Chemical Engineering Journal 162 (2010) 669–676

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Minimisation of organosulphur compounds by activated carbon from commercial diesel fuel: Mechanistic study

Mohammad A. Al-Ghouti[a,*], Yahya S. Al-Degs[b], Fawwaz I. Khalili[c]

[a] Royal Scientific Society, Industrial Chemistry Centre, P.O. Box 1438, Al-Jubiha, Amman 11941, Jordan
[b] Department of Chemistry, Hashemite University, Zarqa, Jordan
[c] Department of Chemistry, University of Jordan, Amman 11942, Jordan

ARTICLE INFO

Article history:
Received 21 April 2010
Received in revised form 14 June 2010
Accepted 15 June 2010

Keywords:
Diesel
Organosulphur compounds
Activated carbon
Adsorption

ABSTRACT

The removal of organosulphur compounds (ORS) from diesel fuel is an important aspect of Jordanian's effort to reduce air pollution by sulphur oxides. The results of this work revealed that activated carbon (AC) has an excellent adsorption for the ORS from non-aqueous diesel medium. Experimental data revealed that percentage removal of the ORS was slightly affected with particle size of the adsorbent, which indicates that elimination of the ORS mainly occurred on the external surface area and the adsorption onto the pores of the adsorbent has a small effect on the entire elimination process. Removal of the ORS by the AC has an endothermic nature where percentage removal values were increased by temperature. The maximum percentage removal value was 72% which was reported at: 2.0 g, 300–500 μm, 25 °C, and 3 days shaking. The experimental results were plotted and treated with Langmuir isotherm, uncommon isotherm shapes were obtained. Therefore, it was not fitted to the experimental results which might reflect a complex nature of adsorbing the ORS onto the AC. However, this behaviour gives an indication on the complex adsorption mechanisms. Finally, the mode of interaction between the ORS and the AC was characterised by comparing the changes in the position and intensity of the surface functional groups using FTIR technique.

1. Introduction

Organosulphur compounds (OSC) in fuels cause toxic emissions and inefficient performance of exhaust catalysts; thus, processes for their removal have been widely explored [1]. OSC are usually present in almost all fractions of crude oil distillation. Higher boiling fractions contain relatively more sulphur and the compounds are of higher molecular weight. The low boiling crude oil fractions contain mainly the aliphatic organosulphur compounds and the higher boiling crude oil fractions boiling above 250 °C predominantly contain thiophenic rings [1].

Thiophene, benzothiophene (BT), and their alkyl derivatives are the most abundant organosulphur compounds in diesel fuel; more reactive sulphides, disulphides, and mercaptans are present as minor components. Thiophene represents a particular challenge, because it resembles abundant arenes and alkenes in electron density and basicity, thus making chemical specificity difficult during adsorption and catalysis. The high specific area, surface functional groups, and structural and compositional flexibility make activated carbon (AC) potential candidates for thiophene adsorption [2,3].

Due to the increasingly stringent environmental regulations on the sulphur content in transportation fuels, desulphurisation of diesel fuel has become a very important research topic. The ORS are the main cause of acid rain and poisoning of catalysts in CO and NO_x catalytic converters [4]. The ORS in diesel fuel have a detrimental effect on the performance of catalysts used in vehicle and have environmental problems. It is generally agreed that the sulphur content in hydrocarbon fuels has to be reduced to less than 35–350 ppmw for vehicle applications. Currently, total sulphur content in Jordanian diesel oil is 12000 ppm (1.2%, m/m). Therefore, there is a dire need to incorporate desulphurisation technologies into the fuel processor.

Hydrodesulphurisation (HDS) with unsupported transition metal sulphide still seems to be the only practical solution to achieve low sulphur diesel less than 10 ppmw [5]. The challenge for desulphurisation of diesel fuels is the difficulty of removing the refractory sulphur compounds, particularly dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (DMDBT) with conventional HDS processes. Alternative technologies need to be developed for desulphurisation of liquid fuels due to the significant content of refractory sulphur compounds. In addition, as the diesel fuel contains not only sulphur compounds and nitrogen compounds but also a large number of aromatic compounds that have aromatic skeleton structure similar to the coexisting sul-

---

* Corresponding author. Tel.: +962796406789.
E-mail addresses: mghouti@rss.gov.jo, ghoutijo@yahoo.co.uk (M.A. Al-Ghouti).

1385-8947/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2010.06.019

phur compounds, a great challenge in development of an effective adsorptive desulphurisation process is to develop an adsorbent which can adsorb the ORS and can perform at ambient temperature and pressure. Recently, many attempts have been made to develop adsorbents for desulphurisation of liquid hydrocarbon fuels [2,3].

The ORS are known to be slightly polar than hydrocarbons of similar nature. The exploitation of the polarity factor has been the subject of numerous investigations for processes based on oxidation/extraction and adsorption [2,3]. A typical adsorption process is expected to offer selective removal of the ORS, to operate at normal temperatures and pressures with ease of operation/ease of process control and economically achieve near total elimination of the ORS from transportation fuels. At the same time, ease of regeneration with minimum requirement of chemical and energy is also expected from the point of view of commercial viability. A wide variety of materials starting from activated carbon, silica-based sorbents, zeolites and metal exchanged/ impregnated activated carbon/zeolites/mesoporous materials have been reported in the past for adsorption [6].

Activated carbons are widely used as adsorbents. They represent extremely versatile adsorbents of industrial significance and are widely used in many applications which concern principally with the removal of undesirable species from liquids or gases. They are also used as catalysts or catalyst supports or gas storages [7,8]. The surface functional groups anchored on/within carbons were found to be responsible for the variety in physicochemical and catalytic properties of the matters considered [8]. So, many researchers focused on how to modify as well as to characterise the surface functional groups of carbon materials in order to improve or extend their practical applications.

The heteroatoms on the surface of the AC took significant role on its application [9]. The heteroatoms of porous carbon surface mainly contained oxygen, nitrogen, hydrogen, halogen, etc, which bonded to the edges of the carbon layers and governed the surface chemistry of the activated carbon [9]. Among these heteroatoms, the oxygen-containing functional groups (also denoted as surface oxides) were the widely recognized and the most common species formed on the surface of carbons, which significantly influenced their performance in conversion systems, catalytic reactions, and adsorptions [10]. Carboxyl, carbonyl, phenol, quinone and lactone surface functional groups attached to aromatic sheets and strips, containing various slit-shaped voids, i.e. the micropores are reported in the literature [9].

