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Adsorptive Desulfurization of Commercial Diesel oil Using Granular Activated Charcoal

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Abstract---The adsorption of sulfur compounds form commercial diesel oil on a granular activated charcoal (GAC) was investigated. The equilibrium of sulfur adsorption on GAC was examined. The adsorption isotherms were determined and correlated with two well-known isotherm equations: Langmuir and Freundlich. The surface chemistry and structure of the sorbent material was studied using nitrogen sorption isotherm and scanning electron microscopy (SEM) integrated with energy dispersive spectroscopy (EDS). The sulfur and other metal contents in diesel oil were evaluated using X-ray fluorescence analyzer. Results showed that the sulfur content was reduced by 20.9 % compared to the original sample. The metal content of the sorbent materials, before and after desulfurization process, was determined using microwave acid digestion system followed by inductively coupled plasma (ICP) technique.

Keywords---granular activated charcoal, adsorption, isotherm equations, desulfurization, diesel fuel

I. Introduction

THE production of diesel oil with low sulfur content in the petroleum refineries is highly driven by the environmental legislations and air quality standards to minimize the environmental hazards and health problems associated with the direct emissions from the diesel powered vehicles. Such emission might contain particulate matter (PM) and toxic gases such as NOx, SOx, and CO. This has forced the petroleum refining industry to produce clean petroleum products by removing the impurities from their major products, diesel and gasoline [1-2]. Selective adsorption of sulfur compounds from diesel oil is an economically acceptable method for the attainment of diesel oil with low sulfur content [3]. Adsorptive desulfurization processes are considered among the most economically attractive techniques due to their simple operating conditions and the availability of inexpensive and re-generable adsorbents such as reduced metals, metal oxides, alumina, metal sulfides, zeolites, silica, and activated carbon [4-5].

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Several studies explored the adsorption of different sulfur compounds, such as benzothiophene (BT), dibenzothiophene (DBT), and their alkyl derivatives, from both model and commercial diesel fuels using different types of adsorbents. In one study [6], granular activated carbon (GAC), produced from dates' stones through chemical activation using $ZnCl_2$ as an activator, was used as a sorbent for sulfur compounds. The activated carbon particle size used in that study was 1.71 mm. Moreover, model diesel oil of n-$C_{10}H_{34}$ and dibenzothiophene (DBT) was used. The results of the study showed that approximately 86% of the DBT was adsorbed during the first three hours. Sulfur adsorption increased gradually to reach equilibrium at around 92.6% in 48 hours and no more sulfur is removed afterward.

In this study, the adsorption efficiency of GAC for sulfur compounds from diesel oil was investigated. The adsorption conditions were examined. The surface of the sorbent material was evaluated before and after the adsorption process using a variety of techniques.

II. Experimental work

A. Material

GAC was supplied from a local chemical company in Sharjah / UAE. The BET surface area was determined using sorption of nitrogen and was found to be 218.387 m^2/g. The GAC sample was dried at 110 ^oC in an oven for 16 h. The diesel oil used was supplied from local Adnoc petrol station in Sharjah/UAE. The initial sulfur content was determined using Energy Dispersive X-ray Fluorescence Spectrophotometer and was found to be 398.3 ppm.

B. Adsorption study

The adsorption desulfurization of diesel oil was conducted in batch series. In each case, variable amounts of GAC were added to diesel oil and ranged between 0 to 10 % by weight. All the experiments were conducted at room temperature. The samples were mixed using a flask shaker oscillating at 300 oscillations/min for 1 h. The resulting mixtures were filtered using vacuum filtration process. The initial and final concentrations of sulfur in diesel oil were measured using Energy Dispersive X-ray Fluorescence Spectrophotometer.

