Deep Desulfurization of Diesel Fuel by Guard Bed Adsorption of Activated Carbon and Locally Prepared Cu-Y Zeolite

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ABSTRACT

Desulfurization of a simulated diesel fuel by different adsorbents was studied in a fixed-bed adsorption process operated at ambient temperature and pressure. Three different adsorption beds were used, commercial activated carbon, Cu-Y zeolite, and layered bed of 15wt% activated carbon followed by Cu-Y zeolite.Initially Y-zeolite was prepared from Iraqi rice husk and then impregnated with copper.

In general, the adsorbents tested for total sulfur adsorption capacity at break through followed the order Ac/Cu-Y zeolite>Cu-Y zeolite>Ac. The best adsorbent, Ac/Cu-Y zeolite is capable of producing more than 30 cm^3 of simulated diesel fuel per gram of adsorbent with a weighted average content of 5 ppm-S, while Cu-Y zeolite producing of about 20 cm^3 of diesel fuel per gram of adsorbent with a weighted average content of 2ppm-S. Activated carbon breaks through almost immediately.

Key words: Desulfurization of diesel fuel, desulfurization by adsorption, guard bed adsorption, Y- zeolite from rice husk

ازالة كبيرة للمركبات الكبريتيه من وقود الديزل باستخدام عمود امتزاز مكون من كاربون منشط و Cu-Y zeolite محضر محليا

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الخلاصة

تمت دراسة ازاله المركبات الكبريتية من وقود الديزل باستخدام العمود الثابت لعمليه الامتزاز تحت ظروف اعتياديه من درجه حراره وضغط. تمت العمليه باستخدام ثلاثه انواع من الاعمدة المحشوة بالمواد الممتزة وهي الكاربون المنشط (Ac) والنحاس المحمل على الزيولات Cu-Y zeolite وعمود مزدوج من 15% وزنا كاربون منشط والنحاس المحمل على الزيولايت تم تحضير الزيولايت Y من قشور الرز العراقي. اظهرت الدراسه ان سعة الامتزاز للمواد الممتزة كانت على الترتيب Ac/Cu-Y zeolite>Cu-Y zeolite>Ac حيث استطاع العمود الافضل Ac/Cu-Y zeolite , من انتاج اكثر من 30 سم مكعب من وقود الديزل الخالي من المركبات الكبريتيه لكل غرام من المادة الممتزة وبمعدل وزني للمركبات الكبريتية بحدود 5 ملغم/لتر. بينما كان انتاج المادة الممتزة Cu-Y zeolite من وقود الديزل الخالي من المركبات الكبريتية

بحدود 20 سم مكعب لكل غرام من المادة الممتزة وبمعدل وزني للمركبات الكبريتية بحدود 2 ملغم/لتر.بينما لم يتمكن العمود المحشو بالكاربون المنشط من انتاج وقود الديزل خالي من المركبات الكبريتية

INTRODUCTION

Ultra deep removal of sulfur from transportation fuels has become more and more important in research and development worldwide, not only because of the heightened interest for cleaner air and environmental protection but also due to the great need for making ultralow-sulfur fuels for use in fuel cells. Fuel cells are attractive for electric power generation because significantly higher efficiencies can be achieved in a more environmentally friendly way than in combustion engines for the automotive fuel cells and the portable fuel cells, liquid hydrocarbon fuels are candidate fuels due to their higher energy density and safety for transportation and storage **,Song, 2003, Babich, 2003**. This is why governments all over the world are implementing more stringent regulations and fuel specifications. The EU legislation set the upper limit of sulfur content in diesel fuel as well as gasoline fuels for 2009 to 10 mg/kg. The US Environmental Protection Agency (EPA) since 2006 reduced the limit for sulfur content of diesel to 15 mg/kg and gasoline fuel to 30 mg/kg **Jiang, et.al, 2006,**and **Ma. X., et.al, Sun2002**.

