Selective adsorptive desulfurization of diesel fuel on carbon nanospheres

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Abstract:

Adsorptive desulfurization of diesel fuel is a non-invasive approach and viable alternative to the conventional hydrodesulfurization(HDS) process that it can be potentially used in industrial desulfurization but in most cases cannot attain the ultra-low sulfur content of below 10 ppm.
In the present work, we report studies on sulfur removal to acceptable levels by using a selective adsorptive desulfurization process at room temperature and atmospheric pressure. A synthesized Carbon Nano sphere, have been studied for their usefulness in desulfurization of diesel. Studies have been carried out on actual diesel fuel. The results showed that the carbon nanospheres(CNSs) can be used as a good adsorbent for the desulfurization of liquid fuels. Optimum adsorbent dose was found to be 7, 5 g/L. The proposed method can remove poly aromatic heterocyclic (PAHs) and polyaromatic sulfur heterocyclic (PAHSs) compounds from diesel fuel of high sulfur contents up to 87% in the total.

1. Introduction:

Sulfur-containing compounds during transportation fuels are converted by combustion to SOx , which is a major source of acid rain and air pollution [1]. For environmental protection purposes, many countries have mandated a reduction in fuels sulfur level down to 10 ppm by 2009 [2,3], and with more and more stringent regulatory constraints, it is a trend to achieve little to no sulfur fuels in the next several years.

Therefore in commercial diesel or gasoline it is demanded to reduce the content of sulfur-containing compounds such as thiophene, benzothiophene (BT), dibenzothiophene (DBT) and 4,6- dimethyldibenzothiophene (DMDBT) to very low levels in order to prevent air pollution from SOx and deactivation of catalysts[4].

Conventionally, hydrodesulphurization (HDS) [5] is used to bring down sulphur concentration in liquid fuels. However, with existing stringent norms for drastically lower sulphur concentrations, HDS processes have severe limitations in bringing down sulphur concentrations to desired levels both technically and economically. Hydrodesulphurization process requires suitable catalyst such as Co–Mo/Al_2O_3, Ni–Mo/Al_2O_3or Ni–W/$Al_2O_3$for removal of sulphur compounds.

The dis-advantages of this process are (a) the catalytic processes operated at elevated temperatures (300–400°C) and elevated pressures (20–100atm of H_2) and (b) the 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 such as 4-methyldibenzothiophene (MDBT) [6].

It is therefore instructive to evaluate alternate solutions to this problem and possible alternatives include, biodesulphurization [7] and oxidative desulphurization [8], and selective adsorption of organic sulfur compounds over various adsorbents [9] have been extensively investigated. The most well-known adsorbents are activated carbons [10], zeolites [11] and mesoporous materials [12].

The adsorption method is a low-energy demanding process and has attracted much attention,and has some advantages such as low operating temperature and pressure, and the adsorbent can be regenerated. Extensive research has been done to find adsorbed materials that are highly selective to sulfur-containing compounds in the presence of the coexisting aromatic hydrocarbons and olefins[13].

Among the adsorbents, the activated carbon nanospheres (ACNS) have many unique properties including smooth surface, good fluidity, low ash content, high mechanical strength, and abundant micropores, which make them an attractive and superior adsorbent to the powdered or granular activated carbons[14].

In order to enhance the adsorption capacity of sulfur compounds on to carbon materials,chemical surface modifications by impregnation [15], oxidation [16] and heat treatments [17] have been previously studied. Although some of these treatments can modify textural properties, the incorporation of oxygen groups on surface adsorbent can increase the adsorption capacity for carbon because of the generation of hydrogen bond between sulphur atom and the oxygen atom from oxygen surface groups [18,19]. Previously, it has been pointed out that the adsorbent modification by oxidation leads to the fixation of a high

number of acidic functional groups [20]. Moreno-Castilla et al. [21] studied the effect of different oxidation treatments based on hydrogen peroxide, ammonium peroxide and nitric acid on the chemical surface of activated carbon.They found that the treatment with nitric acid produced a significant loss of microporosity but it also fixed the largest number of oxygen groups such as carboxylic, anhydric, lactonic and phenolic on the surface.

The bulk of the research is directed towards finding high capacity adsorbents that selectively adsorb the sulfur compounds which are mainly polycyclic aromatic hydrocarbons and organo-sulfur compounds. Accordingly, in this study we have used Carbon nano-sphere (CNSs) synthesized in our laboratory and evaluated their performance for the adsorption of Alkylthiophene, alkylbenzothiophene, and alkyldibenzothiopheneextract from diesel fuel under middles experimental conditions.

