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Adsorption of Thiophenic Compounds from n-Hexane Using Activated Carbon Adsorbent

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Abstract

The aim of this work is to study the adsorption of thiophenic compounds (thiophene and benzo thiophene) on activated carbon by studying the effects of various important variables such as height of the bed (4, 6, and 8 cm) , inlet sulfur concentration (50, 75, 90, and 100 PPM), and flow rate of the liquid n-hexane feed (4, 13, and 20 ml/min.).

The activated carbon has very high affinity for the sulfur compounds in the order benzo thiophene > thiophene. In Fixed bed experiments the concentration of sulfur out (Co) with time decreases with increasing of bed height, flow rate, and the initial concentration of sulfur compounds. The maximum percent removal of thiophene was reached to 70% at initial concentration 50PPM at bed height 6 cm and feed flow rate of 4 ml/min., while the maximum percent removal of benzo thiophene was reached to 73% at initial concentration 75PPM at bed height 4 cm and feed flow rate of 4 ml/min.

Introduction …

A desulfurization process is usually carried out to remove sulfur(S) from natural gas and petroleum products such as gasoline or petrol , jet fuel , kerosene , diesel fuel and fuel oils.[1]

The refinery feed stock (naphtha , Kerosene , diesel oil and heavier oils) contains a wide range of organic sulfur compounds , including thiols , thiophenes , organic sulfides , disulfides and many others.[2]

There are several methods such as oxidative desulfurization and bio desulfurization which have shown good potential for removing refractory sulfur under mild conditions. [3, 4]

This process is based on the well known propensity of organic sulfur compounds to be oxidized; it consists of an oxidation followed by the extraction of the oxidized products. [5]

The greatest advantage of oxidative desulfurization and bio desulfurization compared with the conventional hydro desulfurization technology is that they can be carried out in the liquid phase under very mild conditions near room temperature and under atmospheric pressure. However, all these methods have their own advantages and disadvantages. [6, 7]

Adsorption is a process of accumulation substances that are in the solution, called solute, on a suitable interface. Adsorption is the most commonly used process because it is fairly simple and convenient unit operation and that the cost for its application is relatively low compared to other treatment processes. Adsorption can be equally effective in removing trace component from the liquid phase and may be used either to recover the component or simply to rid an industrial effluent of a noxious substance [8].

Several polishing processes such as reactive adsorption, non-destructive adsorption, extraction, and oxidative desulfurization are suggested to supplement the conventional desulfurization process and produce ultra-clean fuels. [9]

Adsorption processes are some of the most economically attractive methods because of the straight operating conditions and availability of inexpensive and re-generable adsorbents including zeolites, metal-based adsorbents, silica, alumina, and activated carbon. [10]

Metal based adsorbents or metal-organic framework (MOF)is one of the interesting class of porous materials that can be used to adsorb selectively organo-sulfur compounds.MOF compounds consists of metal cations linked by polyfunctional organic linkers yielding porous three-dimensional networks with large pore volumes and high inner surface area.[11,12,13]

Activated carbon due to their low cost , high surface area, thermal and chemical stability under anoxic conditions , receptivity for modification , and high affinity toward adsorption of aromatic and refractory sulfur compounds have been extensively studied for the removal of thiophenic compounds from different fuels. [14, 15]

The objective of the present study is to:

- Understanding the mechanism of sulfur compounds adsorption using influent absorbent (activated carbon) through the evaluation of the outlet concentrations (C_0) and the extraction percent (%E).
- Study the effects of various important parameters such as height of the bed, inlet sulfur concentration, and flow rate of the adsorption desulfurization process using fixed bed activated carbon techniques.

Materials and Experimental work …

1. Materials:

1.1. Adsorbate:

The liquid hydrocarbon used in this study is n-hexane containing various molar concentrations of thiophene and benzothiophene (100, 90, 75 and 50 PPM).

1.2. Adsorbent:

Granulated activated carbon (GAC) was used as an adsorbent in the present work. It was produced by Thomas Baker, India. The physical properties were measured by the oil research and development center and were coincided with that supplied by the manufacturer. These physical properties are listed in table (1).

Table (1). Physical properties of activated carbon

Bulk Density (kg/m^3)	**0.35*10^3**
Particle Density (kg/m^3)	**1.8*10^3**
Surface Area(m^2/g)	**850**
Void Fraction supplied from	**0.4**
Internal Porosity	**0.2**
Pore volume	**0.4871**

The adsorbents were first washed with distilled water and then dried in oven at 110^{o}c for one hour, to remove undesired moisture within particles.

2. Experimental work:

2.1. Equipment:

The fixed bed adsorber studies were carried out in Q.V.F. glass column of (1.2cm) I.D. and 30 cm in height. The activated carbon bed was confined in the column by fine screen with mesh size equal to (50) micron at the bottom and a glass ball packing (2 mm diameter) at the top of the bed to ensure a uniform distribution of influent through the carbon bed. The temperature of the liquid in the feed tank was kept at room temperature ≈ 15°C ± 1 which varied very little through the day. Dozing pump (MAGDOS LB4, JESCO, GERMANY) was used to measure the flow rate to the adsorber. Cylindrical calibration tube (burette) of volume (100) ml and stop watch was used to check the influence flow rate to the adsorber. The general arrangement of fixed bed adsorber is shown in Fig (1).