III. Results and Discussions

A. Equilibrium Adsorption

The percentage of sulfur removal SR% and the amount of sulfur adsorbed by GAC at equilibrium, qe (mg/g), were calculated from the following equations:

$$SR\,\% = \frac{(C_o - C_{eq})}{C_o} * 100$$

$$q_e = V * \frac{(C_o - C_{eq})}{m_s} * 100$$

Where, q_e is the amount of sulfur compounds adsorbed per unit weight of the adsorbent, V is the volume of the liquid phase, C_o and C_{eq} (mg/L) are the initial and the final concentrations of sulfur in diesel oil, respectively, and m_s is the weight of adsorbent.

B. *Adsorption effectiveness of GAC*

The amount of commercial GAC was varied between 0-10 wt. %. The sulfur content was plotted vs. amount of GAC as shown in Figure 1. The curve showed continuous decrease of sulfur content.

When 10 wt% of GAC was mixed with diesel oil at room temperature, the sulfur content in diesel oil was reduced by 20.91%. Moreover, the sulfur breakthrough curve (Figure. 2) showed that the sulfur removal was 8.109 % by adding 3 %wt. GAC and this removal percentage was increased to about 12.38 % by adding 5 %wt. and further increase to 20.94 % by increasing the GAC to 10%wt. This would lead to very important improvement in the physical properties and in the amounts of the emitted gases into the atmosphere.

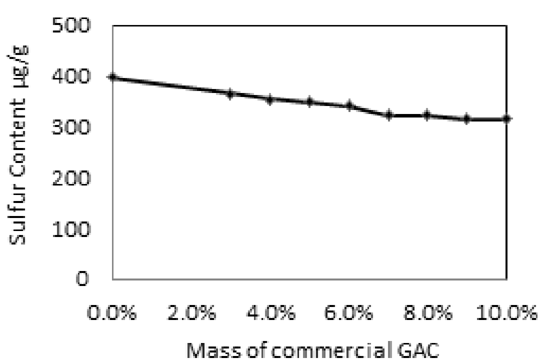

Fig1. Effect of the amount of Commercial GAC on Sulfur removal at Room Temperature and 1 hr.

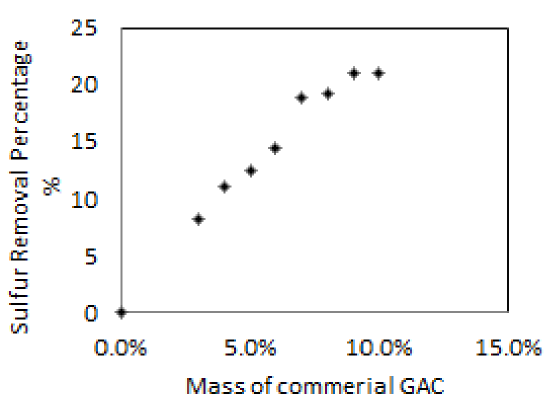

Fig 2. Sulfur breakthrough curve using commercial GAC at room temperature and 1 hr

C. *Diesel oil characterization*

The physical properties of diesel oil before and after the adsorption process were evaluated as shown in Tables 1 and 2. The calculated diesel index and accordingly the cetane number of the diesel oil used, before and after adsorption desulfurization process, showed an improvement in its ignition quality after desulfurization. The results showed an increase in the diesel index from 69.1 to 71.3 and in the corresponding cetane number from 59.7 to 61.3. This improvement is believed to be associated with the removal of some aromatic compounds and heavy metal from diesel oil sample. This is supported by the decrease in the carbon residue and the flash point properties. The viscosity values are in agreement with this conclusion

TABLE I
PHYSICAL PROPERTIES OF DIESEL OIL

Property	ASTM number	Diesel oil	Desulfurized diesel oil
Specific gravity @15/15°C	D98	0.819	0.817
Water content, vol. %	D96	Nil	Nil
Water and sediment, vol. %	D1796	Nil	Nil
Conradson Carbon residue, wt. %	D189–97	0.100	0.035
Ash content, wt. %	D482	0.099	0.062
Kinematic viscosity @ 40 oC, cSt	D445	9.03	8.92
Flash point, CCPM, oC	D 93	81.2	81
Aniline point, °C	D 611	75.0	77
Diesel index	D611	69.1	71.3
Cetane index	Ref. 8	59.7	61.3
Calorific value, J/g	D 240	46,000	~46,000
Sulfur content, ppm	D7220-06	398	315

TABLE II
HEAVY METALS IN DIESEL OIL.