The literature on adsorptive desulphurisation studies reveal rather a conflicting picture with many studies showing substantially lower capacities for sulphur removal success with transportation fuels such as commercial diesel is far from being well understood. Further, a variety of the ORS has been studied for their removal and more attention has been paid to most important components such as BT, DBT and DMDBT, which are critical from the point of view of diesel desulphurisation. Recently, the adsorptive capacity of zeolitic tuff toward organosulphur compounds has been evaluated [11]. The earlier study revealed that the zeolitic tuff has a good adsorptive capacity which could reach to 7.15 mg S/g [11]. The favourable interaction between sulphur compounds and zeolite was mainly attributed to C–S bond cleavage in the solutes to form unsaturated fragments on the zeolite acidic sites [11]. In a similar study, a selective adsorbent was made up based on molecular imprinting polymer technology [12]. The prepared polymer was very selective toward dibenzothiophene that present in diesel with adsorption value of 66 mg/g [12]. Surface modification of chitosan was prepared and used as adsorbent for removing dibenzothiophene sulfone, dibenzothiophene, fluorine, and 4,6-dimethyl DBT that usually found in diesel fuel [13]. van Rheinberg et al. were effectively eliminated 4,6-dimethyldibenzothiophene and other sulphur compounds (final content 0.2 ppm) from diesel using Ni/NiO-adsorbent [14]. The earlier researchers used Gas chromatography/mass spectrometric detection (GC/MS) for separating and detecting fuel components [14]. In a unique study, Zhou et al. have oxidized the surface of activated carbon and applied it for removing number of organosulphur compounds from diesel fuel [15]. The earlier authors used the fixed-bed flow system and the level of sulphur compounds has been greatly reduced using initial effluent level of 400 ppmv [15]. Activated carbon based date' stones and treated with $ZnCl_2$ was used for diesel desulphurisation, the adsorption data of sulphur compounds were fitted to both Freundlich and Langmuir isotherms to estimate the adsorption parameters [16]. From the earlier discussion, it is interested to note that different adsorbents were tested for diesel desulphurisation and these adsorbents include inorganic material like zeolite and polymers and activated carbon. Relatively speaking, most studies was used activated carbon as adsorbent for selective removing of organic sulphur compounds from diesel and this is expected as activated carbon has many surface functional groups and large surface area that enable it for absorbing wide range of pollutants from different media.

Thus, a more systematic work in terms of stock diesel having all important elements such as BT, DBT and 4,6-DMDBT would help in understanding the adsorption behaviour. Also, there is a need to evaluate the effect of various other process parameters such as particle size, temperature, and concentration of the ORS. The present study aims at initiating work in this regard. In the second part of our work, we will report more detailed sulphur removal studies onto the AC after various chemical modifications.

The main objective of this investigation is to study the physical characteristics of this adsorbent such as $pH_{solution}$, pH_{zpc}, surface acidity and basicity. Furthermore, the capability of the AC to adsorb the ORS will be ascertained. The study will also investigate the effect of key parameters such as particle size, initial total sulphur concentration, and temperature on the adsorption process and the nature of the mechanisms involved.

2. Experimental

2.1. Adsorbent and adsorbate

Activated carbon, NORIT PK 1–3 was obtained from NORIT, Holland in a granular bead form. It was produced by steam activation. Some of the physical and chemical properties for NORIT PK 1–3 are presented in Table 1. It was crushed by using a hammer mill and sieved, HAVER & BOECKER EML, into several discrete particle sizes ranging, namely 150–300, 300–500, and 500–800 μm. Table 2 represents the physical and chemical properties of the diesel fuel sample.

Table 1
Some chemical properties for NORIT PK 1–3.

Typical analysis (NORIT Americas technical datasheet)		
Type of test	Unit	Result
Apparent bulk density	g/L	260
Total surface area (N_2, BET method),	m^2/g	1100
Iodine adsorption	mg/g	800
Ash content	%	7
Moisture (as packed)	%	2
Particle size		
>3.4 mm	%	1
>2.4 mm	%	25
>1.7mm	%	55
>1.0 mm	%	92
Density backwashed and drained	g/L	230
D60/D10		1.9
Total pore volume	cm^3/g	1.2
Supernatant, pH		9.49

Table 2
Some physical and chemical properties for the diesel fuel sample used.

Type of test	Unit	Result	According to
Density @ 15 °C	kg/m^3	845	IP-190
Cetane Index	–	52	ASTM D 976-06
Total sulphur content	%m/m	1.20	ASTM D 4294-03
Flash point (PMCC)	°C	75	ASTM D 93-07
Conradson carbon residue (@ 10% residue after distillation)	%m/m	0.136	ASTM D 189-06 $^{\varepsilon 1}$
Ash content	%m/m	0	ASTM D 482-03
Water concentration	mg/kg	120	ASTM D 6304-07
Copper corrosion, 3 h@50 °C	–	1a	ASTM D 130-04 $^{\varepsilon 1}$
Kinematic viscosity @ 40 °C	cSt	3.743	ASTM D 445-09
Distillation			ASTM D 86-07a
Distillate @ 250 °C	% (V/V)	30	
Distillate @ 350 °C	% (V/V)	90	
Temperature @ 95%	°C	375	

IP: Institute of Petroleum, ASTM: American Standard for Testing and Materials, PMCC: Pensky-Martens flash point.