2.2. Experiments:

- Feed liquid hydrocarbon was prepared by adding (50) ppm of either thiophene or benzothiophene into liquid alkane (n-hexane (C_6)). The adsorber column is filled with the activated carbon with sieve opening size (1.5) mm for the desired bed height (6) cm under (2) cm of glass ball packing. The solution is passed to the adsorber column at room temperature (15°C ± 1) through the calibrated dozing pump (MAGDOS LB4, JESCO, GERMANY) at the flow rate (4 ml/min).
- The procedure above was repeated three times: First by varying the concentration of either thiophene or benzothiophene with (100, 90, and75) ppm and fix the bed height to (6) cm, and the flow rate to (4 ml/min) to Study the effect of the concentration. Second by varying the flow rate of the feed to the equipment with (13, and 20) ml/min and fixing the bed height to (6) cm, and the concentration of either **thiophene** or benzothiophene with (75) ppm as moderate value. Third by varying the bed height with (4, and 8) cm and fixing the flow rate to (4 ml/min) and the concentration of either thiophene or benzothiophene with (75) ppm to study the bed height.
- The samples are taken in certain periods of time (5 min), and the concentration of sulfur compounds in each sample is measured using 6800 UV/vis spectrophotometer Jenway. And the experimental curve is determined by plotting the concentration out (C_o) and the extraction percent (E %) of thiophene and benzo thiophene with time (t).

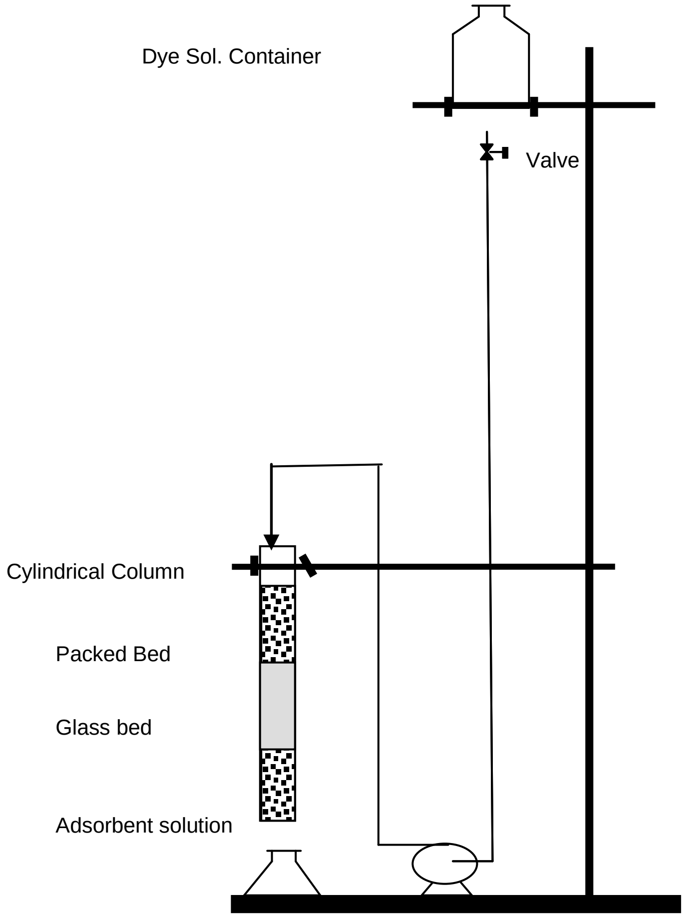


Figure (1): Schematic Representation of Experimental Apparatus

Results and Discussion

The variation of output concentration (C_0) and the extraction percent (%E) with time was studied using different parameters such as initial concentration of either thiophene or benzo thiophene compounds (C_i), bed height (L) , and the flow rate (Q).

1. Effect of Initial Concentration :

Figs.(2) ,and (3) show the effect of different initial concentration of either thiophene or benzo thiophene which was varied from 50 PPM to 100 PPM.it was found that any increasing in sulfur concentration leads to increasing in the outlet concentration with values of concentration in fig.(2) higher than what obtained in fig.(3),that's because the high initial concentration lead to increasing in the driving force of mass transfer rather than the low values. The output concentration was decreased with time because at the beginning of the process the activated carbon adsorbed the sulfur compounds strongly leads to drop in the output concentration after (15)min. of the beginning of the process especially with the using of thiophene as adsorbete, after (15)min. almost values of output concentration kept constant until it reached to (1)hr. of the process. also the (E%) of sulfur compound decreased with increasing the initial concentration and increased with time because it has an inversely proportional with the output concentration.