Symbol	Unit	Diesel oil
Magnesium (Mg)	ppm	< 9.1
Aluminum (Al)	ppm	4.9
Silicon (Si)	ppm	14
Phosphorous (P)	ppm	4.6
Chlorine (Cl)	ppm	4.1
Potassium (K)	ppm	< 2.2
Calcium (Ca)	ppm	2.2
Vanadium (V)	ppm	< 1.0
Chromium (Cr)	ppm	< 1.0
Manganese (Mn)	ppm	8.2
Iron (Fe)	ppm	1.2
Nickel (Ni)	ppm	< 0.1
Copper (Cu)	ppm	2.1
Zinc (Zn)	ppm	1.9
Molybdenum (Mo)	ppm	< 1.0
Barium (Ba)	ppm	< 3.0

D. Sorbent surface characterization

The amount of heavy metals in the adsorbent material before and after sulfur adsorption was determined using the inductively coupled plasma (ICP) analysis and the results are shown in Table 3. The difference in the amount of the trace metals in the solution, before and after adsorption, provides an indication about the amount of metals leached into the diesel oil from the sorbent material. The results presented in Table 3 showed a decrease in the amount of aluminum, chromium, iron, and nickel on the surface of the adsorbent. Moreover, Scanning Electron Microscopy (SEM) was used to study the structure of the surface of the sorbent material before and after the adsorption process. The results are shown in Figure 3. The SEM images of fresh GAC illustrate that the sorbent material have smooth surface with compact structure (Fig. 3(a)). After adsorption, the sulfur is homogenously adsorbed on the surfaces of the sorbent materials (Fig. 3(b)) which prove the validity of using GAC for the adsorption of sulfur from diesel oil.

TABLE III
HEAVY METALS IN GAC ADSORBENT IN PPM

	GAC(fresh)	GAC(after adsorption)
Aluminum	1204	28.7
Cobalt	0.49	0.30
Chromium	149	0.00
Copper	12.7	2.46
Iron	915.6	3.92
Nickel	578.17	6.57
Lead	9.98	2.69

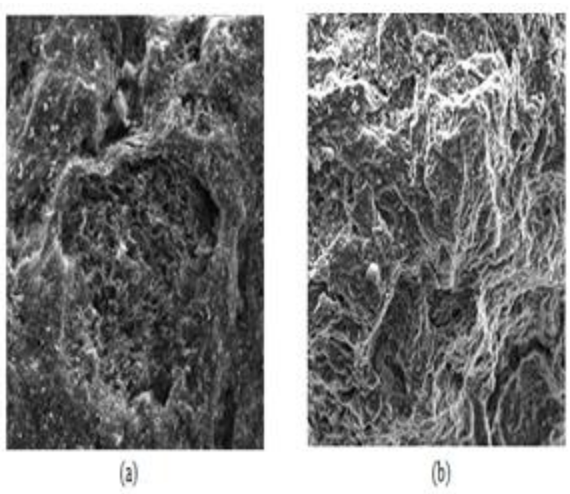

Figure 3: Scanning Electron Micrographs of the GAC before (a) and after (b) adsorption process

The metal contents on the GAC surface before and after the adsorption process are shown in Table 4. The results show no significant variation in the metal concentrations on the surface of the sorbent material as a result of the adsorption process.