2.2. pH$_{solution}$ and pH$_{zpc}$

The pH$_{\text{solution}}$ of the adsorbent was carried out in 60 cm^3 glass bottle where 2.5 g of the adsorbent and 25 cm^3 of deionised water were added. The mixture was then agitated (shaking water bath, GFL (Gesellschaft für Lbortechnik mbH), Germany) for 24 h. The pH of the mixture was recorded using a pH meter and was determined using American Standard for Testing and Material (ASTM) ASTM D-3838/2001 [17]. Furthermore, the surface charge density, σ, of the adsorbent was estimated by following alkalimetric titration method [18,19]. A series of the adsorbent samples at a fixed particle size were spiked with varying amounts of 0.25 M HCl and 0.25 M NaOH solutions to give different pH values. The volume of acid or base was carefully transferred using 1.00 cm^3 micropipette. The samples were then diluted to a final volume of 25 cm^3 with deionised water in a 50 cm^3 bottle. Then, the bottles were tightly sealed and shaken for 24 h at room temperature (22 °C). After that, the equilibrium pH of the solutions was measured and the concentration of H$^+$ and OH$^-$ were calculated. Surface charge density of each solution was calculated using Eqs. (1) and (2) and a plot versus pH values was constructed. The value of zero point of charge, pH$_{\text{zpc}}$, was determined from the σ–pH curve to the pH at zero net adsorption of protons and hydroxide ions, i.e. the intersection of the curve with x-axis at σ equals zero, gives pH$_{\text{zpc}}$ [18,19].

$$\frac{C_A - C_B + [\mathrm{OH}^-] - [\mathrm{H}^+]}{m} = Q \tag{1}$$

$$\sigma = \frac{QF_c}{S} \tag{2}$$

where C_A, C_B represent the concentration of the base and acid added, while [OH$^-$] and [H$^+$] are the equilibrium concentration of the base and acid, respectively. Surface charge, Q (mol/g), m mass of adsorbent, surface area S (m^2/g) of the adsorbent, and F_c is the Faraday's constant (96,500 C/mol) [18].

2.3. Surface acidity

Boehm titrations have been widely used to determine the acidic and basic surface oxides [20]. A 50.0 cm^3 solution of sodium hydroxide (0.01 M) was measured with a clean pipette into a 60 cm^3 sample bottle followed by the addition of 0.5000 g of the adsorbent. The bottle was sealed with its cap and Parafilm and shaken mechanically at 150 rpm for 24 h. The resulting solution was filtered with a filter paper and then titrated against a standard hydrochloric acid solution (0.01 M) using 50.0 cm^3 burette. Phenolphthalein was used as an indicator, which changed the solution from pink to colourless at the end point. Each experiment was carried out two times to reduce the possible error. Concentration of sodium hydroxide in solution was calculated based on the amount of hydrochloric acid used. The number of moles of sodium hydroxide neutralised by the acidic functional groups on the surface of that 0.5000 g of the adsorbent was defined as the surface acidity of the adsorbent (mol/g).

2.4. Surface basicity

A 50.0 cm^3 solution of HCl (0.01 M) was measured with a clean pipette into a 60 cm^3 sample bottle followed by the addition of 0.5 g the adsorbent. The bottle was sealed with its cap and Parafilm and shaken mechanically (shaking water bath, GFL (Gesellschaft für Lbortechnik mbH), 1083, Germany) at 120 rpm for 24 h. The resulting solution was filtered with a filter paper and then titrated against a standard sodium hydroxide solution (0.01 M) using 50.0 cm^3 burette. Phenolphthalein was used as an indicator, which changed the solution from colourless to pink at the end point. Each sample experiment was carried out two times to reduce the possible error. Concentration of hydrochloric acid in solution was calculated based on the amount of sodium hydroxide used. The number of moles of hydrochloric acid neutralised by the basic functional groups on the surface of that 0.5 g of the adsorbent was defined as the surface basicity of the adsorbent (mol/g).

2.5. FTIR measurements

Analytical spectra were taken using a Shimadzu IR Prestige-21/FTIR-8400S with a resolution of 4 cm^{-1} at 64 scans. The data interval provided by the instrument for a resolution of 4 cm^{-1} is 1 cm^{-1}. Samples of particle size <66 μm were first dried at 110 °C for 24 h. The dried samples were mixed with finely divided KBr at a ratio of 1:300. Duplicate spectra were collected for the same sample. A previously recorded background spectrum was subtracted from the spectrum. All spectra were recorded from 4000 to 400 cm^{-1} and the spectra were collected using a Shimadzu IR Prestige-21 Windows Software. These tests were conducted at the laboratories of the Royal Scientific Society (RSS), Amman, Jordan.

Adsorbent spent samples were removed from the diesel sample after equilibration and were freed from the diesel by drying at 65 °C in preparation for the FTIR analysis. Small quantities of the adsorbent were grinded with KBr and pressed by a provided tool. Then the disc, which is formed, was placed in the instrument. It was scanned in transmission mode through wavenumber range from 400 to 4000 cm^{-1}. Before each measurement, the background was collected, which was then automatically subtracted from the sample spectrum.

2.6. Adsorption isotherms

A stock Jordanian diesel fuel, 7000 parts per million by weight sulphur (ppmw S) and various concentrations composed of n-heptane are prepared and used for all desulphurisation experiments. The AC samples are sieved and the fraction with particle size ranges from 150 to 300, 300 to 500, and 500 to 800 μm were chosen for adsorption measurements. Before performing the experiment, the AC sample was washed using distilled water to remove any dust and contaminants, filtered and dried at 100 °C overnight in drying oven. To exactly 1.000 g of the AC, 20.0 ml sample of the diesel fuel is added in 100 ml stoppered glass bottle. Thirteen of different sulphur concentrations are prepared and placed in a shaker (shaking water bath, GFL (Gesellschaft für Lbortechnik mbH), Germany) at 25, 35, and 45 °C. Enough shaking was performed to ensure a reasonably good relative movement between the AC particles and the liquid. At predetermined times a sample is withdrawn, filtered on filter paper and the filtrate is subjected to analysis by sulphur analyser, (SLFA-2100/2800 X-ray Fluorescence Sulfur-in-Oil Analyzers, Horiba). This is done according to ASDTM D2622 [21].

Removal of total ORS are calculated according to the following equation,

$$\text{removal of total ORS}\,(\%) = \frac{(S_o - S_e)}{S_o} \times 100\%$$

where S_o and S_e are the initial total ORS and the equilibrium total ORS concentrations, respectively.