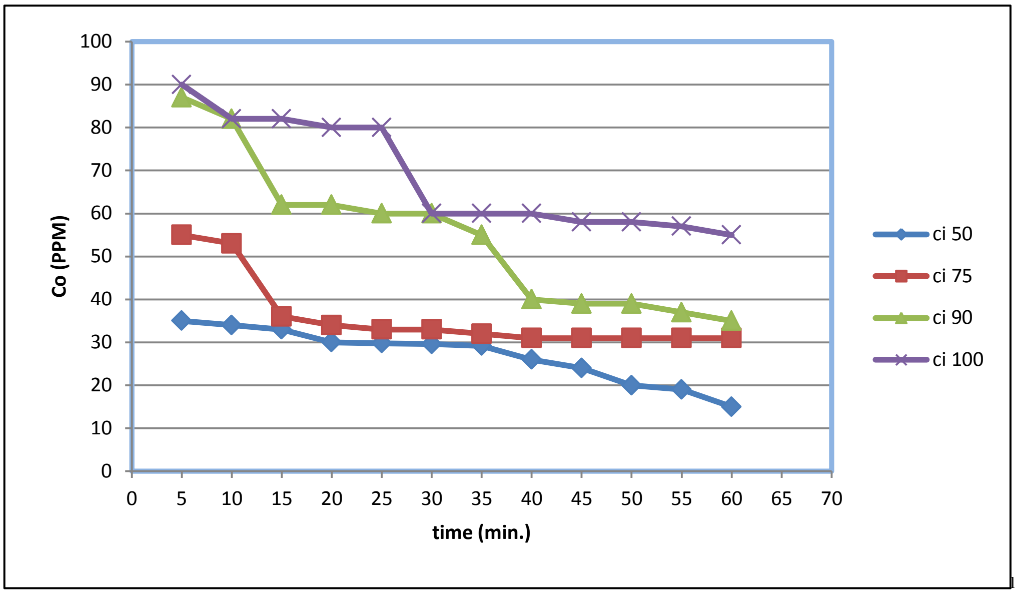


Figure (2): the experimental curves of thiophene at different initial concentrations (Ci), bed height (L) =6 cm, Flow rate (Q) =4 ml/ min.

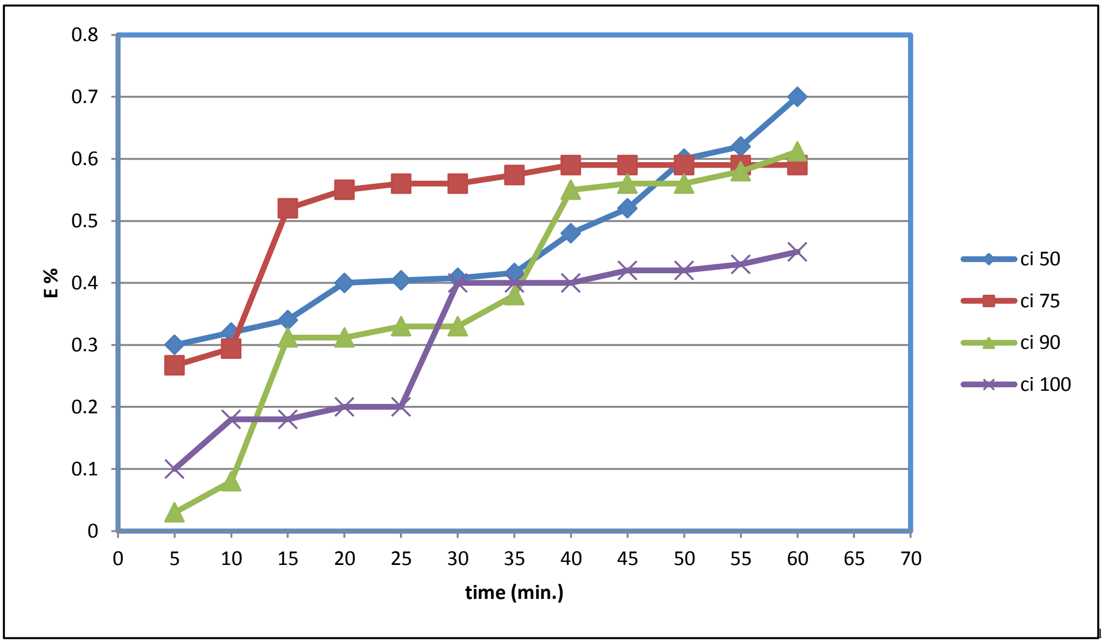


Figure (3): the extraction curves of thiophene at different initial concentrations (Ci), bed height (L) =6 cm, Flow rate (Q) =4 ml/ min.

