

Desulphurization of commercial diesel fuel using carbon-based metal oxide nanocomposites

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Research Article

Keywords: diesel desulphurization, carbon-based metal oxide, adsorption, nanocomposite, graphite oxide

Posted Date: March 23rd, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-353427/v1>

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Abstract

This paper presents a slight on desulphurization process of the commercial diesel fuel using the carbon-based metal oxide nanocomposites such as graphene oxide, ZnO, rGO as a nano-adsorbent, activated carbon (PAC and AC) and charcoal Granular active carbon (GAC) to produce a fuel of less than 10 ppm sulphur content. The synthesised of sorbents were achieved using incipient impregnation, microwaved-assisted and chemical exfoliation methods. The materials were characterized using Thermogravimetric Analyzer (TGA), Fourier transform infrared spectroscopy (FTIR) and X-ray diffractometer (XRD), Brunauer, Emmett and Teller (BET). The examination effect of operating conditions on the adsorption capacity with DBT and Sulphur compounds adsorption, the isotherms and the adsorption kinetic models were evaluated. The experimental data for PAC and AC were well suited to Freundlich isotherm and pseudo second-order kinetic models. The results shown that the sulphur feed concentration, the space velocity and the functional groups of the adsorbents have a considerable effect on the adsorption. In addition, it was observed that the temperature in the range of 30 to 80°C has a significant effect on the adsorption of Sulphur compounds from diesel fuel using 20 wt% of sorbents. The rGO substrate which contained abundant oxygen functional groups was confirmed to promote the dispersion metal oxide and increased the adsorption efficiency of sulphur compounds (H_2S and SO_2) by providing oxygen ions weakly bound to the sulphur molecules. For the desulfurization process by adsorption, PAC and AC exhibited a better affinity for 80% removal of sulphur compared to the GAC and GO.

1. Introduction

The Sulphur compound has been known as a contaminant in different forms to the environment and causes environmental damages especially as acid rain, corrosion of equipment and deactivation of catalysts in the industries ^[1, 2]. Diesel fuel has been known to be the principal contributor to the environmental pollution after emission from the automotive combustion engines ^[3]. Therefore, the reduction of the released sulphur and sulphur oxides into the air from the combustion increases attention on the chemistry of diesel fuel processes with regard to challenges on desulphurisation ^[4, 5]. Hence, several diesel desulphurization processes have been proposed and used in the industry to produce low diesel sulphur content from various material resources such as coal, natural gas, crude oil as well as an under-product. At the same time, an increase attention on the absorbents has been directed to carbon-based materials such as activated carbon, carbon nanotubes and graphene ^[6 - 9]. The main activities causing emissions of SO_x , NO_x , CO_2 and CO pollutants are associated with transportation and combustion of diesel fuels from a combustible engine which led to new regulation to lower sulphur content in fuel oils by responsible government. These emissions can be decreased through the reduction/removal of the amount of sulphur compounds contained in the diesel fuel. Different desulphurization processes can be used to achieve this. It is commonly implemented using the catalytic hydrogen processing techniques, or by removing sulphur compounds contained in stack gases ^[10, 11]. However, the small changes in the fuel quality can result in a good control of the environmental impact due to pollution from the end-users ^[12, 13]. Various studies have investigated the adsorption of different