3. Results and discussion

3.1. Characterisation of the AC

Surface properties of an adsorbent play an important role in the adsorption process [22]. Adsorbents may contain chemical functional groups on their surface of acidic or alkaline nature. Such groups often have an effect on the adsorption process of pollutants in various matrices. However, the value of solution pH will be affected by the particular conditions under which an adsorbent used, such as adsorbent concentration, the time and the temperature [22]. The solution pH of the adsorbents at a given concentration of adsorbent (23 °C, 10%, m/m) is 8.4. The acidity (0.678 mmol/g) and basicity (0.654 mmol/g) values of adsorbent refer to acidic and basic sites, which are available in the adsorbent surface. Moreover, the surface contains acid sites, HA, and basic sites, B, usually ionised according to these equilibria [22]:

$$HA_{(s)} \rightleftharpoons H^+_{(aq)} + A^-_{(s)} \tag{3}$$

$$B_{(s)} + H^+ \rightleftharpoons BH^+_{(s)} \tag{4}$$

The AC contains heteroatoms on its surface and the main heteroatom is oxygen. Different functional groups can be derived from these chemical heteroatoms. The most common are: carboxyl, lactonic, carbonyl and phenolic [23]. Moreover, the AC can show acidic and basic pH values in solution. The basic properties are ascribed to the presence of basic surface oxides. Carbons with low oxygen content show basic properties and anion exchange behaviour. The acidic surface properties are due to the presence of acidic surface groups. Carbons with high oxygen content, on the other hand, show acidic surface properties and cation exchange behaviour [23]. It is clear that the acidic characteristic of the AC is slightly higher than its basic characteristic. Generally, carboxylic groups have the strongest character in determining the acidity value of carbon.

The AC contains heteroatoms on its surface and the main heteroatom is oxygen. Different functional groups can be derived from these chemical heteroatoms, which exhibit electrical charge properties having a strong influence on the adsorption of ionic and polar species such as ORS. Thus, the charge on the surface of the AC must be counterbalanced in the solution phase to maintain electroneutrality.

Surface charge densities, σ, of the AC as a function of pH (Figure is not shown here). The intersection of the curve with x-axis at y equal to zero, gives the zero point of charge (pH_{zpc}). Here, the total charge from the cations and anions at the adsorbent surface is equal to zero. The zero point of charge occurred at pH value of 7.3 under the same experimental conditions.

The total surface functional groups and pH_{pzc} are important characteristics for any AC, as such characteristics can indicate the acidity/basicity, the type of adsorbent and indicate if it is H-type (is hydrophobic and takes on a positive charge by absorbing hydrogen (H^+) ions when immersed in water) or L-type (is hydrophilic and absorbs hydroxyl (OH^-) ions when immersed in water. It indicates that the AC has both basic and acidic properties. As already known, the acid functional groups are: carboxylic, lactonic, and phenolic, while, basic functional groups include oxygen-containing species such as ketonic, pyronic, chromenic, and p-electron system of carbon basal planes [24].

The AC has more acidic properties with maximum positive surface charge of 0.25 Coulomb/m^2 (C/m^2) at pH close to 1.0 and a maximum negative charge of 0.081 C/m^2 at pH 12. The density of surface functional groups depends on the preparation conditions and on the nature of the precursor of the AC [25]. Due to their importance in the attraction of polar-solutes from solution, many chemical treatment procedures are employed to increase the density of surface functional groups of the ACs [25]. The estimated pH_{zpc} is 7.3 and the type of this AC is L-type according to the Mattson and Mark classification of the ACs [26]. When added to distilled water, L-carbon type has a neutral solution. Accordingly, the L-type AC is a potential adsorbent for polar ORS in diesel.

3.2. Adsorption isotherms

Adsorption technology has been proposed for the removal of the ORS in fuels [2,3]. Compared to the hydrodesulphurisation process, the adsorptive removal of the ORS seems very promising since adsorption can be accomplished at ambient temperature and pressure and the sulphur in fuels can be removed to a very low level [27].

The AC is porous sorbents that can be utilized in removing ORS [28], but offer relatively low sulphur adsorption capacity at ambient temperature. The adsorption capacity of the AC is determined by their physical or porous structure, but is also strongly influenced by their chemical structure. To improve the sorbent performance, surface modification by acid incorporation or metal impregnation will be applied and verified in the next coming publications. These methods can create large amounts of acid groups and more adsorption sites on the surface of the AC, which can increase sulphur capacity. The use of inorganic metals in carbon modification can form catalytically active metals on the AC surface that serve as adsorption active points. These different functional groups and metal ions on the carbon surface play important roles in the adsorption of the ORS.

One of the attractive approaches for sulphur reduction that relies on the physical adsorption of the ORS rather than the chemical interaction was recently demonstrated by many studies [29]. It is reported that the diesel fuel with 50–330 ppm sulphur could be desulphurised to less than 10 ppm by adsorption over active carbon fiber at room temperature. The research on the adsorption removal of the ORS from the petroleum oil distillates seems to be attractive; however, it is still in its preliminary stages. Adsorption removal of the sulphur compounds could prove its economic feasibility and efficiency at the industrial level. It could rather be promising for further development and improvement. The challenge is to find