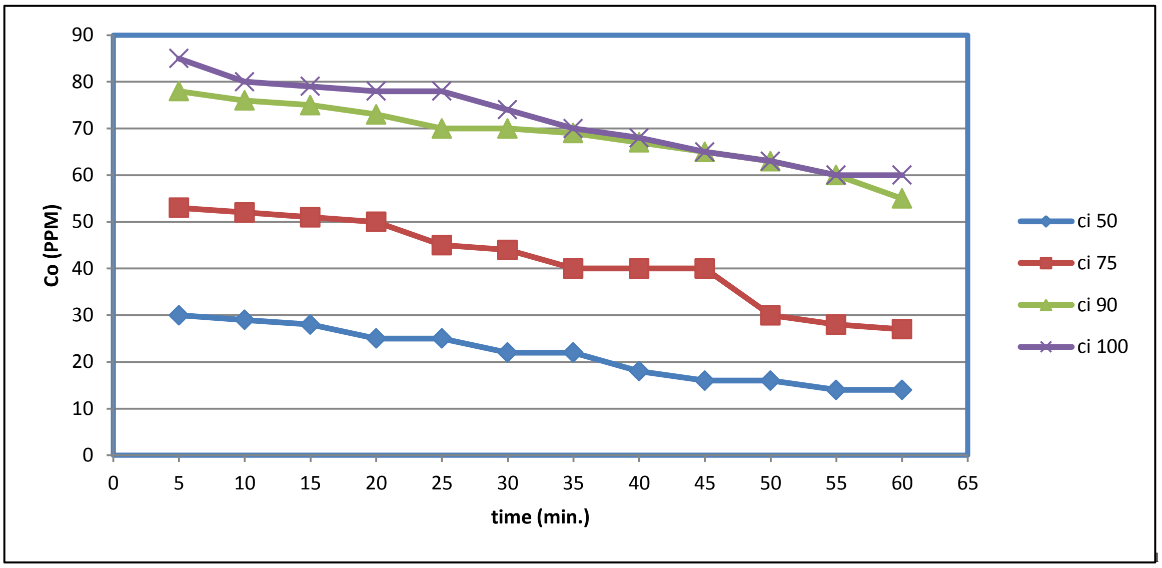
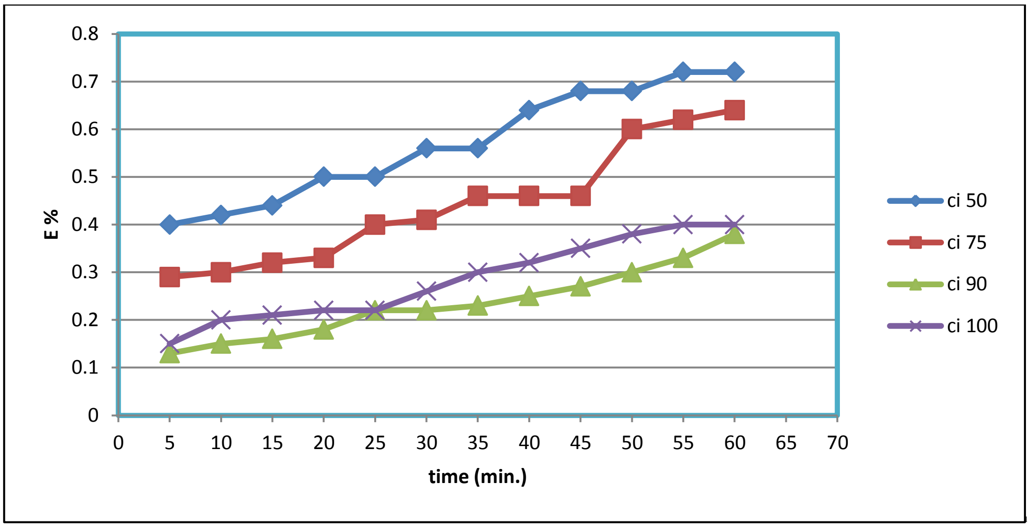


Figure (4): the experimental curves of benzo thiophene at different initial concentrations (Ci), bed height (L) =6 cm, Flow rate (Q) =4 ml/ min.



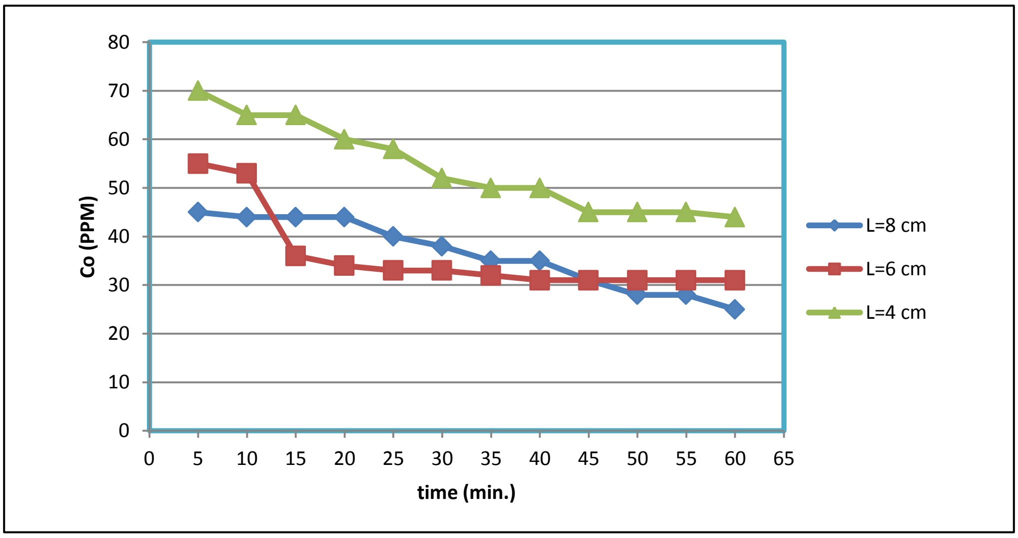


Figure (5): the extraction curves of benzo thiophene at different initial concentrations (Ci), bed height (L) =6 cm, Flow rate (Q) =4 ml/ min