sulphur compounds, including BT, DBT and 4,6 –DMDBT, modified composite oxides, activated carbon, mesoporous and microporous zeolites, etc. from both model and commercial fuels [14, 15]. Activated carbons (AC) are identified by their low cost, both chemical and thermal stability under anoxic conditions, high and tuneable surface area that is considerably affected by the precursors of carbonaceous materials and the preparation techniques, modification receptivity, and high adsorption affinity for both aromatic and refractory sulphur compounds [8,16, 17]. The gas-adsorbing carbons typically have more micropores whereas; the liquid-adsorbing carbons have crucial mesopores that are significant because of the great size of liquid molecules [9, 11]. According to Bamufleh [1], granular activated carbon (GAC) was made from dates' stones through chemical activation using $ZnCl_2$ as an activator was employed as a sorbent for sulphur compounds removal [2, 6]. In the area of adsorptive desulphurization, the study found that activated carbons can remove both nitrogen compounds and refractory sulphur compounds simultaneously [2,4]. Al Zubaidy [18] investigated the adsorptive desulphurization process using carbonized date palm kernel powder and commercial activated carbon at room temperature. Diesel oil used had a total sulphur content of 410 ppmw. Used activated carbon decreased the sulphur content by more than 54% as results, whereas the carbonized date palm kernel powder exhibited lower sulphur removal efficiency. Again, the work done by Chandra and Kumar [2] in which response surface methodology was applied for sulphur removal from model oil (dibenzothiophene; DBT dissolved in isooctane) using commercial activated carbon (CAC) as a sorbent material. Lonkar and his colleagues [19] worked in the field of adsorptive desulphurization of H_2S and developed a simple and scalable approach for one-step synthesis of CuO/reduced graphene nanocomposites. The objectives of this study are to evaluate the desulphurization on commercial diesel fuel using metal carbon-based nanocomposites, re-generable performance of activated carbon-based adsorbents and graphene-based adsorbents. Then synthesize MeO/GAC and MeO/GO nanocomposites with the use of chemical and thermal methods. The adsorbents characterisation before and after each sulphidation stage was performed using different experimental analysis technics and procedures. In that regards, the investigation effects of each operational conditions on desulphurization efficiency by using different sorbents (PAC, GAC, AC, GO, ZnO, rGO) at different wet percentages (2 wt% to 20 wt%). The different temperature rages were used to study the adsorption isotherms and the kinetic models of sorbents for each experimental sample. The characterisation of rGO and ZnO was conducted at different temperatures while bore in mind to produce diesel fuel with sulphur content below 10 ppm. The effect on feedstock used against the variables such as time, temperatures, concentration, the process efficiency of the sulphur adsorption from the feed to the final product were also taken in consideration.

2. Experimental

2.1. Preparations

2.1.1. Preparation of model diesel

The raw diesel fuel material “commercial ultra-low Sulphur 50 ppm Diesel” was purchased from a local petrol station. A wide variety of materials, including metal ions loaded on mesoporous materials, mixed metal oxides, metal modified activated carbon, supported metals and others were tested as adsorbents. Most of these materials were synthesized in our laboratory to treat the diesel fuel feedstock. The adsorbent was stored in a stainless-steel column with an internal diameter of 0.36 m, length of 1.2 m and the adsorbent bed volume of 2.49 mL. The sulphur removal efficiencies were done with different carbon-based adsorbents for the adsorptive in diesel fuel while bear in mind the ignition quality of diesel fuel after the absorption process.

2.1.2. Preparation of graphite oxide using a chemical exfoliation method

Graphite oxide (GO) was synthesized using the modified Hummers method [20]. Sulphuric acid (Minema chemicals, 95.0 – 98.0%) as a strong oxidizing acid was mixed with sodium nitrate (Labchem, $\geq 85\%$ by weight). Once the sodium nitrate dissolved, the mixture of graphite powder (Control laboratories, $\geq 99.99\%$) was added and the mixture ultrasonicated to exfoliate the GO sheets. This mixture was then put in an ice bath and continuously stirred as potassium permanganate (Labchem, $> 99.0\%$) was added dropwise for about 30 mins. The mixture was then transferred to a heated magnetic stirrer where the oxidation process took place for 20 additional hours. Once the mixture has cooled down to room temperature, the oxidation reaction was completed by progressively adding a solution of hydrogen peroxide (Labchem, 30% by weight in H_2O) and de-ionized water. The colour of the mixture changed from dark brown to bright yellow. Finally, the GO solids centrifuged and washed twice using a solution of hydrogen chloride (Labchem, 37%) and de-ionized water. The filtrate was then rinsed until the pH of the de-ionized water went neutral. The graphite oxide was then dried in an oven at $80^\circ C$ for 10 hrs.

2.1.3. Synthesis of adsorbents using a microwave-assisted chemical reduction method

The metal oxide nanocomposites were synthesized by dissolving a known mass (weight at different mass, 20 to 200 g) of either granular activated carbon (monitoring and control laboratories) and graphite oxide, in ethylene glycol (Labchem, Anhydrous, 99.8%), the mixture was then ultra-sonicated for 1hr. Sodium hydroxide solution (Labchem, $\geq 97.0\%$) was added, and the mixture ultra-sonicated for a further 30 mins. Aqueous metal acetate solutions (zinc, copper, manganese, cobalt) (Monitoring and control laboratories, $\geq 98.0\%$) with the desired weight of metal species (5 to 150 mg) were added drop wise into the mixture. The mixture was chemically reduced using a hydrazine solution (Labchem, 35 wt%). The mixture was then further reduced using a hydrothermal method, by exposing it to microwave irradiation for periods ranging from 3 to 10 mins. Once the mixture had cooled down to an ambient temperature, was centrifuged and washed with de-ionized water until the rinsing water pH went to neutral. The metal oxide nanocomposites dried in an oven for approximately 18 hrs.