2. Experimental

2.1.Chemical and solvents

-carbon nanospheres: was produced by pyrolysis of crude oil.

-Diesel fuel: An actual diesel was used as the feedstock for desulfurization-adsorption process. physical and chemical properties of typical diesel fuels that were used are presented in Table. 1.

Table 1: Physical and chemical properties of a typical diesel fuel

Test description	Norme	value
Color	ASTM	0,5
Cetane index	D1500	51,6
Density at 15°C,	ASTM D976	830
(Kg/m^3)	ASTM	80
Flash point, (°C)	D1298	
Distillation, (°C)		
65% vol		310
90% vol	ASTM D86	350
PF		380
Could point	ASTM D97	-4
Pour point	ASTM D97	-6
Sulfurcontent (ppm)	ASTMD2622	450

All chemical such as benzene, DMF, iron chloride and other reagents used in the preparation methods were of analytical reagent grade and were obtained from Sigma-Aldrich chemical reagents.

2.2.Synthesis and activation of carbon nanospheres :

CNSs were prepared by pyrolysis of crude oil under atmospheric pressure (1 atm) in the presence of $FeCl_3.6H_2O$ as catalyst (mass ratio catalyst/crude oil is 0.00083 g / g) at a temperature of 900 ° C using Ar as the carrier gas. CNS product was washed and treated with benzene to remove soluble impurities and polyaromatic.

The resulting spheres were then activated as follows: 500 mg of the solid sample was heated to reflux for 2 h in 100 ml of $(HNO_3(65\%)/HCl(37\%)$ at 115 ° C. The solution was then cooled to room temperature, CNS were filtered and washed with distilled water. The structure was confirmed by SEM / EDAX and µXrf.[22]

2.3. Adsorption desulfurization of diesel fuel

Adsorptive desulfurization was carried out in a liquid-phase glass batch reactor operating at atmospheric pressure and room temperature under stirring.Each experience increasing the amount of the adsorbent from: 0.05g,0.1g,0.15g,0.2g,0.25g,0.3g,0.35g,0.4g,0.45g and the quantity of diesel used in each run was 40ml. The sorbent was suspended in solution of pretreated diesel. This mixture was kept under vigorous stirring for all overnight, to reach the thermodynamic equilibrium. The solid was then filtered for its characterization (SEM/EDAX), µXrf.

The liquid product was washed using distillate water and dried then analyzed by GC-MS to evaluate the sulfur compound concentration.

2.4 Characterization and analysis methods:

2.4.1. Characterization of adsorbent

-**Scanning Electron Microscopy(SEM)**: The surface morphology of the samples was examined with scanning electron microscopy (SEM) using a Scanning Electron Microscope FEI QUANTA 600W were used in order to check purity, phase's structure, surface morphology of the products. Parameters used are: accelerating voltage 5kEv, high vacuum, ETD detector, Working Distance 10 mm.

- **The micro X-ray fluorescence**: (µXrf) is a technique for non-destructive elemental analysis, qualitative and / or quantitative applies on solid samples, liquid or gaseous. However, the limitation of the XRF analytical boils down to the inability to detect light elements (low atomic number) Hydrogen measures (H), Lithium (Li) and beryllium (Be) are impossible, those Boron (B), carbon (C), nitrogen (N), oxygen (O) and the fluorine (F) are very delicate.TheµXrf used is HORIBA brand (Department Vehicle Examination NCIC-GN) XGT model 5000 with an X-ray source Rhodium. The analyses were performed with a voltage of 30 KV and a current of 0.8 to 1 mA.

2.4.2. Sulfur analysis:

-**X-ray fluorescent analysis:** the total concentration of sulfur in diesel samples was analyzed using X-ray fluorescence (X-ray fluorescence spectrometer OXFORD Lab X-3500 (ASTM 2622 method) which was calibrated with six liquid calibration standards (obtained from AccuStandard), and concentration ranging from 0, 200, 400, 500, 600, 800, 1000 ppm sulfur by wt%.

-**Gas-chromatography–mass spectrometry:**To identify the organo-sulfur compounds degradation products, the mixture was centrifuged and the upper solution was injected to a GC-MS instrument (Marque; thermo Scientific, Model, Trace GC, DSQII, Column, Tr-5ms) with a flame ionization

detector (GC-FID) and HP-5 MS column (30 m x250 µm x0.25 µm). The analysis conditions were as follows: injector temperature is 300°C; detector temperature, 290°C; column temperature, 100°C for 2 min, then heated to 250°C in rate of 3 °C/min; the carrier gas was nitrogen. Before the analysis, the sample was diluted to the concentration in the range of 1µL for extracted sample of PAHs/PASHs.