2. Effect of Bed Height (L):

The bed depth is one of the major parameters in the design of fixed bed adsorption column. The effect of bed height on the experimental curves was studied for thiophene, and benzo thiophene respectively for adsorption onto activated carbon at constant flow rate, and constant concentration are presented in Figs. (4) and (5). It is clear from the figures that any increasing in bed height leads to decreasing at the output concentration of sulfur compounds increasing in (%E) for example the output concentration of thiophene in (4 cm) bed height is (65 ppm) while it reaches to (43 ppm) in the bed height (8 cm), the reason of this behavior is at smaller bed height the bed is saturated in less time produced higher values of sulfur compounds at the outlet of the bed, while at higher bed height interaction with the adsorbent leads to small values of sulfur compounds in the outlet.

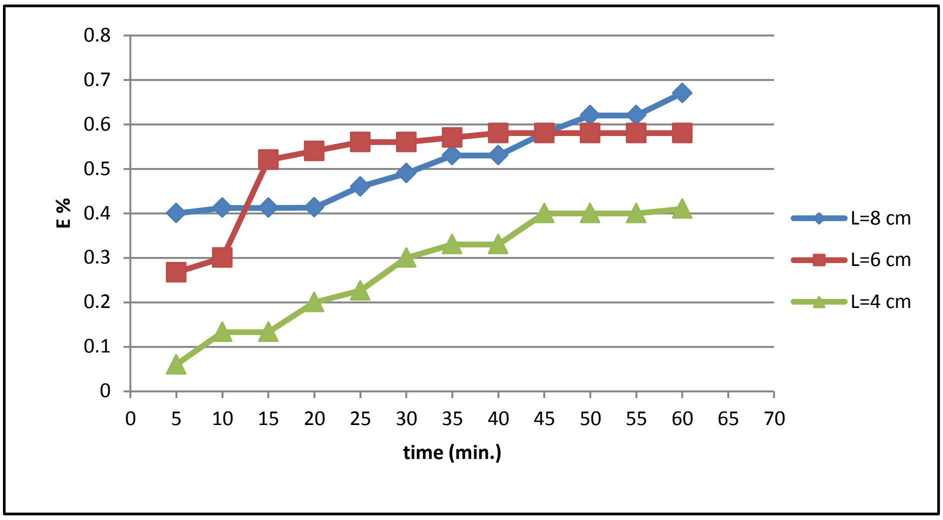


Figure (6): the extraction curves of thiophene at different bed height (L), initial concentration (Ci) =75 ppm, Flow rate (Q) =4 ml/ min

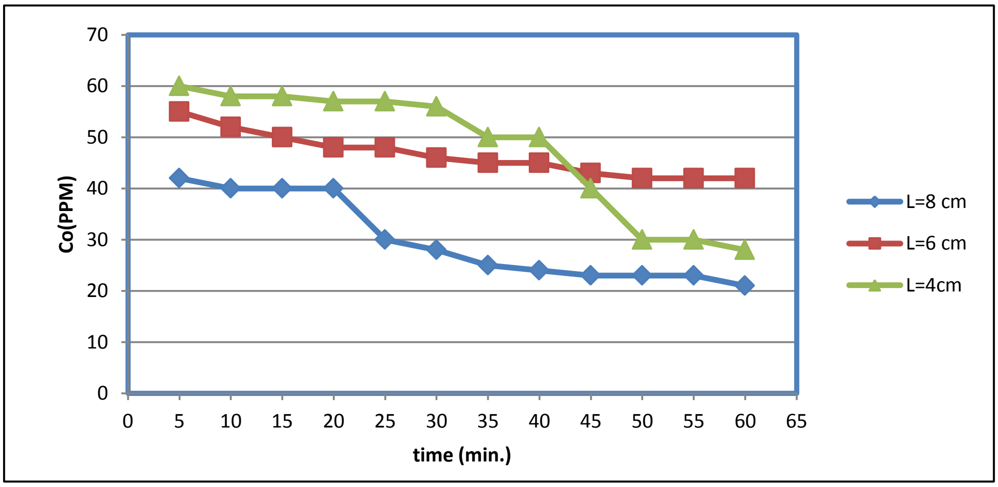


Figure (7): the experimental curves of benzo thiophene at different bed height (L), initial concentration (Ci) =75 ppm, Flow rate (Q) =4 ml/ min.