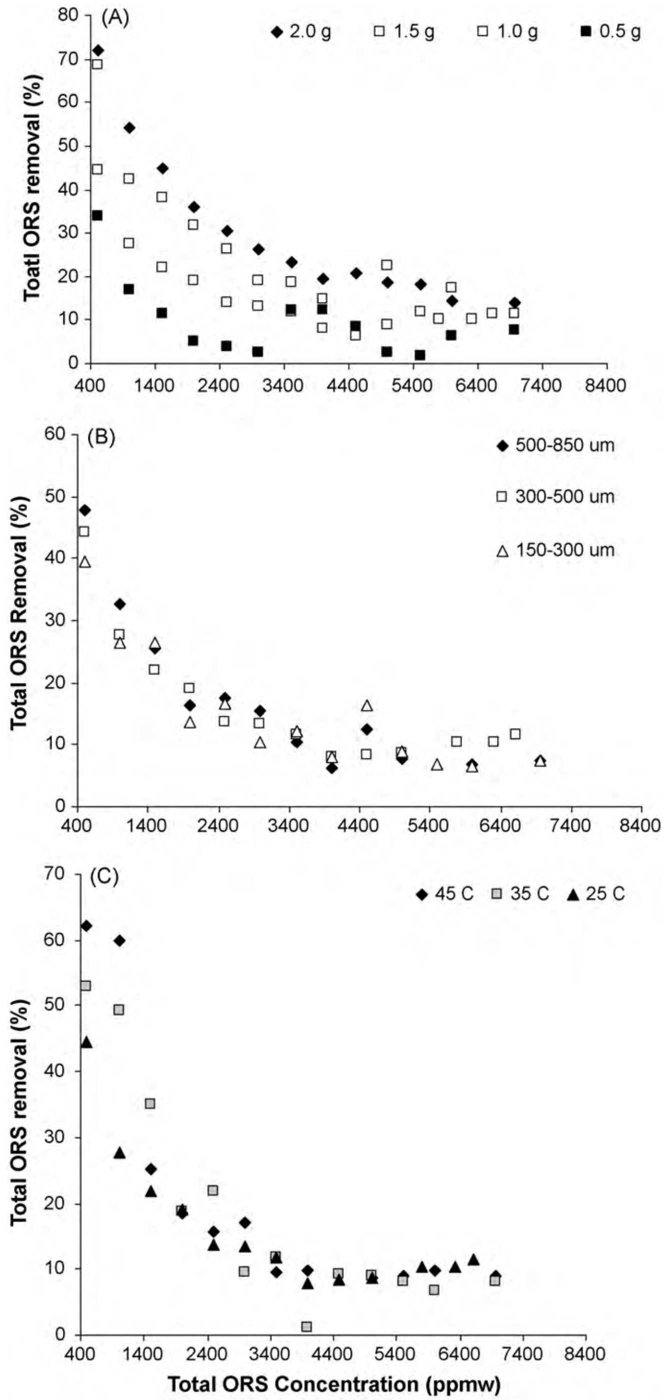

Fig. 1. Effect of mass (A), particle size (B) and temperature (C) on the adsorption of ORS onto AC.

a proper sorbent with high capacity and selectivity toward the polyaromatic sulphur compound and to be regenerable. The experimental results were plotted and treated with Langmuir isotherm, uncommon isotherm shapes were obtained. Therefore, it was not fitted to the experimental results which might reflect a complex nature of adsorbing the ORS onto the AC. However, this behaviour gives an indication on the complex adsorption mechanisms.

3.2.1. *Effect of mass of adsorbent*

Effect of the AC mass on the total ORS removal was studied over a wide mass range: 0.5–2.0 g and the results were depicted in Fig. 1. The total ORS content in the diesel fuel at low concentration was shifted from 500 ppm, the original content before adsorption, down to 141 ppm after adsorption. A substantial quantitative removal of the total ORS species from the diesel fuel by the adsorption process over the AC was obviously achieved. In the contrary, a slightly small shift was observed for the adsorption of a high concentration of the ORS onto the AC. This could be attributed to the aromatics present at a high sulphur concentration in the diesel fuel strongly compete with the ORS for the available adsorption active sites. Aromatics in the diesel fuel sample (∼22%, m/m) also possess a considerable polarisability, which is more pronounced for the polynuclear like species. Although the AC shows a relatively higher percentage removal in terms of adsorbing the sulphur containing compounds it is not directly linked with the surface area and/or porosity. However, the sulphur and oxygen content of the AC could be comprised in this respect.

In fact, the AC mass has a large effect on removal of the ORS. At 3000 ppmw, the ORS percentage removal values were 2.5%, 13.3%, 19.25, and 26.8% at 0.5, 1.0, 1.5, and 2.0 g, respectively. A clear picture was observed at 3000 ppmw and the process seems to be very complex to be explained.

3.2.2. *Effect of particle size*

Fig. 1 shows total ORS adsorption at 25 °C under various total ORS concentrations by the AC sample having three different particle sizes. For these particle sizes, the slightly different equilibrium steady-state values were attained. The amount of total ORS adsorbed at different total ORS concentrations was changed depending on the particle size of the sample. When the total ORS concentrations were decreased and the particle size of the sample was increased, the amount of the total ORS adsorbed increased. It is clear that particle size has a slight effect in total ORS adsorption on the AC especially at high levels (>2400 ppmw). On average, the removal of total ORS was about 8% at 5000 ppmw level regardless the particle size of the AC. A slight deviation in percentage removal was noted at 500 ppmw and this observation will be discussed later. This behaviour indicates that the mechanism of adsorption does not depend only on the particle size (i.e. surface area or channels) [30].

3.2.3. *Effect of temperature*

Effect of temperature on removal of the ORS was studied at wide concentration range from 500 to 7000 ppmw and at 25, 35, and 45 °C. The adsorption behaviour of the ORS is presented in Fig. 1. Generally speaking, temperature has a large effect on removal of total ORS over the range 500–2400 ppmw and at higher concentration range the temperature has little or no effect on total ORS removal. For example, at 3500 ppmw the percentage removal of total ORS was 11.62%, 11.65% and 10.5% at 25, 35, and 45 °C, respectively. The reason is considered to be the fact that during the adsorption, the organosulphur molecules loose their kinetic energies, so that the adsorption became an exothermic process. Therefore, the higher the adsorption temperature, the lower would be the amount adsorbed. At lower concentration, the adsorption is endothermic. While at higher concentrations there is some kind of saturation and there is no effect.

The earlier observation may indicate that the ORS adsorbed on the external surface of the adsorbent. On the other hand, mass of adsorbent has a significant effect on the ORS uptake. The percentage removal of the ORS has been increased by 112% by increasing the mass from 0.5 to 2.0 g. The earlier observation is often occurring because more active sites are available for adsorption at higher masses. The process of the ORS removal is endothermic and this is clear from the data presented in Table 3. The percentage removal has been increased from 44.4 to 62.2 by increasing solution temperature from 25 to 45 °C. Using Clausius–Clapeyron equation [31], the enthalpy and entropy of the adsorption process (ΔH_{ads} and ΔS_{ads}) were estimated and found to be 13.3 kJ/mol and 75.0 J/mol/K. Phys-

Table 3
Percentage removal of ORS compounds at 500 ppmw level and at different experimental conditions.

Experimental parameter	ORS removal[d]
Particle diameter[a] (μm)	
150–300	39.4
300–500	44.4
500–850	47.7
Carbon mass[b] (g)	
0.5	33.8
1.0	44.4
1.5	68.4
2.0	71.8
Temperature[c] (°C)	
25	44.4
35	52.9
45	62.2

[a] Mass: 1.0 g, $T = 25\,^{\circ}\mathrm{C}$, diesel volume: 20 mL, shaking time: 3 days.

[b] Particle diameter: 300–500 μm, $T = 25\,^{\circ}\mathrm{C}$, diesel volume: 20 mL, shaking time: 3 days.

[c] Particle diameter: 300–500 μm, diesel volume: 20 mL, shaking time: 3 days.