2.1.4 Synthesis of adsorbents using an incipient impregnation/ thermal reduction method

Metal species of manganese zinc, cobalt and copper were loaded on granular activated charcoal (GAC) (monitoring and control laboratories) and graphite oxide (GO) using the incipient wetness impregnation

method. First, the amount of de-ionized water that was fully absorbed by (20 to 250 mg) mass of GAC and GO. Metal acetates carefully weighed with the desired weight percent of metal species and dissolved in de-ionized water while keeping in mind the water solubility of the acetates. A slowly addition of aqueous solutions of metal acetates was stirred in carbonaceous materials. The resulting mixtures was then ultra-sonicated for 2 hrs, by ensuring a uniform deposition. The mixture was then dried in an oven for approximately 18 to 24 hrs at 120°C. The solids result was torched at temperatures ranging from 200°C to 500°C.

2.2. Carbon materials

The range of three activated carbons (powdered activated carbon (PAC), activated carbon (AC) and granular activated charcoal (GAC)) were used as adsorbents in this study and were purchased from Monitoring & Control Laboratories company.

2.3. Characterizations

The morphology of the MeO/GO and MeO/GAC sorbents was determined using a Scanning Electron Microscope (SEM), whereby the cross-sectional area of adsorbents was observed before and after each sulphidation regeneration cycle. The observation provided information such as pores, size, shape, distribution, element determination and density. An X-Ray Diffractometer (XRD) was used to identify and characterize the crystal phases present on the sorbents, their atomic structure and size. An X-ray beam scattered when it hits the atoms in a crystal. XRD patterns were generated using a stationary X-ray source (typically Cu K α , $\lambda = 0.154$ nm operating at 30 mA and 35 kV with a scan rate of 1 deg/min), and the scattered X-rays were detected by a mobile detector.

The Fourier Transformer Infrared Spectroscopy (FTIR) was used to identify the types of functional groups present on the surface of the MeO/GO and MeO/GAC sorbents before and after each sulphidation regeneration cycle. Analysis was performed using a Nicolet Magna-IR 830 spectrometer using the Attenuated Total Reflectance (ATR) method. Brunauer, Emmett and Teller (BET) analyser was used to measure the surface area and pore size distribution of MeO/GO and MeO/GAC of sorbents. The BET measurements for pure MeO/GAC and MeO/GO composites were conducted using a Micromeritics Gemini 32375. The surface area was measured at the boiling point of nitrogen 77°K within a P/P₀ range between 0.05 to 0.5 Pa. The thermogravimetric analysis (TGA) was used to measure the mass characterization of the desulphurization samples during a given time at a given temperature. The IHFB-TGA was used as an instrument.

2.4. Performance testing

2.4.1. DBT and H₂S adsorption tests

The adsorption was carried out using batch and packed bed reactors, at varying temperatures and atmospheric pressure. In batch experiments, the investigation effects of adsorbent composition,

adsorption temperature, and mixing speed were conducted. The desulphurized diesel products were analysed using liquid gas chromatography. Experimental data used to determine the adsorbents breakthrough capacity, adsorption isotherms and kinetics. The packed bed adsorbents regenerated through solvent washing with a toluene/methanol mixture, followed by oxidation using an O_2/N_2 gas mixture. The adsorption of 200 ppm H_2S from a H_2S/N_2 gas mixture was conducted using a stainless-steel packed bed tube reactor. The syngas passed through the adsorbent bed at a fixed flow rate and adsorbent temperature. The outlet sulphur gas concentration was determined using a H_2S analyzer. The experiments (see the experimental setup Figure 1) were carried out until the output H_2S concentration reached 5 ppm from the analyzer reading [14].

The experimental breakthrough time was established when the outlet concentration of H_2S reaches 1 ppm and regeneration tests, the adsorbent spent was heated to the temperature of $600^\circ C$ in N_2 approximately for 1 hour. After the hydrothermal decomposition, the adsorbent was cooled down to the $200^\circ C$ reaction temperature in N_2 for another sulphidation reaction.