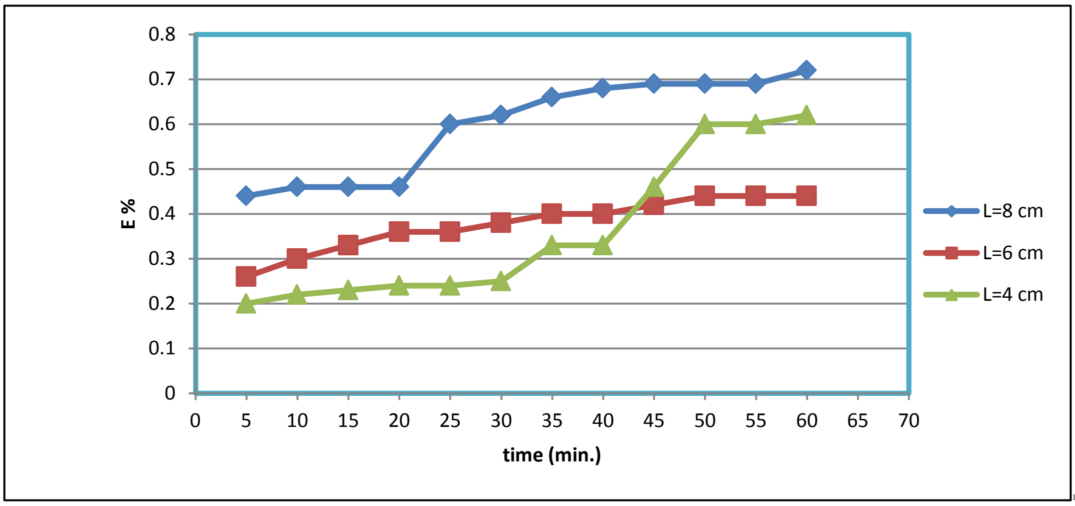


Figure (8): the extraction curves of benzo thiophene at different bed height (L), initial concentration (Ci) =75 ppm, Flow rate (Q) =4 ml/ min.

3. Effect of flow rate:

The contact time is an important variable in the design of a fixed bed adsorption column; therefore the flow rate is one of the major design parameter. The effect of varying flow rate on the experimental curve was studied for all the systems. Fig. (6) And (7) show the experimental curves for thiophene, and benzo thiophene respectively obtained for different flow rates and at constant bed height, and constant concentration in term of C_o versus time.

It is clear from the figures below that the output concentration of sulfur compounds decreased with time, but at each period of time there was a proportional relationship between the flow rates of the output concentration. This is because the residence time of solute in the bed decreased as the flow rate increased and there is no enough time to complete adsorption. It is expected that the change in flow rate will affect the film diffusion but not the internal diffusion, the higher flow rate lead to smaller film resistance to mass transfer.

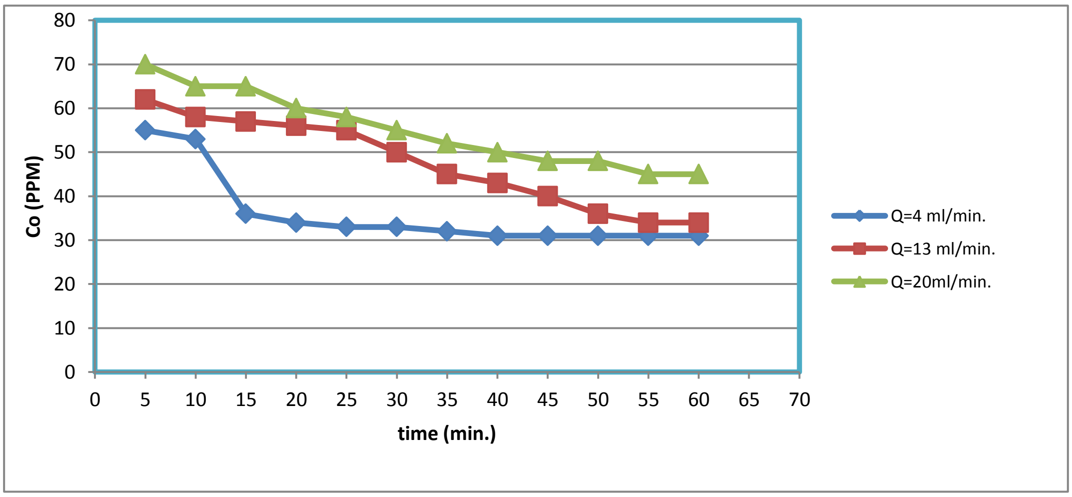


Figure (9): the experimental curves of thiophene at different flow rate (Q), initial concentration (Ci) =75 ppm, bed height = 6 cm