[d] The presented data were taken as average of three or four trials (RSD ± 4.5%).

ical adsorption and chemisorption can be classified, to a certain extent, by the magnitude of the enthalpy change. It is accepted that bonding strengths of 84 kJ/mol or less are typically those of physical adsorption type bonds. Chemisorption bond strengths can range from 84 to 420 kJ/mol [32]. Based on this, the adsorption of polar ORS by hydrophilic AC appears to be a physical adsorption process. The positive value of ΔS_{ads} indicates that the total entropy of the system has been increased after the ORS removal. Removal of the ORS by the AC is a spontaneous process, the estimated ΔG_{ads} were −9.1, −9.8, −10.6 kJ/mol at 25, 35, and 45 °C, respectively. The maximum removal of the ORS (~72%) was observed at the following conditions: particle diameter: 300–500 μm, temperature: 25 °C, diesel volume: 20 mL, ORS level 500 ppmw, mass of the AC: 2 g, and shaking time: 3 days.

For more investigation, the percentage removal of the ORS at different experimental conditions and at 500 ppmw level is presented in Table 3. As shown in Table 3, the removal of the ORS was not highly affected by changing the diameter of the adsorbent and a better uptake was observed at larger diameter.

3.3. FTIR analysis

Understanding the mechanism of the ORS adsorption on the adsorbent surface is essential for the removal of the ORS from liquid fuel [30]. The ORS present in fuel are of varying chemical and physical properties and as a result, interact differently with various types of adsorbents. The driving force for adsorption results from: (i) specific character of the solute relative to the particular solvent (i.e. solubility) and (ii) a specific affinity of the solute for the solid. This kind of attraction may be predominantly one of electrical, van der Waals or of a chemical nature. Consequently, the surface chemistry of the adsorbents and its effect on the adsorption process was investigated in order to interpret the ORS adsorption results on various adsorbents.

Fourier transform infrared (FTIR) technique is an interesting application for studying the interaction between an adsorbate and the active groups on the surface of the adsorbent. Parameters like particle size and temperature play very important roles in determining the adsorption mechanism [30]. A systematic approach relating the ORS adsorption performance of the AC to their surface chemistry was investigated.

The surface chemistry of the adsorbent and its effect on the adsorption process was investigated in order to interpret some results of the ORS adsorption experiments. Infrared spectra were useful in identifying functional groups since many have characteristic stretching frequencies between 4000 and 1600 cm^{-1}. The region between 1600 and 400 cm^{-1} is referred to as the fingerprint region. Absorptions in this region are unique for each compound and may be used to confirm that two substances are identical. An increasing awareness of the effect of the chemistry of the adsorbent surface on the adsorption behaviour at the solid/liquid interface allowed the development of techniques that characterised the main functional groups on the adsorbent surface.

The adsorptive capacity is not only determined by the adsorbent's textural porous structure but is also influenced by the chemical structures of the surface. This is because on the adsorbent surface there might be unpaired electrons, incompletely saturated valences and/or certain functional groups, which would undoubtedly, influence the surface attraction force and ultimately the adsorptive capacity, particularly when additional amounts of adsorbate are taken up onto the adsorbent via chemisorption. Since the ORS are acidic compounds, active sites responsible for adsorption should have a basic character. The basic sites have been related to the surface oxygen.

FTIR was mainly used as a qualitative technique for the evaluation of the chemical structure of carbon materials. It was not easy to get good spectra because carbons are black materials that absorbed almost all of the radiation in the IR spectrum, and the peaks obtained were usually a sum of the interactions of different types of groups [8].

Functional surface groups of the AC sample were examined by the FTIR and Boehm titration. Fig. 2 represents the FTIR spectrum of the AC sample. All of the samples show a broad band between 900 and 1300 cm^{-1} region. The broad band extended between 900 and 1300 cm^{-1} is assigned to both –C–O stretching and –O–H bending modes of alcoholic, phenolic, and carboxylic groups [33]. Loaded AC (7000 ppm) sample has much stronger peaks in the 2700–3000 cm^{-1} region (representing aliphatic CH, CH_2, CH_3 stretching modes). It is given that the 1540–1800 cm^{-1} band was associated with C=O stretching mode in carbonyls, carboxylic acids and lactones, whereas the 1000–1440 cm^{-1} band was assigned to the C–O stretching and O–H bending modes in phenols and carboxylic acids.

Shifts or changes of these peaks indicate interactions of the ORS with the functional groups onto the AC surface, and can be interpreted as adsorption on neutral sites. As it is shown from Fig. 2 (AC-500 ppm) a slight shift is observed for the 3446 and 1114 cm^{-1} bands. This would be attributed to interaction of the ORS onto the O–H groups on the surface of the AC. While changes were observed

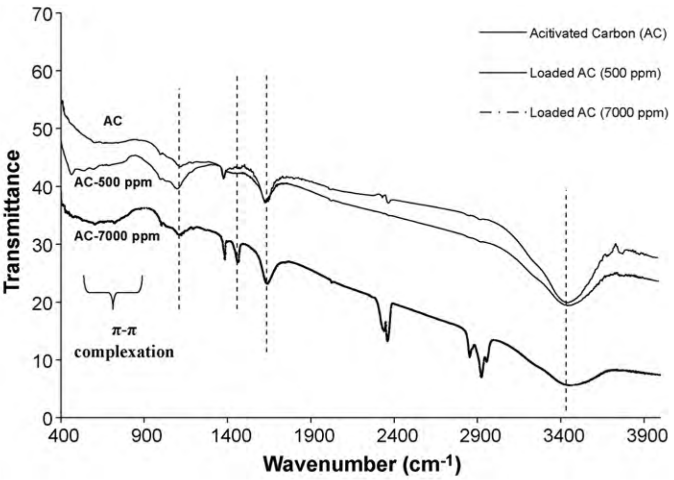

Fig. 2. FTIR spectra of AC before and after removing total ORS.

Table 4
Peak assignments for the AC before and after ORS adsorption.