Industrially, the elimination of sulfur is carried out through the process called hydro desulfurization (HDS). This process uses Ni-MolAl_2O_3 and Co-Mo/Al_2O_3 catalysts. The disadvantages of this process are (i) the catalytic processes operated at elevated temperatures (320-380)^{o}C and elevated pressures 3-7 Mpa and (ii) HDS process is highly efficient for the removal of sulfur compounds such as thiols, sulfides and thiophenes, but less effective for removing refractory sulfur compounds: benzothiophene (BT), Dibenzothiophene (DBT), and their alkyl derivatives . These molecules are common in diesel fuels. The methyl groups in these species create a steric effect that hinders the capacity of HDS catalyst to chemisorb the sulfur atoms,**Baeza, et.al 2008**.

Adsorption is a viable option for motor fuel desulfurization and the idea behind this approach is to selectively separate less than 1wt% of fuel mass using selective adsorption for removing sulfur and leave the 99wt% of non-sulfur containing fuel mass untouched, besides to adsorption can be accomplished at low temperature and pressure (ambient conditions) **Ma, X., et.al, 2002,**and **Jiang, et.al, 2005.** Recently, many attempts have been made to develop adsorbents for desulfurization of liquid hydrocarbon fuels **C.S.Song, 2003,M.Breysse,et.al,2003, C.Song, et.al, 2003, and P.T.Vasudevan, et.al, 1996**.The reported adsorbents include the reduced metals**G.W.Bailey, et.al, 1987, L.J.Bonvillr, et.al,2000, R.R.Lesieur, et.al, 2002, X.Ma, et.al, 2002, T.Fukunaga, et.al, 2003, X.Ma, et.al,2005, and X.Ma,M. et.al, 2005**, metal oxides **B.S.Turk, et.al.2001,S.Watanabe,et.al. 2004]**, metal sulfides **[X.Ma.et.al., 2003]**, zeolite-based materials **[R.T.Yang , et.al., 2003, A.J.Hernandez-M, et.al., 2003, S.Velu, et.al., 2003, and A.J.Hernandez, 2004** and carbon materials, **S.Haji, et.al., 2003,Y.Sano, et.al.,2004 and ,A,Zhou, et.al. 2004]**.

Activated carbons and zeolites have been widely used as adsorbents in the separation and purification processes for gaseous or aqueous solution systems. Activated carbons have high adsorption capacity towards some organic and inorganic compounds due to large specific surface area, high adsorbate-adsorbent physical and chemical attraction and balanced macro-, meso- and micro-porosity while at the same time the steric hindrance of particle diffusion is minimized with regard to the size of the molecules being adsorbed. Zeolite can be successfully used for the selective adsorption of polar or polarization molecules such as water and CO_2 and sulfur-containing molecules from some petroleum fractions. These adsorbents are hydrophilic and contain large void fraction. Synthetic zeolites have a well-defined crystalline lattice of metal alumina silicates which contains uniform pore size **Bagreev, et.al. 2004, and Johns, et.al. 1999]**.

There are several published reports investigating the use of activated carbons and zeolite for sulfur removal from hydrocarbon liquids **, Bakr, et.al. 1997, Lee, et.al. 2002, Sano, et.al, 2005, and Kim, et.al. 2006**.

In this study the ability of preparing Cu(I)-Y-zeolite by using Iraqi rice husk as agricultural residues to prepare Na-Y—zeolite adsorbents then activated it by copper using ion-exchange process and finally reduce Cu^{+2} species to Cu^{+} which is desired for π -complexation.

Also, adsorptive desulfurization of a model diesel fuel, which contained the same molar concentration of the species examined, including sulfur compounds, over three beds, commercial AC, Cu (I)-Y-zeolite prepared from rice husk and AC/Cu (I)-Y-zeolite as a guard bed were conducted in a fixed bed system to evaluate the performance of the prepared adsorbent.

1. MATERIALS AND METHODS

1.1 Preparation of Rice Husk Ash

Rice Husk (RH) is a forming waste, obtained from the rice mills, it needs some treatments to convert it to rice husk ash. It was treated with 10% sulfuric acid for 24 h for preliminary removing all impurities. Then washed, filtered, dried in air, and calcined at 750°C for 6 h. The calcined rice husk subjected for dissolution with 4M sodium hydroxide followed by refluxing at 90°C for 12 h. Concentrated hydrochloric acid was then added to the a forementioned base dissolved for complete precipitation, then filtered, washed and dried in an oven at 120°C for 6 h. The chemical composition of rice husk ash is showed in **Table 1**.