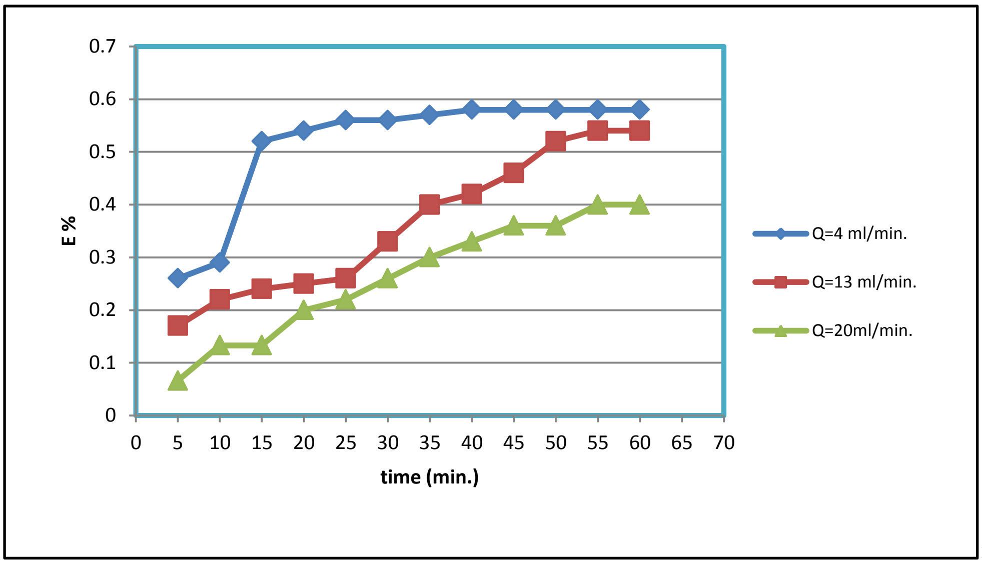


Figure (10): the extraction curves of thiophene at different flow rate (Q), initial concentration (Ci) =75 ppm, bed height = 6 cm

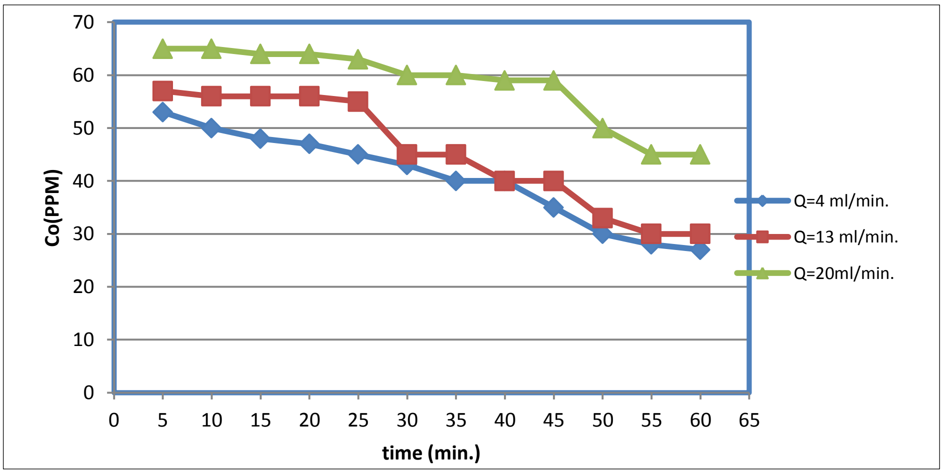


Figure (11): the experimental curves of benzo thiophene at different flow rate (Q), initial concentration (Ci) =75 ppm, bed height = 6 cm

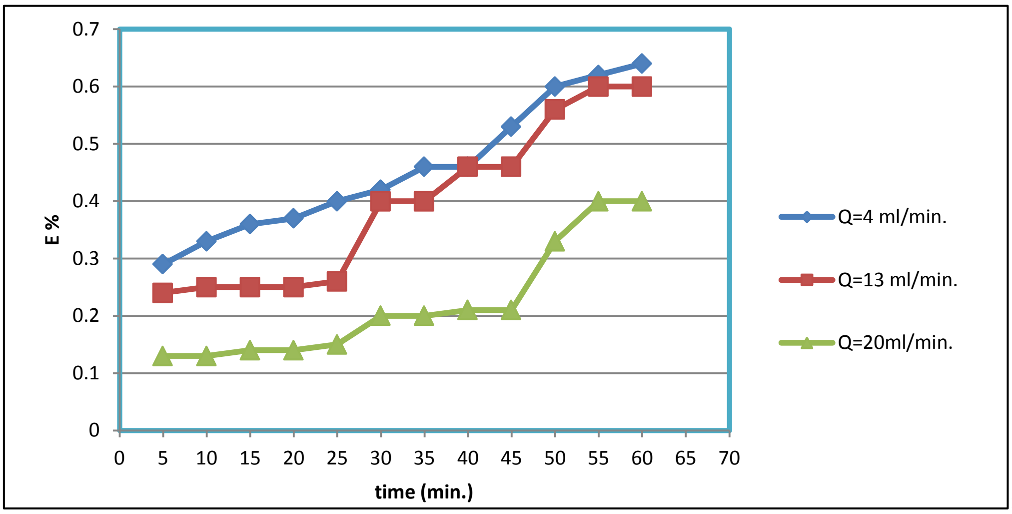


Figure (12): the extraction curves of benzo thiophene at different flow rate (Q), initial concentration (Ci) =75 ppm, bed height = 6 cm

Conclusions:

In the present work the adsorption of sulfur compounds named thiophene, or benzo thiophene onto activated carbon for single component system lead to the following conclusions:

1. The concentration of sulfur out (Co) decreases with:
   - A. The decrease in bed height.
   - B. The increase in flow rate.
   - C. The decrease in initial concentration of sulfur compounds.
2. The activated carbon has very high affinity for the sulfur compounds in the order

   Benzo thiophene > thiophene.