2.5. Desulphurization process

The desulphurization process with the three adsorbents was studied at different volume levels of sorbent materials (1wt% - 20 wt%), with the operating temperatures (room temperature, $30^\circ C$ and $80^\circ C$) and the contact time (1 - 3 hrs) in accordance with the following procedures:

- Three adsorbents (PAC, AC and GO/GAC) were dried at $100^\circ C$ for at least one hour and half.
- 10 L of commercial diesel fuel was mixed with adsorbents and stirred using a glass stirrer oscillating at 310 to 450 oscillations/min ranges.
- Filtration of the mixtures was performed to separate the sorbent solids from the filtrate.
- Sulphur and metal contents were analysed in the samples of diesel fuel using an ED-XRF spectrophotometer.
- During the formation of two layers, the mixture was heated in a bath water at a controlled temperature and at which the rate of sample recovery was recorded.
- A range of 2 to 20 wt% of adsorbents were mixed in the range of 10 to 20 g of dual metal oxides to the feedstock at controlled room temperature with the interval stated above to achieve equilibrium time for high sulphur removal after one hour.

3. Results And Discussion

3.1. Kinetics and Isotherm model Adsorptions

3.1.1. Kinetics models

The adsorption capacity of sorbent materials (PAC, GAC and AC) slowly increased after one hour, the increase of time had an impact on the adsorption results of sulphur compounds. The rate constants of

the adsorption processes were determined using the pseudo first order model (Equation 1).

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t / 2.303 \quad (1)$$

where:

- q_e, q_t (mg/g) were the amounts of sulphur adsorbed at equilibrium and time t (min) respectively.
- k_1 (min^{-1}) as the equilibrium rate constant of the pseudo-first-order adsorption.

The experimental made k_1 was found to be constants throughout and the plots of $\ln(q_e - q_t)$ versus t for each sorbent material (see Figure 2 A) had a R^2 of 0.9319. The results obtained showed that the experiment values of q_e do not agree with the calculated values for all the adsorbents. Thus, this demonstrates that the adsorption kinetics of sulphur compounds employing the three adsorbents does not follow the first order kinetic model. The sample temperature used for the three sorbents varied from room temperature to 80°C. But, at some point for the first order model, as the time increased, $\ln(q_e - q_t)$ showed a maximum point (Figure 2A) and slowly slopping down. Alternatively, a pseudo second order model equation (Equation 2) was employed. The calculated values q_e corresponded to the values of equilibrium capacity acquired experimentally for this model. Likewise, the graphs of t/q_t versus t were drawn. Line graphs (see Figure 2B) with R^2 of 0.9715) started a good agreement between the experimental and calculated values of q_e for all the adsorbents.

$$\frac{t}{q_t} = \frac{t}{k_2 \cdot q_e^2} + \frac{1}{q_e} t \quad (2)$$

where:

- k_2 (min^{-1}) as the equilibrium rate constant of the pseudo-second-order adsorption.
- q_e and q_t (mg.g^{-1}) are adsorption capacities at equilibrium and adsorption capacities at time t of sulphur compound adsorbed per mass of adsorbent.
- t (s) is the time taken for the sulphur compound be adsorbed.

To compare kinetics on Figure 4, the correlation on both graphs when using 20 wt% PAC for the sulphur content removal, the second order was the best as the results indicate with the higher percentage removal and the reduction for the hour used and R^2 was found to be 0.9715 compare to $R^2 = 0.9319$ of fist order using a 20 wt% of sorbent.

3.1.2. Isotherm models

3.1.2.1. Freundlich isotherm

The Freundlich adsorption isotherms for GO and GAC were done at room temperature (Figure 4). The Freundlich isotherm constants were calculated using non-linear regression and are presented in Table 2, respectively.

3.1.2.2. Langmuir isotherm

The Langmuir adsorption isotherms for GO and GAC were studied at room temperature (Figure 3). The Langmuir isotherm constants were determined using non-linear regression and are shown in Table 1.

At the equilibrium, the fitting of Langmuir adsorption on GO had R^2 of 0.9756 while GAC had R^2 of 0.9757. those two sorbents had almost the same amount of sulphur removal concentration for each 60 min contact time used. Hence the highest % desulphurisation increased on both as the time was increased from 64% to 78% on 3 hrs basis as also the change in temperatures and concentration of the sorbents. Figures 5 and 6 shown a great impact on sulphur adsorption using GO and GAC as sorbents. At equilibrium reactions, the quantities of sulphur adsorbed were impacted with the change of concentration at each interval time.

TABLE 1. Langmuir Adsorption Parameters.