2.2 Synthesis of Y-zeolite

Type Y-zeolite was synthesized using Iraq rice husk as a silica source. A 500 ml Teflon beaker containing a magnetic stirrer was washed with deionized water. Sodium hydroxide of 1.6616 g was added slowly to deionized water and stir until clear and homogenous solution appeared for about 5 minutes. The aqueous solution of sodium hydroxide was ready for the preparation of seed. The gel was prepared according to the following molar chemical composition:

$$10.67Na_2O:1\ Al_2O_3:10SiO_2:180H_2O$$

2-milliliter aqueous solution of sodium hydroxide was added to 0.7515g sodium aluminate oxide until a homogenous mixture was formed; Iraq rice husk 1.5361g was added separately to 5.5ml sodium hydroxide aqueous until homogenously mixed. Both of preparations were heated under vigorous stirring to obtain a homogenous mixture. The sample was aged for 24 h at room temperature in the Teflon bottle. The aluminate and silicate solutions were mixed together in the polypropylene beaker, subsequently stirred for 2 h with the purpose of making it completely homogenized. This combined solution was used as the feed stock gel **M.M.Rahman, et.al.,**

2009, Mohammed.N, and Wadood, T.M. 2011.,The flow chart of the process is shown in **Fig. 1.**

2.3 Adsorbent Preparation

Cu(I)-Y zeolite (i.e. reduced Cu(II)-Y zeolite) was prepared by first ion exchanging Na-Y zeolite with a $Cu(NO_3)_2$ aqueous solution of 0.5 M for 48 hours followed by reduction of Cu^{+2} to Cu^{+}. The amount of copper (Cu) in the ion exchange solution was equivalent to a 10-fold cation exchange capacity. The adsorbent was recovered by filtration and washed with large amount of deionized water, followed by drying at 100°C for about 24 h. Activation of the adsorbent was performed at 450°C to promote auto reduction of Cu^{+2} to Cu^{+} , which is desired for π -complexation. A more detailed discussion on the Cu (I)-Y zeolite autoreduction process can be found elsewhere **,Johns, 1999, M., .Rahman, 2009, Iwamoto, et.al. 1991,Parrillo, et.al., 1993,Larsen, et.al., 1994,Takahashi, et.al., 2001, Takahashi, et.al., 2002, and Hernandez, et.al., 2003**.

2.4 Commercial Activated Carbon (AC)

Table 2 shows the physical properties of the commerical activated carbon .

2.5 Simulated Diesel Fuel

The detailed composition of the model fuel is listed in **Table 3**. The diesel was type “simulate Diesel - 40” according to British Petroleum BP`s specifactions. The average total sulfur concentration for the diesel was reported to be Benzothiophene (BT) and Dibenzothiophene (DBT) standards were purchased from sigma-Aldrich.

2.6 Fixed-Bed Adsorption/ Breakthrough

All adsorption/breakthrough experiments were perfermed in vertical column made quartz adsorbers equipped with a supporting glass fits. The setup consisted of a low-flow liquid pump, two pyrex feed tanks, and a heating element. Initially, the adsorbents were loaded inside the adsorber, and heated in situ at desired temperature. Both Cu-Yzeolite and activated carbon adsorbents were activated at about 300°C. After activation treatment, both the adsorbents under study were allowed to cool down to room temperture. Next, a sulfur-free hydrocarbone was allowed to flow through the sorbent. After wetting the adsorbent for about 10 min, the feed was switched to the simulated one to flow. Effluent samples were collected at regular intervals until saturation was achieved, which depended on the adsorption dynamics and the amount of adsorbent.