References…

1. Atsushi Ishihara*, Danhong Wang, Franck Dumeignil, 2004," Oxidative desulfurization and denitrogenation of a light gas oil using an oxidation/adsorption continuous flow process", Tokyo University of Agriculture and Technology, Japan.

2. Ryszard A. Wolny, 2010,"Desulfurization and Denitrogenation with Ionic Liquids and Metal Ion Systems" BRACEWELL & GIULIANI LLP, HOUSTON, TX US.

3. Yu, M.; Li, Z.; Xia, Q.; Xi, H.; Wang, H. desorption activation energy of dibenzothiophene on the activated carbons modified by different metal salt solutions. Chem.Eng. J. 2007, 132, 233, 239.

4. Campos-martin J.M., Capel-Sanchez M.C., Perez-Presas P. and Fierro J.L.G.(2010) Oxidative processes of desulfurization of liquid fuels ,j.chem.tech.Biotech.,85(7).

5. Jeon H.J.,Ko, C.H., Kim S.H.and Kim J.N.(2009) removal of refractory sulfur compounds in diesel using activated carbon with controlled porosity,energy fuels 23 (5).

6. Li J.R., Kuppler R.J. and Zhou H.C.(2009)Selective gas adsorption and separation in metal –organic frameworks,Chem.Soc.Rev.,38.

7. Yang R.T., Hernandez-Maldonado, A.J. and Yang F.H.,(2003)desulfurization of transportation fuels with zeolites under ambient conditions, science 301.

8. Kim, J.H.; Ma, X.; Zhou, A.; Song, C. Ultra-deep desulfurization and denitrogenation of diesel fuel by selective adsorption over three different adsorbents: A study on adsorptive selectivity and mechanism. Catal. Today 2006, 111, 74-83.

9. Xiaoliang Ma, Uday Turaga, Shingo Watanabe, Subramani Velu and Chunshan Song .Deep Desulfurization of Diesel Fuels by a Nival Integrated Approach.2004.

10. Richard A. Wolny, Desulfurization and denitrogenation with ionic liquids and metal ion systems, 2010BRACEWELL & GIULIANILLP, HOUSTON, TX US.

11. RUTHVEN, D.M. principles of adsorption and adsorption processes, 3th ed., New York: Wiley intercience, 1984.

12. Fallah, R.N.;Azizian, S.Removal of thiophenic compounds from liquid fuel by different modified activated carbon cloths.fuel process. Technol.2012.

13. Hu, Z.; Srinivasan, M.P.; Novel activation process for preparing highly microporous and mesoporous activated carbons.carbon 2001, 39.

14. Tanase Dobre, Oana Cristina Parvulescu, Gustav Iavorschi, 2010, "Experimental Study of Vocs Adsorption onto Fixed Bed Activated Carbon", University Politehnica of Bucharest, Faculty Applied Chemistry and Material Science.

أمتزاز مركبات الثايوفين من الهكسان بأستخدام الكربون المنشط

يسرى صابر كريم
قسم الهندسة الكيمياوية
جامعة النهرين- كلية الهندسة

الخلاصة ...

ان عملية استخلاص المركبات الكبريتية من وقود المكائن هي طريقة فعالة للحصول على وقود نقي ،يهدف هذا البحث الى دراسة عملية استخلاص نوعين من المركبات الكبريتية وهي الثايوفين والبنزو ثايوفين من السائل الهيدروكاربوني (هكسان) باستخدام تجارب عمود الحشوة الثابت والكاربون المنشط كمادة مازة من خلال دراسة تأثير كل من التركيز الابتدائي للمركبات الكبريتية (100,90,75,50) جزء من المليون،أارتفاع عمودالكاربون المنشط (8,6,4) سم و معدل جريان السائل (20,13,4) مل/دقيقة.
وجد من خلال التجارب العملية ان للكاربون المنشط الفة للمركبات الكبريتية وبمستوى بنزو ثايوفين > ثايوفين وان التركيز النهائي للكبريت المستخلص يقل بزيادة التركيز الابتدائي للمركبات الكبريتية ,ارتفاع عمود الحشوة , معدل جريان السائل.أن أعلى نسبة مئوية لأستخلاص مركبات الثايوفين وصلت الى 70% بأستخدام تركيز أبتدائي 50 جزء من المليون، أرتفاع عمود الكربون المنشط 6 سم و معدل جريان السائل 4 مل / دقيقة، بينما أعلى نسبة مئوية لأستخلاص مركبات البنزو الثايوفين وصلت الى 73% بأستخدام تركيز أبتدائي 75 جزء من المليون، أرتفاع عمود الكربون المنشط 4 سم و معدل جريان السائل 4 مل / دقيقة .