Group or functionality	Assignment peak/region (cm^{-1})		
	AC	AC-500 ppm	AC-7000 ppm
Alcohol (O–H stretching), phenol (O–H stretching)	3446	3436	3460
Carbonyls, carboxylic acids and lactones	1624	1624	1635
C–O stretching and O–H bending modes in phenols and carboxylic acids	1114	1097	1109
Methylene scissoring	–	–	1463
Methylene asymmetric C–H stretching	–	–	2929
Methylene asymmetric C–H bending	1375	1375	1384
Out-of-plane C–H bending (aromatic)	900–690		

for AC-7000 ppm at 3446, 1624, 1114, and 1375 cm^{-1}. New peaks were also detected at 1463 and 2929 cm^{-1} (Table 4). These changes could be attributed to the involving of the O–H groups and the carbonyls, carboxylic acids and lactones groups in the adsorption of the ORS from diesel fuel. Here, it would be expected that all ORS (aliphatic and aromatic) participate in the adsorption process. This phenomenon is supported by formation of new peaks when a high ORS (AC-7000 ppm) was used in the adsorption. While, only aromatic ORS were participated in the adsorption process when low ORS concentration was used.

The following FTIR signals were observed in the spectrum of the AC 1105, 1382, 1652, and 3412 cm^{-1}. The earlier signals are attributed to C–OH stretching, carboxylic acid group, lactonic group, and alcoholic groups. In fact, FTIR revealed the polar nature of surface functional groups of the AC. Two spectra were also taken, the AC after removal of low level ORS (500 ppmw) and the AC after removal of large amount of the ORS (7000 ppmw). The spectrum of the AC-500 ppmw was identical to the original the AC and no new peaks appeared in the spectrum. However, the spectrum the AC-7000 ppmw retained the original beside four new peaks appeared at 1456, 2355, 2846, 2918 cm^{-1}. In fact, the appearance of new peaks could be attributed to: (a) the ORS that accumulated at the surface and this is possible because the earlier peaks are attributed to polar S–C bond stretching and bending, (b) adsorption of the ORS by polar functional groups of the AC may affect their strength and hence create new types of absorptions bands, and (c) the new peaks could be attributed to the π–π interactions that developed between cyclic ORS and the sheets of the AC. In conclusion, FTIR indicate the involvement of surface functional groups of the AC in the uptake of the ORS.

During batch adsorption experiments, a gas was evolved. This gas might be H_2S forms via C–S bond cleavage in thiophene-derived carbocations to form unsaturated fragments on Brønsted acid sites [1].

A clear change in the spectral range, 900–690 cm^{-1}, for both loaded samples (loaded AC-500 and loaded AC-7000) was observed. This spectral range would be attributed to the π–π interactions between the aromatic nature of the ORS and aromatic sheets of the AC. The π–π complexation bond is typically a weak bond that can be formed between the adsorbent and adsorbate [34]. The extent of π-complexation between the adsorbate and adsorbent depends, for a given adsorbent, on the density of the π-electrons in the adsorbate molecule. Thus, very strong bonds can be formed with molecules with more than two double bonds (e.g., dienes), triple bonds, and polynuclear aromatics. At the same time, for a given adsorbate, the adsorbent can be tailored to yield the desired bond strength, by choosing the appropriate cation.

The results revealed that the aromatics present in the diesel fuel strongly compete with the ORS for the available adsorption active sites. Diesel fuel typically contains a considerable amount of aromatics in addition to relatively small amounts of refractory sulphur containing compounds. Thus, in the adsorption process, a likely tough and mandatory competition between aromatics and the sulphur containing compounds for the active sites will detriment the adsorbent capacity and selectivity as well. In such a competitive environment, adsorbent identity definitely plays a role in this respect.

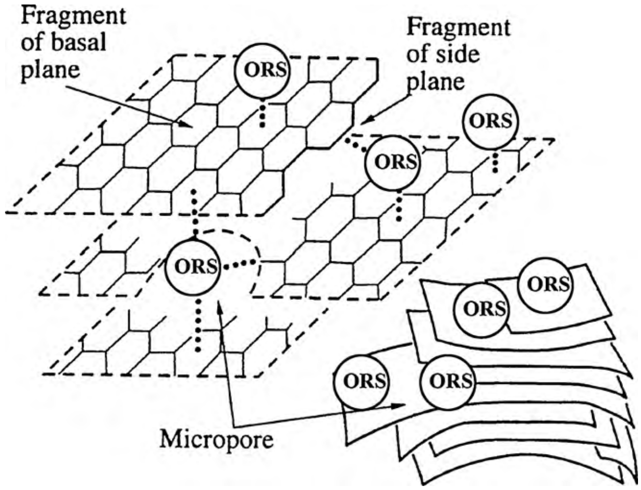

Fig. 3. Probable positions of ORS adsorption on the surface of the AC.

The first process may take place near the exterior surface of the AC particles and the external functional groups will participate in the adsorption. The second process may take place on the entire surface of the surface and results in a uniform distribution of adsorbed ORS. The ORS adsorbed on the AC surface resulting in the formation of π complexes with the C=C fragments of the AC network. On the AC surface at least three types of adsorption sites might occur on: basal plane, edge plane and micropores, as shown in Fig. 3.

4. Conclusions

This study would end up with following conclusions: (1) the AC is an expensive adsorbent, however, it showed an excellent adsorption for the ORS present diesel, (2) The removal capacity of the AC is high when the ORS present at lower level (500 ppmw) and the capacity is reduced when the level reached 7000 ppmw, (3) The removal of the ORS at 500 ppmw is highly affected by the AC mass and temperature, while, not affected by particle size. Thermodynamic studies showed that the ORS adsorption is a physisorption process with ΔH around 13 kJ/mol, (4) The removal of the ORS is a favourable process over the temperature range 25–45 °C, and (5) To a large extent, FTIR studies revealed that surface functional groups played a significant role for attracting the ORS and the adsorption mechanism is mainly π–π attraction.

Acknowledgements

The authors would like to thank the Ministry of Higher Education and Scientific Research-Scientific research Fund/Jordan for the financial support of the project “Selective Adsorption of Sulphur Compounds in Diesel Fuel Using Novel Jordanian Natural Adsorbents” within the scientific research fund programme-2008, project reference no. 2008/05/1/s. Financial support from the Royal Scientific Society/Jordan is also gratefully acknowledged. The authors also greatly thank Mr. Abd Alwhab Badawi, Mr. Habib Al-Ghoul, Eng. Nour AlJammal, and Eng. Da’a Aljelani for technical assistance on the experimental parts in this project.