2.7 Total Sulfur Analysis

The total sulfur concentration in the simulated diesel fuel and desulfurized diesel fuel were detrmined using an Antek 9000s total sulfur analyzer. The instrument was calibrated to at least four different sulfur concentation rangs using standard samples, and linear calibration curves were obtained for each calibration range. The sulfur detection limit of the total sulfur analyzer in the normal working range is 0.5 ppmw sulfur.

3.RESULTS AND DISCUSSION

3.1 Adsorbent Characterization

The concentrations of Na and Al were determined based on comparison with two replicates of the standard reference material NIST1633A; the determination of Cu content was determined relative to high-purity copper wire. As seen in the **Table 4** below, ion-exchanging Na-Y with Cu^{++} resulted in incomplete ion exchange. If it is assumed that one Cu^{++} cation compensates for two aluminium tetrahedra, then, for our experiment the ion exchange resulted in only 78% substitution of the original sodium ions, the others were compensating for aluminum tetrahedra. This is the simplest way to describe these zeolites.

3.2 Adsorption Equilibrium Analysis

Equilibrium adsorption data collected in this work is presented in **Fig. 2** , where it can be seen that saturation loading of the three tested adsorbents AC, Cu-Yzeolite, and AC-Cu Y zeolite were (0.28, 0.35, 0.39) mg/g respectively. These result are inline with generally accepted notions that adsorption process on activated carbon is in most cases of physical nature, when chemical bond is not formed. However adsorption on zeolite is supposed to be mainly chemisorption. Higher adsorption capacities that were obtained indicate the ability to form mild chemical bonds with organic sulfur compounds.

The idea of using a guard bed is to extend the capacity of Cu-Y zeolite for smaller S-compound because activated carbon adsorbs both aromatic and thiophenic compounds by vander waals and electrostatic interactions. Thus larger molecules were preferentially adsorbed by carbon, with no selectivity for thiophenic molecules **Takahashi, et.al., 2002,and Hernandez, et.al., 2003**.

3.3 Fixed-Bed Adsorption.

3.3.1 Adsorption on activated carbon bed

Fig.3 illustrated that total sulfur content during experiments with activated carbon breaks through almost immediately. This is expected with AC because activated carbon adsorbs both thiophenic and aromatic compounds by vander waals and electrostatic interaction with no selectivity for thiophenic molecules. Thus larger molecules with higher polarizabilities were preferentially adsorbed by activated carbon. These result are in agreement with the others **,Takahashi, et.al., 2002, and Hernandez, et.al., 2003b**.

3.3.2 Adsorption on Cu Y-zeolite bed

As seen in **Fig.4**, Cu-Y zeolite alone is capable of processing 20 Cm^3 of simulated diesel fuel per grams of adsorbent to be sulfur free. Among the many thiophenic compounds present in diesel fuel, only two were selected for the experiments:benzothiophene(BT) and dibenzothiophene (DBT). The last one molecules are the most difficult to remove in desulfrization treatment processes for transportation fuels. The order of breakthrough followed that of molecular weights **, Arturo, 2004**. For Cu-Y zeolite, the long delay of the breakyhrough of these thiophenic compounds was a direct result of π –complication and followed that of molecular weights. It also indicated some degree of diffusion limitation in zeolite.

3.3.3 Adsorption on guard Bed of Cu-Yzeolite and AC

The idea of using a guard bed of AC/Cu-Yzeolite is that to presorb not only aromatics, but also the largest sulfur-containing compounds, thus extending the capacity of Cu Yzeolite for smaller sulfur compounds.

Two guarded bed was used(i.e 5and 15 wt% of AC of the total bed weight). The results shown in **Fig. 5** indicated that the combination of activated carbon and Cu-Y zeolite as layers had high selectivities for these large molecules, and, hence, prevented them from entering the Cu-Yzeolite bed. Without these layers of AC/Cu-Yzeolite, these largest molecules would have entered the mainbed of Cu-Yzeolite and subsequently occupied the adsorption site as well as partially blocking the pores of the zeolite. Thus ,the quard bed not only delayed the breakthrough of the sulfur compounds, but also sharpend their wavefronts by eliminating pore blockge.