The percentage removal of sulfur and equilibrium adsorption uptake in the solid phase (mg/g) was calculated using the following relationships:

% removal sulfur= 100 (C0- Ct)/C0

*C0:*the initial concentration of sulfur compounds in the diesel fuel before adsorption (450 ppm)

*Ct:*the concentration of sulfur compounds in the diesel fuel after adsorption in ppm

3. Results and discussions:

3.1.Identification of Poly Aromatic heterocyclic (PHAs) and Poly Aromatic Sulfur heterocyclic (PASHs) compounds in diesel fuel:

Amount of 100 mL of diesel fuel was mixed 50 mL of polar solvent dimethylformamide DMF then heated to 60°C for 02h.The bottom DMF layer was separated from the upper hydrocarbon layer. About 100 mL of hot distilled water was added to the DMF layer. A ring of chestnut colored liquid separated on the upper, which was the polar compound. 5 mL of octane was then added and the contents mixed for 20 min. This upper organic layer was isolated, washed with distillate water, dried and filtered. The octane was evaporated under a stream of nitrogen and this organic layer (Figure.1) analyzed by GC-MS.
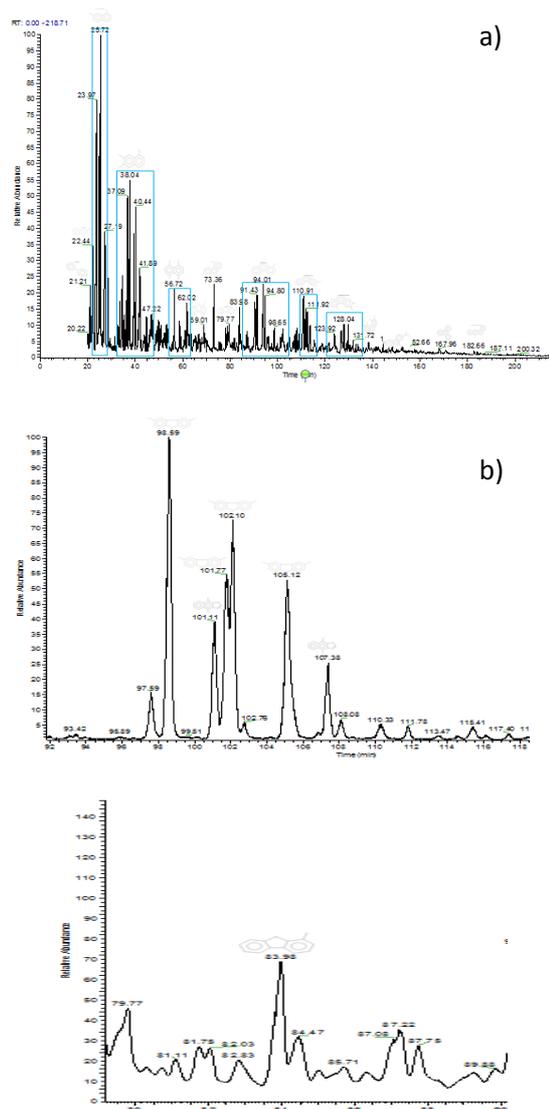

Figure 1: CGMS spectra of used diesel, a/CGMS spectra of Poly Aromatic heterocyclic (PHAs) compounds in diesel fuel, b/CGMS spectra of Poly Aromatic Sulfur heterocyclic (PASHs) compounds in diesel fuel.

As shown in Figure.1, the major sulfur compounds existing in the diesel fuel are:benzothiophene,alkylbenzothiophene,alkyl dibenzothiophene indicating that most sulfur compounds with higher HDS reactivity, including alkylated condensed aromatic derivatives of naphthalene,alkylnaphthalene, anthracene, alkylanthracene, phenanthrene, have been removed from the diesel fuel in current processes.

3.2 Characterization of CNS

As showing in figure.2 the SEM image of the typical morphology of carbon structures, including nanospheres after activation and before adsorption. The particles appear to agglomerate to each other as a sphere form a dimeter less than 500 nm with well-defined pores.Chemical analysis of the product using EDX,it confirms the high yield of carbon (89.51%) after pyrolysis of crude oil at 900 ° C in the presence of impurities in the carbon spheres are: oxygen (O) that is due to the presence of oxygen-containing group on the surface of the carbon nanospheres, other elements such as molybdenum (Mo), chlorine (Cl), Calicium (Ca).