References

[1] A. Chica, G.S. Karl, I. Enrique, Effects of zeolite structure and aluminium content on thiophene adsorption, desorption, and surface reactions, Appl. Catal. B: Environ. (60) (2005) 231–240.
[2] D. Stirling, The Sulfur Problem: Cleaning up Industrial Feedstocks, The Royal Society of Chemistry, Cambridge, UK, 2000.
[3] J.G. Speight, The Desulfurization of Heavy Oils and Residua, second ed., Marcel Dekker, USA, 1999.
[4] A.A. Yahia, S.B. Hisham, Sulfur removal from model diesel fuel using granular activated carbon from dates stones activated by $ZnCl_2$, Fuel (88) (2009) 87–94.
[5] G.P. Jung, H.K. Chang, B.Y. Kwang, P. Jong-Ho, H. Sang-Sup, C. Soon-Haeng, K. Jong-Nam, Reactive adsorption of sulfur compounds in diesel on nickel supported on mesoporous silica, Appl. Catal. B: Environ. (81) (2008) 244–250.
[6] M.B. Vinay, H.K. Chang, G.P. Jung, H. Sang-Sup, C. Soon-Haeng, K. Jong-Nam, Desulfurization of diesel using ion-exchanged zeolites, Chem. Eng. Sci. 61 (2006) 2599–2608.
[7] A.B.M.N. Allwar, A.B.M.N. Mohd, Textural characteristics of activated carbons prepared from oil palm shells activated with $ZnCl_2$ and pyrolysis under nitrogen and carbon dioxide, J. Phys. Sci. (19) (2008) 93–104.
[8] W. Shen, L. Zhijie, L. Yihong, Surface chemical functional groups modification of porous carbon, Recent Patents Chem. Eng. (1) (2008) 27–40.
[9] Y. El-Sayed, T.J. Bandosz, Adsorption of valeric acid from aqueous solution onto activated carbons: role of surface basic Sites, J. Colloid Interface Sci. (273) (2004) 64–72.
[10] Y.H. Li, C.W. Lee, B.K. Gullett, The effect of activated carbon surface moisture on low temperature mercury adsorption, Carbon (40) (2002) 65–72.
[11] Mustafa F, Al-Ghouti MA., Khalili FI., Al-Degs YS. Characteristics of organosulphur compounds adsorption onto Jordanian zeolitic tuff from diesel fuel. J. Hazard. Mater., doi:10.1016/j.jhazmat.2010.06.003.
[12] B. Castro, M.J. Whitcombe, E.N. Vulfson, R. Vazquez-Duhalt, E. Bárzana, Molecular imprinting for the selective adsorption of organosulphur compounds present in fuels, Anal. Chim. Acta (435) (2001) 83–90.
[13] J. Aburto, A. Mendez-Orozco, S. Le Borgne, Hydrogels as adsorbents of organosulphur compounds currently found in diesel, Chem. Eng. Process. (43) (2004) 1587–1595.
[14] R. van Rheinberg, K. Lucka, H. Köhne, T. Schade, J. Andersson, Selective removal of sulphur in liquid fuels for fuel cell applications, Fuel (87) (2008) 2988–2996.
[15] A. Zhou, X. Ma, C. Song, Effects of oxidative modification of carbon surface on the adsorption of sulfur compounds in diesel fuel, Appl. Catal. B: Environ. (87) (2009) 190–199.
[16] H. Bamufleh, Single and binary sulfur removal components from model diesel fuel using granular activated carbon from dates’ stones activated by $ZnCl_2$, Appl. Catal. A: Gen. (365) (2009) 153–158.
[17] ASTM D3838-05 Standard Test Method for pH of Activated Carbon, vol. 15.01.
[18] J.S. Noh, J.A. Schwarz, Estimation of the point of zero charge of simple oxides by mass titration, J. Colloid Interface Sci. (130) (1989) 157–164.
[19] J.P. Chen, M. Lin, Equilibrium and kinetic of metal ion adsorption onto a commercial H-type granular activated carbon: experimental and modelling studies, Water Res. (35) (2001) 2385–2390.
[20] T. Otowa, Y. Nojima, T. Miyazaki, Development of KOH activated high carbon and its application to water purification, Carbon (35) (1997) 1315–1319.
[21] ASTM D2622-08 Standard Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry, vol. 15.01.
[22] P.J.M. Carrott, F.L. Conceição, M.M.L. Ribeiro Carrott, Use of n-nonane pre-adsorption for the determination of micropore volume of activated carbon aerogels, Carbon (45) (2007) 1310–1313.
[23] K. Laszlo, K. Josepovits, E. Tombacz, Analysis of active sites on synthetic carbon surfaces by various methods, Anal. Sci. (17) (2001) 741–744.
[24] Y. Chun, G. Sheng, C. Chiou, B. Xing, Compositions and sorptive properties of crop residue-derived chars, Environ. Sci. Technol. (38) (2004) 4649–4659.
[25] M. Mazet, B. Farkhani, M. Baudu, Influence of heat or chemical treatment of activated carbon onto the adsorption of organic compounds, Water Res. (28) (1994) 1609.
[26] J. Mattson, H. Mark, Activated Carbon: Surface Chemistry and Adsorption from Solution, Marcel Dekker, New York, 1978.
[27] M. Jiang, T.N. Flora, R. Ataur, P. Viral, Flow calorimetric and thermal gravimetric study of adsorption of thiophenic sulfur compounds on NaY zeolite, Thermochim. Acta (434) (2005) 27–36.
[28] H. Cui, Q.T. Scott, A.R. Mark, Removal of sulfur compounds from utility pipelined synthetic natural gas using modified activated carbons, Catal. Today (139) (2009) 274–279.
[29] H. Farag, Selective adsorption of refractory sulfur species on active carbons and carbon based CoMo catalyst, J. Colloid Interface Sci. (307) (2007) 1–8.
[30] M.A. Al-Ghouti, M.A.M. Khraisheh, S.J. Allen, M.N. Ahmad, The removal of dyes from textile wastewater: a study of the physical characteristics and adsorption mechanisms of diatomaceous earth, J. Environ. Manage. (69) (2003) 229–238.
[31] C. Namasivayam, D. Kavitha, Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste, Dyes Pigments (54) (2002) 47–58.
[32] S. Faust, O. Aly, Adsorption Processes for Water Treatment, Butterworth Publishers, USA, 1987.
[33] V. Gaur, A. Sharma, N. Verma, Preparation and characterization of ACF for the adsorption of BTX and SO_2, Chem. Eng. Process. (45) (2006) 1–13.
[34] R.T. Yang, Adsorption, John Wiley & Sons Inc., USA, 2003.