As seen in **Fig. 5,** the combination of activate carbone (AC) and Cu-Yzeolite is by for the best adsorbent to produce sulfur free diesel fuel that content of equal or less than 1 ppm. The guard bed is capable of processing more than 30 cm^3 of simulated diesel fuel per gram of adsorbent.

Comparison between the two guard beds results (i.e 5 and 15 wt% of activated carbon) showed that there are a number of larger molecules than others. The best bed depends on the exited a significant number of larger aromatic, nonthiophenic compounds. In fact , the commerical diesel typically contains over 150 different compounds. For the present study, 15wt% of AC gives the best results for the simulated diesel fuel metioned previously.

4. CONCLUSION

Results have demonstrated that Y-zeolite prepared from Iraqi rice husk and impregnated with copper gives good results for the removal of sulfur compounds from simulated diesel fuel, based on dynamic fixed-bed adsorption experiment.

When Cu Y-zeolite adsorbent used with activated carbon as a quard bed, Cu-Y zeolite provides by for the best adsorption capacities both at breakthrough point and at saturation.

In general, the adsorbents tested followed the following order for sulfur removal:

AC/Cu-Y zeolite > Cu-Y zeolite > AC.

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NOMENCLATURE

C = sulfur conc. in effluent

Ce = sulfur conc. At equilbrium

C_o = initial conc. of sulfur in feed

q = a mount of ions per gram of adsorbtion

ABBRAVIATION

AC = Activated Carbon

BT = Benzothiophene

BP = British Petroleum

DBT = Dibenzothiophene

EU = European

HDS = Hydrodesulfurization

RH = Rice Husk

US: United State

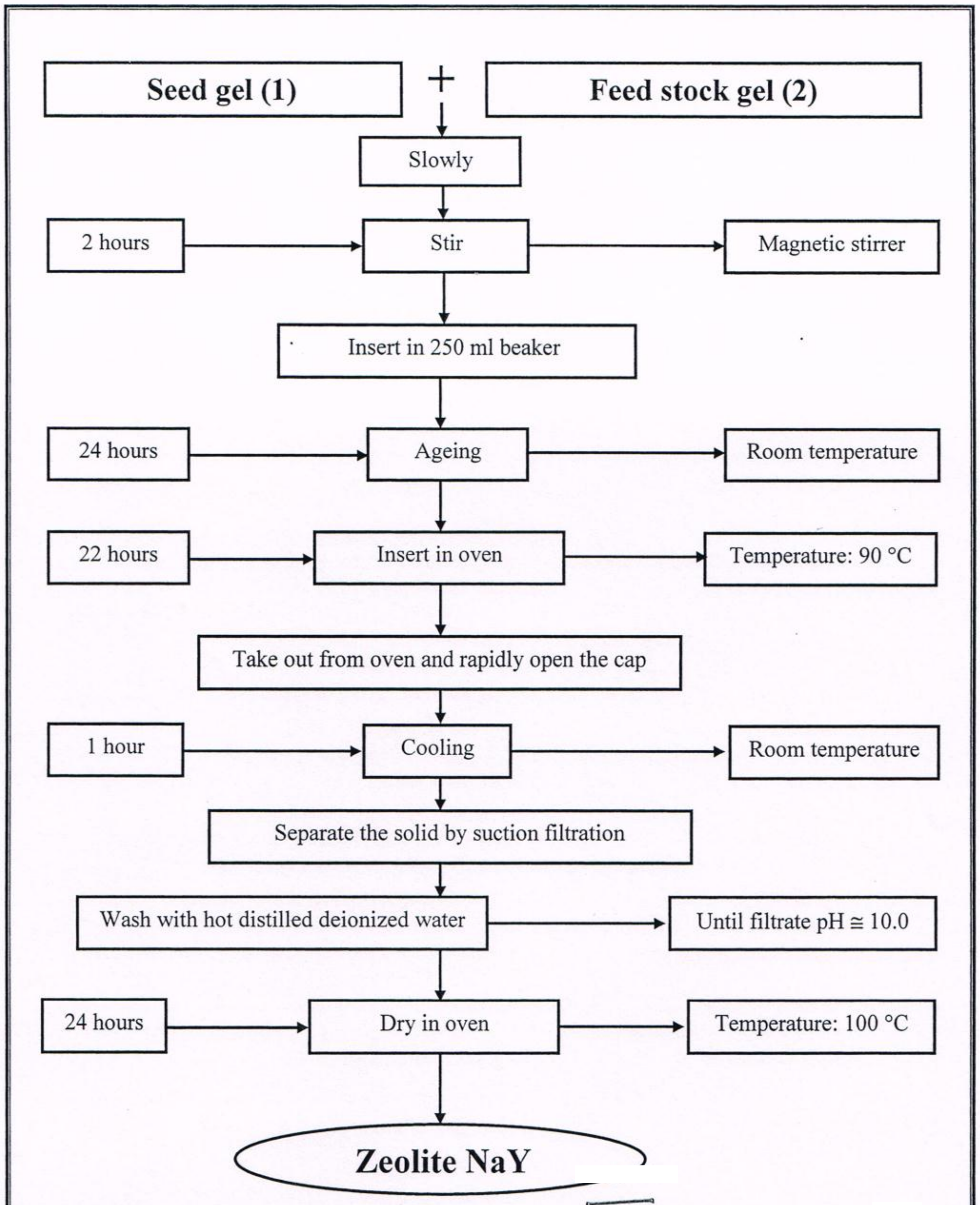

Figure 1. Flow chart of the synthesis of type Y-Zeolite catalyst using Iraqi

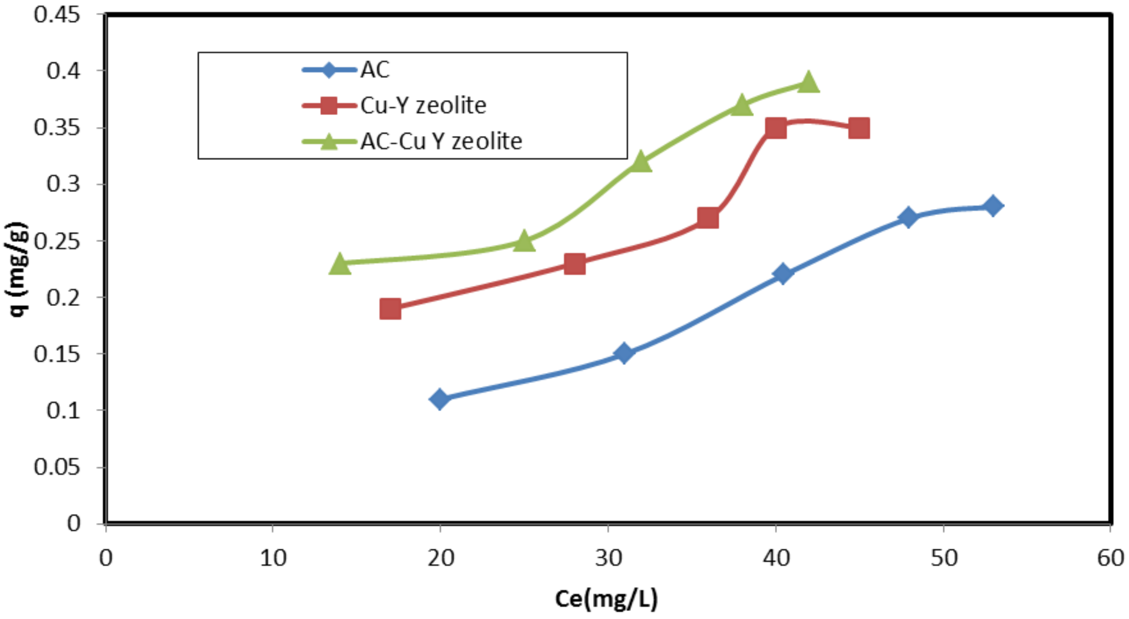

Figure 2. Adsorption Equilibrium Analysis.