Sorbent	GO			GAC		
	q_m	k_{eq}	R^2	q_m	k_{eq}	R^2
Room Temperature	381,6	$5,413 \times 10^{-5}$	0,9756	434	$3,015 \times 10^{-5}$	0,9757
30°C	278,8	$8,334 \times 10^{-5}$	1	244,8	$4,348 \times 10^{-5}$	0,9576
Ce at room temp	49,99	47,64	43,12	37,34	32,78	28,88
	25,55	23,32	19,79	16,12		
Ce at 30°C	49,99	46,67	44,46	38,68	33,31	27,12
	21,12	18,97	15,56	10,32		

TABLE 2. Freundlich Adsorption Parameters.

Sorbent	GO			GAC				
Parameter	K_f	n	R^2	K_f	n	R^2		
Room Temperature	0,004	0,749	0,9919	0,001	0,684	0,9755		
30 °C	0,001	0,579	0,994	$4,480 \times 10^{-5}$	0,410	0,9667		
80 °C	$6,17 \times 10^{-5}$	0,456	0,9646	0,001	0,677	0,9962		
Ce at room temp (GO)	49,99	47,54	42,32	38,34	34,45	30,31	28,45	25,65
Ce at 30°C (GO)	49,99	46,65	40,42	36,65	34,42	28,23	26,32	22,87
Ce at 80°C (GO)	49,99	45,04	40,46	34,68	27,53	22,56	17,56	12,36
Ce at room temp (GAC)	49,99	46,64	43,21	37,44	32,38	28,54	25,33	20,03
Ce at 30°C (GAC)	49,99	44,54	39,89	35,36	30,03	26,60	22,38	18,47
Ce at 80°C (GAC)	49,99	45,24	38,36	32,36	26,54	19,54	14,35	10,12

In the same manner, the studies on samples from the prepared commercial diesel were done using XRD, BET and TGA analysis for their surface porosity to mass characteristics. The equilibrium of sulphur removal percentages was done using a 20 wt% of the adsorbents (MeO, AC, GAC and PAC) at the temperature range from room temperature to 80°C respectively. The equilibrium and kinetics of sulphur adsorption on different adsorbents were determined using two kinetic models (pseudo first order and second order) and tested using Langmuir and Freundlich isotherm equations. An attempt to regenerate the adsorbents by ratio 1:1, 1:2 and 4:1 of methanol and toluene mixture at 30°C and 80°C. To estimate the amount of solvent needed to completely recover 4,6-DMDBT and to regenerate the adsorbent for further use, the solvent fractions were collected and analysed using the total sulphur analyser.

The results stipulate that most of the Sulphur compounds could be recovered using at least 13 cc of solvent per g of adsorbent. Experiments using model fuels have revealed that sulphur compounds are destroyed and converted to the corresponding organic fraction although no hydrogen gas was used during adsorption. The adsorbent was regenerated by treatment with H₂ gas at 450°C for 1 to 2 hrs, and then reused for the next cycle. After the solvent washed, the regenerated adsorbent was flushed with N₂ gas (45 mL/min) for about 1.5 hrs at 320°C to remove all adsorbed solvent molecules.

3.2. Metal-oxide characterizations on graphite oxide

This method was performed before by Liu ^[21] and based on the analysis results, the functional groups on rGO did take part in a critical role to report the ions on the GO surface and the aggregation of the nano-sized ZnO particles. From the SEM analysis, the ZnO particles had thin composite layers arranged in

agglomerates and dispersed on the fuel in which smaller particles of Zn ions to be deposited on rGO sheets. Thus, the roles of rGO for sulphur adsorption were not only ZnO dispersion but also the adjustment of ZnO. In addition, ZnO particles played an important role for the sulphur compounds adsorption. Other metal oxide used was, copper oxide, which was added to the ZnO/rGO composite to increase the adsorption capacity of the sulphur compounds. An increase of the Cu mol% to the one of ZnO, showed an increased capacity from 15 mol% to 45 mol% of the sulphur removal than when ZnO was alone. Various tests were performed to determine the sulphur compounds breakthrough on ZnO and ZnO/rGO in dry and wet conditions.

The DBT (Figure 5) trial tests for adsorption on graphite, GO, rGO, GAC and ZnO adsorbents in regard to the sulphur adsorption, GAC showed a greater desulphurization (89%) than others followed by rGO (68%) while the graphite (39%) had the lowest desulphurization adsorption capacity. Each trial on adsorbents used, both rGO and granular activated charcoal (GAC) showed a significant sulphur removal as a dominant sorbent than others.

With the abundant oxygen functional group in rGO turned it to have a great sulphur adsorption efficiency while the dispersion of metal oxide in the solution. Coming to GAC in regards of sulphur removal, this in turn showed the capacity to compete with a metal oxide due to homogeneous adsorption of sulphur capacity than the remaining sorbent materials from the diesel fuel. The reduction of reflux ratio in the process for the ZnO/rGO allowed their great adsorption capacities.