After the diesel desulfurization-adsorption process, volume of carbon spheres was increased as shown in figure.2 and indicate that the elementary analyses CNSs was adsorbed sulfur in diesel that contains with a concentration of 0.8%.
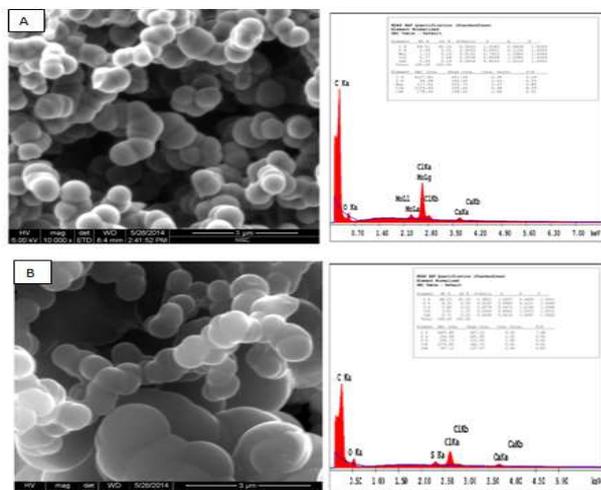

Figure 2: Scanning electron microscopy and EDX of CNSs synthesized at 900°C for 2 hours, A) before adsorption, B) after adsorption

The X-ray microfluorecsence (Figure.3) shows that the carbon nanospheres containing impurities such as Fe, Cl, Zn and Cu, no other atom such as sulfur is detected, temperature of the synthesis reaction is 900°C at this temperature the sulfur evaporates.After the

adsorption process, the CNSs was analyzed by µXRF, this technique has allowed us to see a sulfur adsorption by CNSs with a concentration of 3.96%.

From these results of SEM/EDX and µXRF , the CNSs can used as a good adsorbent of sulfur compounds.
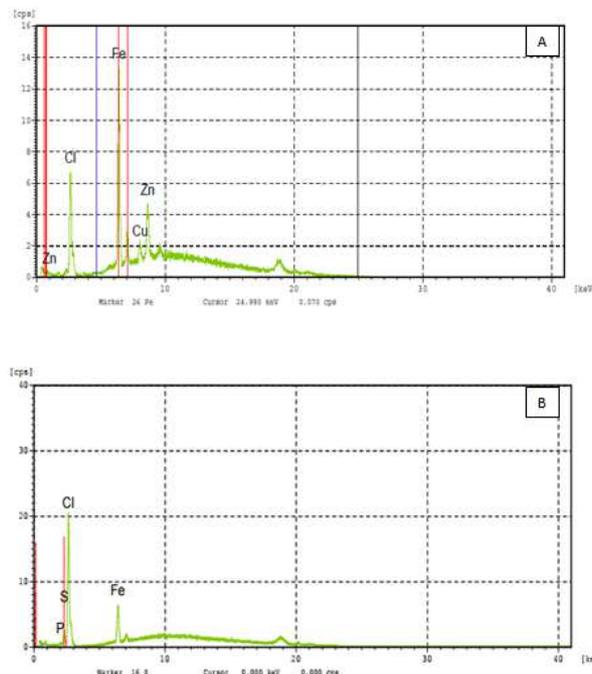
Figure.3:X-Ray fluorescence of carbon nanospheres, a) beforeadsorption, b)after adsorption

3.3. Adsorption of Different Poly Aromatic heterocyclic (PHAs) and Poly Aromatic Sulfur heterocyclic (PASHs) compounds in diesel fuel

It has been shown that the extent of adsorption of the refractory S-containing molecules in middle distillates depends markedly on the nature of the organo-sulfur molecules. The degradation products were analyzed by GC-MS technique (figure4/a). After adsorption, the adsorbent was separated and the solution was again analyzed by GC-MS (Figure 4/b).The alkylBT, alkylDBTand aromatic compounds were relatively easily adsorbed on used CNSs.

The results showed that a most of sulfur containing and aromatic compounds were

adsorbed by CNSs and the remaining compounds were alkanes C_8-C_{24}.