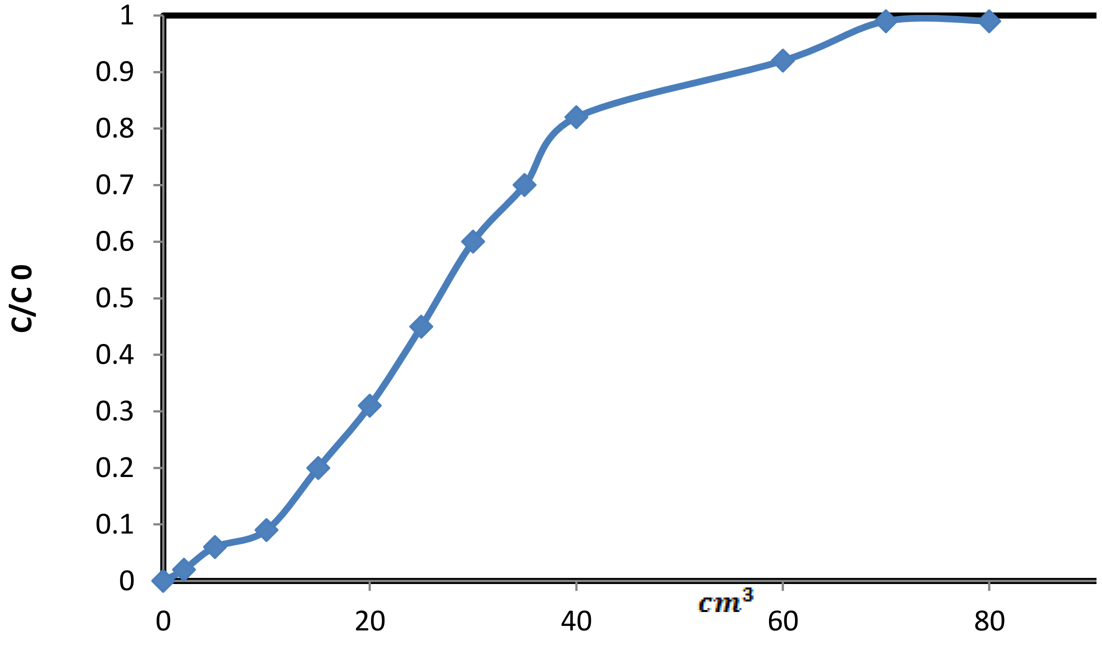

Figure 3. Breakthrough curve of sulfur compounds in a fixed bed adsorber of actived carbon adsorbent.

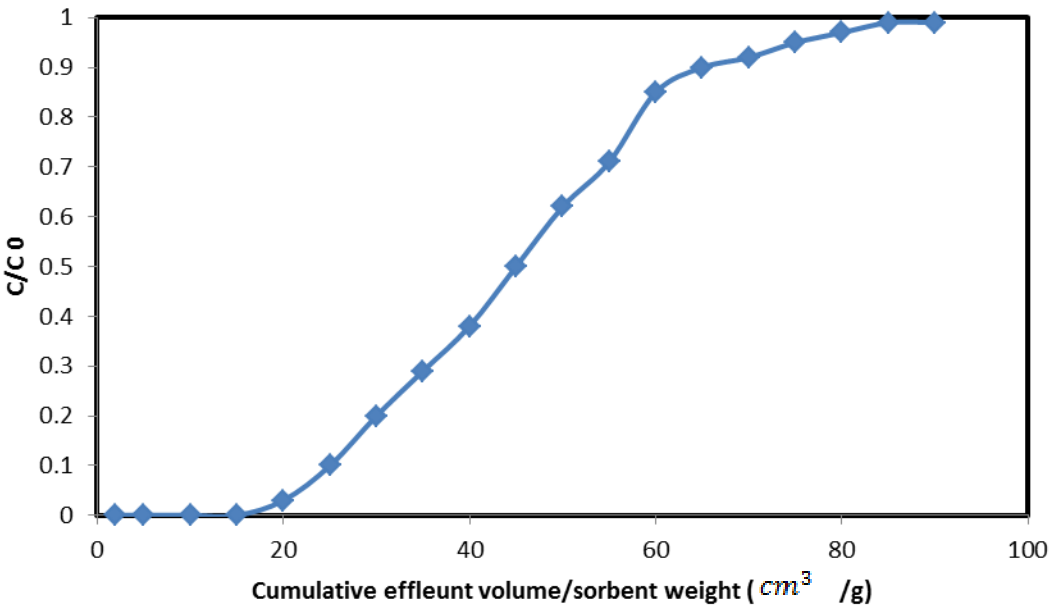

Figure 4. Breakthrough curve of sulfur compounds in a fixed bed adsorber of CuY-zeolit adsorbent.