Figure 6 showing the sulphur removal content at given temperatures (room temperature, 30°C and 80°C) with number of sorbents (2 wt%, 4 wt%, 6 wt%, 8 wt%, 10 wt%, 16 wt%, 18 wt% and 20 wt% which is represented in colour range from blue to gold respectively). The observation on the behaviour of each wet percentage of sorbent on the sulphur removal from the sample showed 9.85 ppmv from the final product at 20 wt% and 80°C. In the same way, the sulphur content from each sample at given temperature and sorbent used gave a great removal each 60 min. The breakthrough time per wet% of adsorbent for ZnO/rGO (685 min/g) was about 10 times longer than PAC/GAC/AC (60 min/g). This could be explained either by oxygen functional groups attach to ZnO/rGO/GO composite and promoted the adsorption capacity of sulphur compounds or either by reduction of reflux ratios.

The graphene materials employed in adsorption were prepared by thermal and chemical reduction procedure, oxidation of graphite to produce GO to attain reduced rGO. A new modification of GO and rGO graphene oxides via the development of nanocomposites with oxide metals and organic molecules improved their sorption characteristics.

The effect of metal oxides and rGO composite in regard to the adsorption capacity of sulphur compounds studied the oxidation changes, specially, on metal species such as copper, zinc oxides, etc. by using crystallite analysis (XRD) (Figure 7) in the identification of the lattice energy of the. The adsorption considered two powdered activated carbon (PAC and GAC) which showed better affinity for removal of sulphur compared to GO. After depletion by reflux and microwave, the characteristic peak of

GO disappeared by eliminating the oxygen functional groups which linked the GO layers. To increase the adsorption ability of GO was done by dispersing metals onto the surface area and showed high percentage removal of sulphur compounds over four cycles which indicated good reusability as the adsorption efficiency was still above 80% over the third cycle.

In addition, the morphology changes, the chemical state of Zn and O in the ZnO matrix was also modified during the sulphidation-regeneration cycles; and it produced a decrease in adsorption capacity over multiple cycles.

3.3. Test Analysis

3.3.1 FTIR and TGA test

The use of FTIR in the identification of the functional group present on the surface of the MeO/GO and MeO/GAC sorbents and were studied before and after each sulphidation regeneration cycle. This helped on identifying the vibration on the structure formed during the contact of the metal oxides onto the prepared diesel samples. The functional groups identification on the metal oxides by FTIR, the Thermogravimetric analysis (TGA) was also performed on the sample to give a clear understand on the mass characterization after and before each desulphurization at a given interval, time and temperature during the whole process. The FTIR spectra of GO, rGO and ZnO/rGO composite (Figure 8), the composites from the microwave method (rGO-M and ZnO/rGO-M) hold stronger peaks of hydroxyl groups than that those acquired from the reflux method (rGO-R and ZnO/rGO-R). In addition, the intensity of Zn-O bond did decrease after three adsorption tests. It was also confirmed that a portion of Zn-O bond reacted with H₂S and converted to ZnS. The vibrational peaks produced by the three different components which make up of oxide groups at the broad band interval from 3250 to 3600 cm⁻¹. The -OH group stretching increased the intensity from 3250 to 1600 cm⁻¹ and shifted slightly to lower wavenumbers (1600 to 1020 cm⁻¹) and ascribed to the presence of inter- and intramolecular hydrogen bonded hydroxyl groups possessing a form association between the three different sorbent components used experimentally.

The TGA analysis method provided the particle size of ZnO deposited on the rGO surface. It was perceived that nano-size ZnO particles were deposited on the surface of rGO. Those ZnO particles are well separated and dispersed from each other on the rGO surface and displayed a good combination between rGO sheet and ZnO nanoparticles. Nevertheless, possible reason was that the rapid and short heating process by microwave decreased the particle size of ZnO and made the surface area of ZnO for the sulphur compounds adsorption increased. The sulphur content and TGA weight loss obtained from different reaction temperatures are displayed in Table 3.

TABLE 3. Surface weight loss percentages for AC, GO, ZnO, rGO, PAC and GAC at given temperature ranges on diesel fuel.