Indeed, the selective adsorption might well be ruled by several factors among which the electronic characteristics of the adsorbate and the surface nature of the adsorbent play a major role. The total removal of sulfur compounds was about 87%.
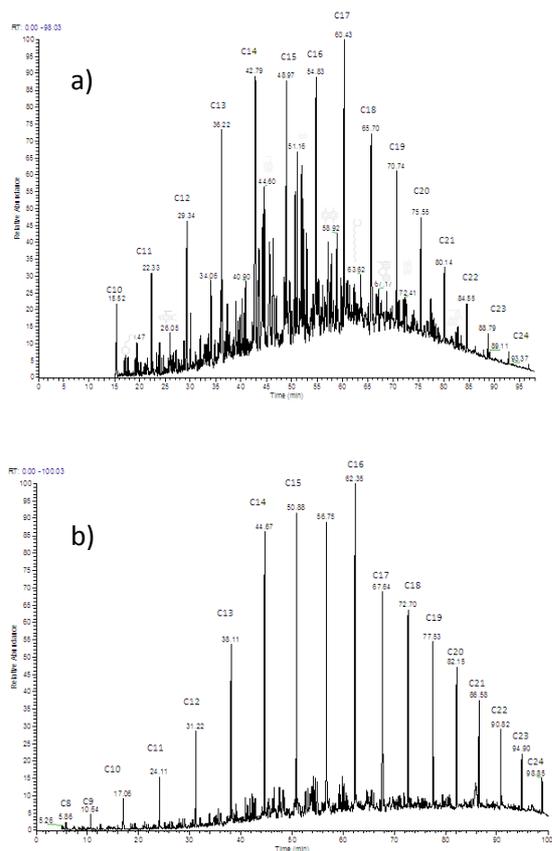

Figure 4: CGMS spectra of diesel a) before adsorptive desulfurization, b) after adsorptive desulfurization.

3.4 Effect of CNSs mass (m)

Many different factors affect the capacity of an adsorbent for a particular fuel. For example, the capacity can vary based on the particle size, the material preparation formulation and technique adsorption, column dimensions, temperature of adsorption, type of sulfur compounds present in the fuel, and presence of existing competitive molecules such as olefins and aromatics.

The effect of adsorbent amount on the diesel fuel was studiedin room temperature with 450 ppm and the results are shown in **Figure.5**.

Amount of CNSs(g)	Concentration of CNSs in 40 ml of diesel (g/l)
0.05	1.25
0.10	2.5
0.15	3.75
0.20	5
0.25	6.25
0.30	**7.5**
0.35	8.75
0.40	10
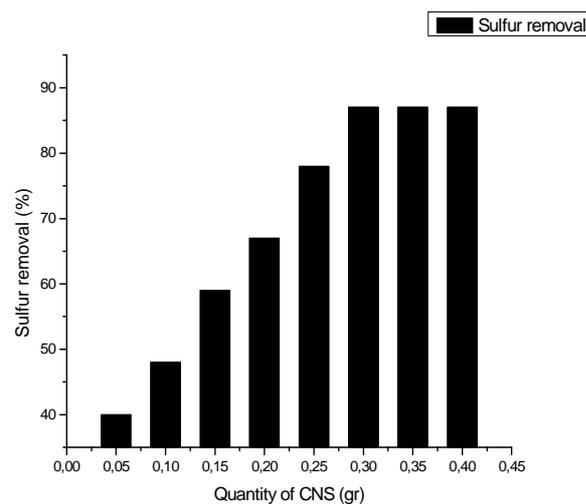
Figure 5: Effect of adsorbent dose on the removal of PASHs.

The removal of organo-sulfur compounds to be increasing with an increase of adsorbent concentration from 1 to 10 g/l. The removal remained unchanged for m> 7,5 g/l (0.3g) for CNSs The increase in the adsorption with the CNSs dosage can be attributed to the availability of greater surface area and more adsorption sites. At m< 6 g/l, the CNSs surface becomes saturated with organo-sulfurcompundsand the residual PASHs concentration in the solution is large. With an increase of concentration , the sulfur removal

increases due to increaseof PASHs uptake by the increased amount of CNSs. For m> 6 g/l, the incremental sulfur removal became low. At about m= 7, 5 g/l, the removal efficiency became almost constant at for sulfur removal by CNSs.

4. Conclusion:

CNSs as promising materials for adsorptive desulfurization of liquid transportation fuels. The aim of the experiment was to determinate the efficiency of removing sulfur from diesel fuel by the adsorption process with CNSs adsorbents.

Application of carbon nanospheres absorbent was an efficient method for removal of sulfur compounds(87%). Since the conventional hydro desulfurization process is not an effective method forremoval dibenzothiophene and its derivatives, the combination of desulfurization-adsorption method used in this research can be used for deep desulfurization of transportation fuels.

Acknowledgements

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