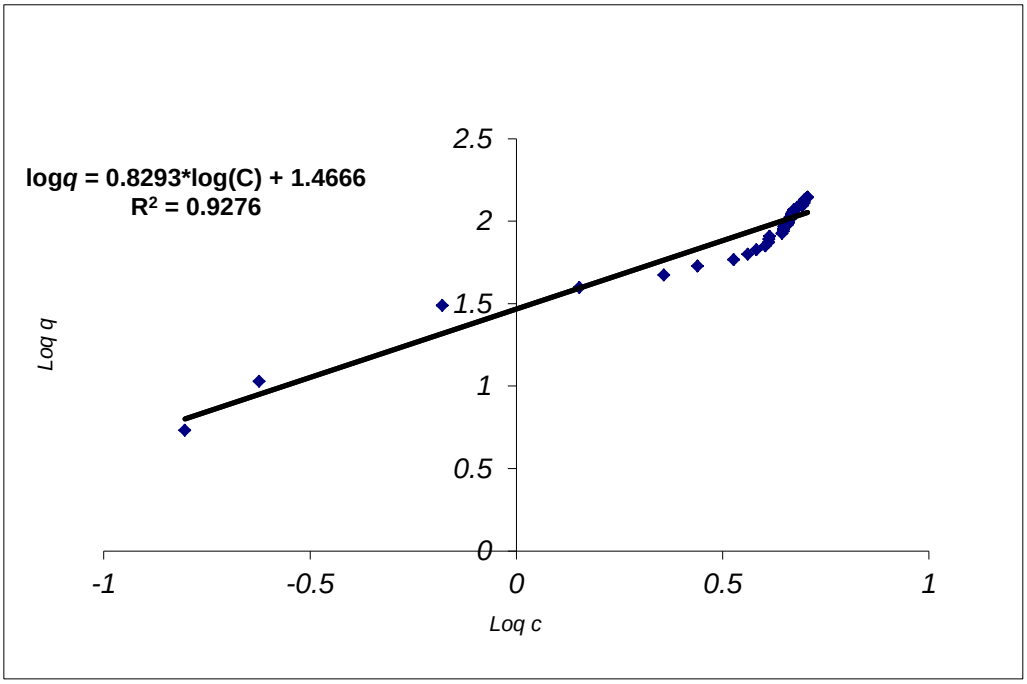

Figure 6: Freundlich isotherm of the DBT, 12 gm adsorbent substance at different initial concentration, 40 C° and flow rate 0.8833 gm/min.

Freundlich constants n,K_F and q listed in Table (2). We note that the correlation factor is smaller than that evaluated by using Langmuir isotherm. This trend is due to the Freundlich isotherm used for multilayer of adsorbent surface area not for monolayer as given by Langmuir isotherm.

b. adsorption of 4,6-dimethyldibenzothiophene:

Figure 7. shows the Freundlich isotherm for the 4, 6 DMBT onto the adsorbent substance. The values of the Freundlich constants n, K_F and q are listed in Table (2). Also correlation factor was lesser than that evaluated by Langmuir isotherm.

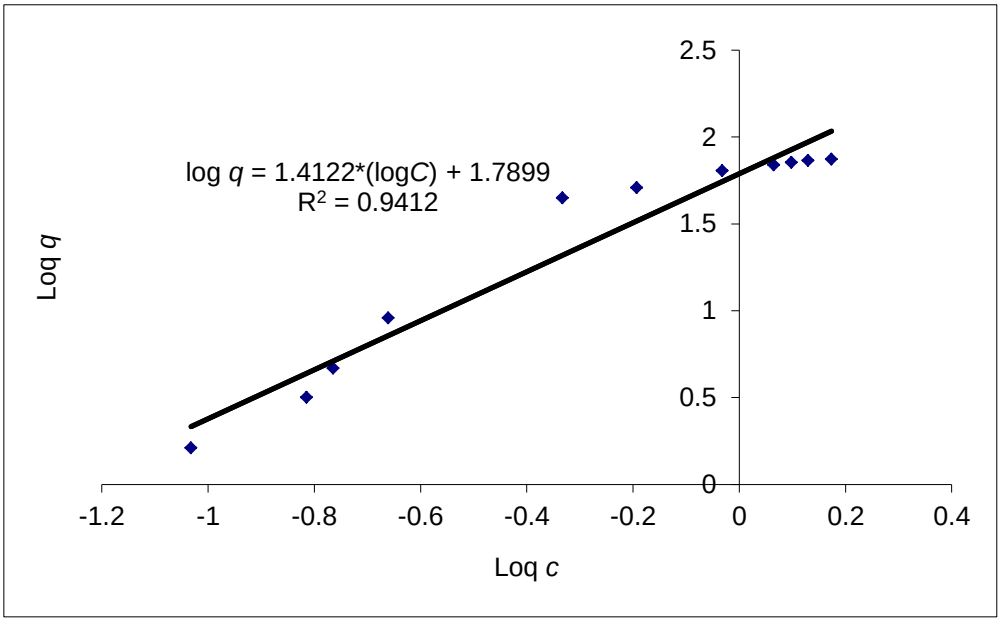

Figure 7: Freundlich isotherm of the 4,6-DMDBT, 12 gm adsorbent substance at different initial concentration, 40 C° and flow rate 0.8833 gm/min.

Table 2: Freundlich adsorption parameters for the sulfur compounds adsorbed onto activated carbon:

compound	Initial Concentration(wt %)	q(mg/gA.C)	K_F(L/gA.C)	n(-)	R(-)
DBT	0.745	139.53	0.0952	1.205	0.9276
4,6DMDBT	0.2276	74.499	3.574*E-3	0.708	0.9412

We note that the Langmuir equation demonstrates the best fit of experimental data than the Freundlich equation. That refers to the monolayer of the grains are saturated, because the shape of the adsorbent is grain.

4.Conclusion.

In Summary, the adsorption isotherms and adsorption efficiency for desulfurization by selective adsorption using a solid adsorbent (activated carbon Eu-GAC) in a fixed bed column have been explained. By raising the contact time until reaching about 13 hours, the adsorption ability grows for both sulfur components. The Langmuir isotherm adsorption shows that the correlation factor is lower than that of DBT, that reflex the low capacity of 4,6 DMBT lesser than DBT because the monolayer saturation capacity was 74.499 mg/g. The correlation of the Freundlich isotherm factor is smaller than that evaluated using Langmuir isotherm.

5.References

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