Temp (°C)	Surface weight loss (%)					
	AC	GO	ZnO	rGO	PAC	GAC
100	88	95	88	90	100	99
140	86	90	84	87	95	90
180	80	90	76	70	83	81
220	68	74	65	64	74	70
260	55	66	56	60	65	65
300	40	56	55	55	56	50
340	33	44	43	44	42	40
380	22	31	33	36	35	35
420	05	03	10	05	08	03

The weight losses in all the samples produced by heating in TGA apparatus are in accordance with the amount of sulphur measured by the apparatus with the temperature range from 100°C temperature to 420°C. For higher Sulphur concentrations in the feed stream, it was seen that, room temperature is enough to achieve high sulphur loading. Therefore, nearly no sulphur loss from these adsorbents would occur in full-scale applications when produced through high temperature impregnation processes. However, more than 260°C temperatures are not desirable since they will produce other pollutants, such as SO_x, H₂S and SO₂, to form and decrease sulphur loading on the carbon surface.

3.3.2 BET test

The surface area and pore size distribution on the metal oxide sorbents species were characterised and analysed by BET analyser as a quantitative analysis (yield percent of carbon and carbon functionality). This was conducted with N₂ adsorption isotherm to find out the pore size distribution and surface area on each used sorbent, and the analysis shown a heterogenous surface and several sizes while the surface roughness indicated high surface area for adhering adsorbate molecules from the prepared feed diesel (Table 4).

TABLE 4. Surface area, pore volume and pore diameter of the adsorbents with 5 wt% impregnation.

Adsorbent	Surface area (m ² /g)	Pore volume (m ³ /g)	Pore diameter (Å)
AC	118	0,45	125,56
GAC	184	0,39	128,40
PAC	217	1,55	122,55
GO	799	0,06	118,30
rGO	825	0,41	120,68

The studied internal surface area from the analysis was confined to the pore structure of the adsorbent materials (AC of 125,56, GAC of 128,40, PAC of 122,55, GO of 118,30 and rGO of 120,68 in pore diameter) while keeping in mind that the pore structure as a major factor which could affect the adsorption process. Also, if the diameter of the adsorbate molecules becomes higher, the lower the adsorption would take place due to steric interferences at low pressure in the N₂ adsorption. The sulphur content removal favoured in the increase in adsorption time, temperature and concentration on all the technics and sorbents used to sulphurise the diesel fuel feedstock.

4. Conclusion

In accordance with the results obtained for commercial diesel fuel in how to reduce its sulphur content with a metal-based nanocomposite. The adsorption capacity of carbon-based adsorbents for the removal of sulphur compounds from diesel fuel was carried out. This provided essential data to model the physical and chemical adsorption process and develop an appropriate regeneration method for the spent sorbent materials for the study. Considering the loss of adsorption capacity of spent sorbent materials after several tests on adsorption regeneration cycles, the study helped to understand the overall sulphur removal process when different adsorbents were used to verify which one is effective and convenient to remove a high percentage of sulphur in a short period of time and other conditions. PAC and GAC showed a better sulphur removal affinity compared to AC, GO and rGO. The removal of sulphur capacity for the three sorbent materials was compared showing the best sulphur removal percentages in the diesel fuel samples while the equilibrium and the kinetics of the sulphur adsorption on the different sorbents were examined using the two equations of the kinetic model (pseudo first order and pseudo second-order) and the adsorption behaviour was best described by the Freundlich isothermal model.

Additionally, to microscopic characterization of GO and rGO, the spectroscopic techniques such as XPS and FTIR and diffraction techniques such as XRD were used to present the structure of the sorbents and the presence of oxygen containing functional compounds. The synthesis of the adsorbents was achieved with a variety of methods and with great control. The heat treatment at different temperature ranges, vacuum promoted exfoliation, physical incorporation of additives, and surface modifications using oxidative agents were among the few techniques employed in the synthesis processes.

Declarations

Acknowledgments

The author expresses deep gratitude to VUT (Vaal University of Technology), my supervisor Dr Kabuba, Prof Rotto and my family by providing necessary support to bring this article to this level.