TABLE IV
SURFACE METALS OF GAC BEFORE AND AFTER ADSORPTION PROCESS IN PPM

Element	GAC	
	Before DS	After DS
Na	0.24	0.08
Mg	1.03	0.34
Al	0.28	1.38
Si	0.27	0.47
P	0.32	0.16
S	0.58	0.17
Ca	1.1	0.73
Ti	0.04	0.09
Cr	0.02	0
Mn	0	0.05
Fe	0.11	0.32
Ni	0.02	0.1
Cu	0.12	0
Zn	0	0.01
Sr	0.17	0.07
Pb	0.42	0

E. Adsorption Isotherms

The adsorption isotherm study was conducted and the experimental isotherm was fitted to Langmuir and Freundlich equations. The Langmuir isotherm assumes a monolayer adsorption on to a surface of the adsorbent where the adsorbent contains a finite number of uniform sites for the adsorption and it assumes that there is no transmigration of adsorbate on the plane of surface. However, the Freundlich isotherm assumes heterogeneous surface energies, where the energy in Langmuir equation varies as a function of the surface coverage [7]. Comparison of the correlation coefficients or (R) can confirm the applicability of any of the studied isotherm equations.

1. Langmuir Isotherm

The linear form of the Langmuir's isotherm is given by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$$

Where C_e is the equilibrium concentration of sulfur in (mg/L), q_e and q_m are the equilibrium and maximum amounts adsorbed per unit mass of adsorbate in (mg/mg), respectively, andK_L is the Langmuir constant related to the rate of adsorption. From the plot of $\frac{C_e}{q_e}$ against C_e if a straight line with slope $\frac{1}{q_m}$ is obtained (Figure 4), indicating that the adsorption on GAC follows the Langmuir isotherm.

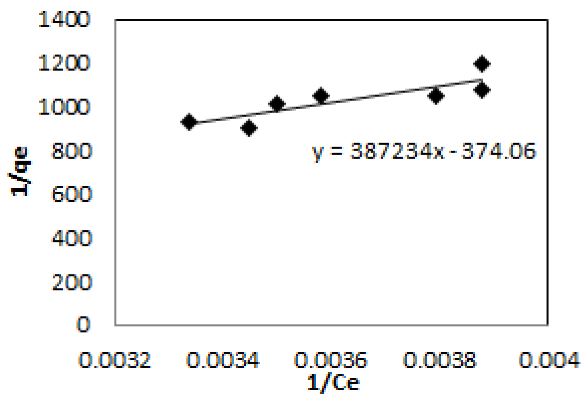

Fig 4. Langmuir adsorption isotherm

2. Freundlich isotherm

The Freundlich model is given by the following equation:

$$q_e = K_F(C_e)^{\frac{1}{n}}$$

And the linear form is given by:

$$Log\ q_e = \log K_F + \frac{1}{n} C_e$$

K_F and n are the Freundlich constants that show the adsorption capacity of the GAC and the affinity between the adsorbent and adsorbate. The plot of log qe versus log Ce gives a straight line with slope '1/n' is shown in Figure 5.

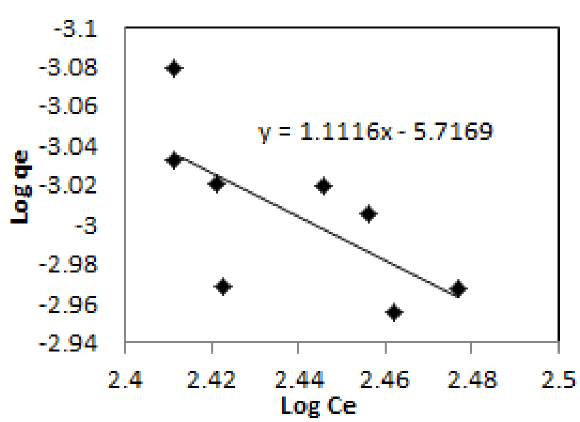

Fig 5. Freundlich adsorption Isotherm

From figures 4 and 5, it is clear that the adsorption desulfurization process is more likely obeys Langmuir isotherm.

IV. Conclusion

The adsorption desulfurization of diesel oil using GAC showed good efficiency for sulfur removal of 20.94% at room temperature. This sulfur removal caused an improvement in all physical properties and especially the ignition quality. The diesel index as well as the cetane number was improved win this adsorption desulfurization process. The kinetic study showed that the adsorption desulfurization process of diesel oil is more concise with Langmuir isotherm.

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