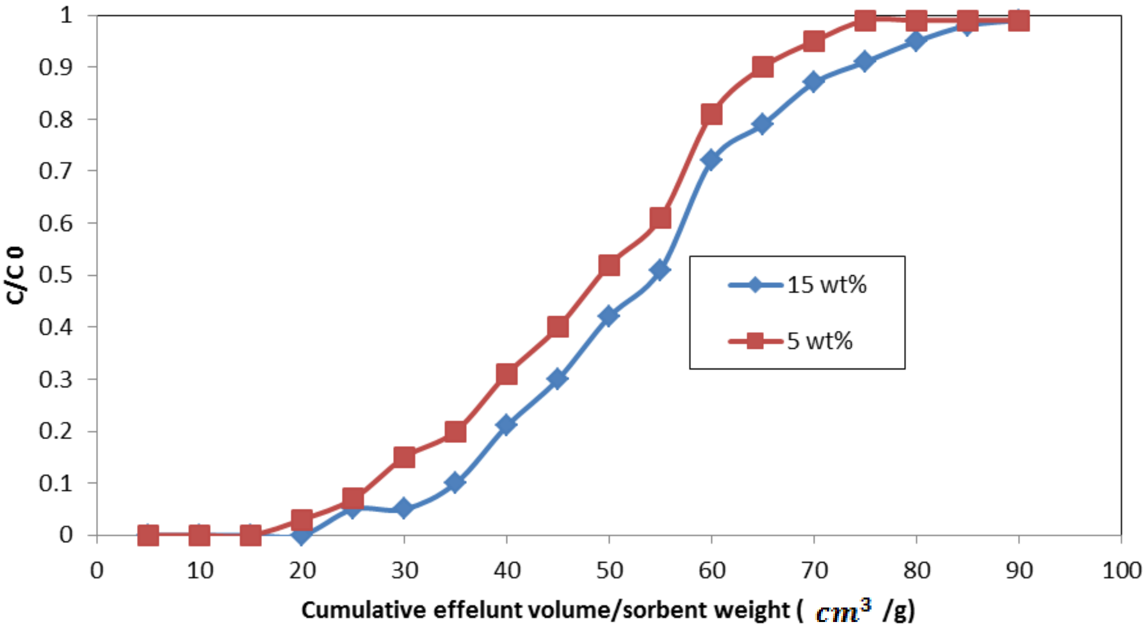

Figure 5. Breakthrough curve of sulfur compounds in a fixed bed adsorber of AC/CuY-zeolit adsorbent.

Table 1. The chemical composition of rice husk ash.

	Wt.%
SiO_2	94.5
Al_2O_3	2.23
Fe_2O_3	0.16
TiO_2	0.115
CaO	0.51
MgO	0.25
Na_2O	0.49
K_2O	0.63
P_2O_5	0.32
LOI	0.73

Table 2. physical properties of AC.

Particle size (mm)	0.006-0.080
Bulk density (g/cm^3)	0.35
Surface area (m^2/g)	1100

Table 3. Composition of the simulated diesel fuels (diesel 40).

compounds	composition
n-Dodecane	80wt%
Toluene	20wt%
Benzothiophene (BT)	150ppm
Dibenzothiophene (DBT)	148ppm

Table 4. Composition Data for Na-Y zeolite and Cu^{+2}-Y zeolite.

Adsorbent	Molar ratios		
	Si/Al	Na/Al	2Cu/Al
Na-Y	2.65	0.92	----
Cu^{+2}-Y	2.65	0.22	0.78