Competing interests

The authors declare no competitor interest for the publication of the article

References

- [1] Bamufleh H.S. General single and binary sulphur removal components from model diesel fuel using granular activated carbon from dates' stones activated by $ZnCl_2$. *Appl. Catal. A: Gen.* **2009**, 365, 153.
- [2] Chandra V, Kumar S.R. "Studies on Adsorptive Desulfurization by Activated Carbon," *Clean-Soil Air Water.* **2012**, 40, 545.
- [3] Balinge K.R, Khiratkar A.G, Krishnamurthy M, Patle S. D, Cheralathan K.K, Bhagat P.R. Deep-desulfurization of the petroleum diesel using the heterogeneous carboxyl functionalized poly-ionic liquid. *Res. Efficient Technol.* **2016**, 2, s105 – s113.
- [4] Choi K.H, Korai Y, Mochida I, Sano Y. Selection, further activation of activated carbons for removal of nitrogen species in gas oil as a pre-treatment for its deep hydrodesulfurization," *Energy Fuels.* **2004**, 18, 644.
- [5] Ma X, Song C, Velu S, "Selective adsorption for removing sulphur from jet fuel over zeolite-based adsorbents," *Ind. Eng. Chem. Res.* **2003**, 42, 5293.
- [6] Darwish N.N. *Adsorption study of desulfurization of diesel oil using activated charcoal.* MS thesis, American University of Sharjah, Sharjah, United Arab Emirates **2015**.
- [7] Katzer J.R, Ramage M.P, Sapre A.V. Petroleum refining: poised for profound changes. *Chem. Eng. Prog.*, **2000**, 6, 41.
- [8] Jeong H.K, Lee Y.P, Lahaye J.W.E.R, Park M.H, An K.H, Kim I.J, Yang C.W, Park C.Y, Ruoff R.S and Lee Y.H. Evidence of Graphitic AB Stacking Order of Graphite Oxides. *J. Am. Chem. Soc.* **2008**, 130, 4, 1362.
- [9] Li D, Li W, Peng J, Xia H, Zhang L, Guo S, Chen G, Wang X. "Optimization of Mesoporous Activated Carbon from Coconut Shells by Chemical Activation with Phosphoric Acid," *BioResources*, **2013**, 8, 6184.

- [10] Kim J.H, Ma X, Zhou A. "Ultra-deep desulfurization and denitrogenation of diesel fuel by selective adsorption over three different adsorbents: a study on adsorptive selectivity and mechanism," *Catal. Today*, **2006**, 111, 74.
- [11] Dubey S.P, Nguyen T.T.M, Kwon Y.N, Lee C. Synthesis and characterization of metal-doped reduced graphene oxide composites, and their application in removal of Escherichia coli, arsenic and 4-nitrophenol. *J. Ind. Eng. Chem.* **2015**, 29, 282.
- [12]. Randal M.C.A. Ecotoxicity and environmental fate of diesel and diesel blends produced by Sasol's Fischer-Tropsch processes using natural gas and coal as feedstock as well as biodiesel and biodiesel blends. PhD thesis, Stellenbosch University, Stellenbosch, South Africa **2012**
- [13] De Klerk. Environmentally friendly refining: Fisher-Tropsch versus crude oil. *Green Chem.*, **2007**, 9, pp 560 – 565.
- [14] Song H.S, *Desulfurization by metal oxide / graphene composites*. UWSpace, Waterloo, Ontario, Canada **2014**.
- [15] Stanislaus A, Marafi A and Rana M.S, Recent advances in the science and technology of ultra-low sulphur diesel (ULSD) production. *Catal. Today*, **2010**, 153, 1.
- [16] Zhou A, Ma X, Song C. "Effects of oxidative modification of carbon surface on the adsorption of sulphur compounds in diesel fuel," *Appl. Catal.: B Environ.* **2009**, 3-4, 190.
- [17] Kabuba J. and Banza M. cobalt and nickel separation in hydrometallurgy using modified clinoptilolite with dialkyl phosphoric and ethylenediaminetetraacetic acid as an ion exchanger. *Can. J. Chem. Eng.* **2021**, 1
- [18] Zubaidy Al, Bin Tarsh F., Darwish N. N., Sweidan B., Abdul Majeed S., Al Sharafi A., and Abu Chacra L, "Adsorption Process of Sulfur Removal from Diesel Oil Using Sorbent Materials," *J. Clean Energy Technol.* **2013**, 1, 66.
- [19] Lonkar S.P, Pillai V.V, Stephen S, Abdala A, Mittal V. Facile in situ fabrication of nanostructured graphene – CuO hybrid with hydrogen sulfide removal capacity. *Nano-Micro Letters.* **2016**, 8, 4, 312.
- [20] Song and Ma, An overview of new approaches to deep desulfurization for ultraclean gasoline, diesel fuel and jet fuel. *J Catal. Today*, **2003**, 86, 1, 211.
- [21] Liu Y., Hu Y., Zhou M., Qian H. and Hu X., Microwave-assisted non-aqueous route to deposit well-dispersed ZnO nanocrystals on reduced graphene oxide sheets with improved photoactivity for the decolorization of dyes under visible light. **2012**. *J. Appl. Catal. B Environ.*, 125, 425.

Figures

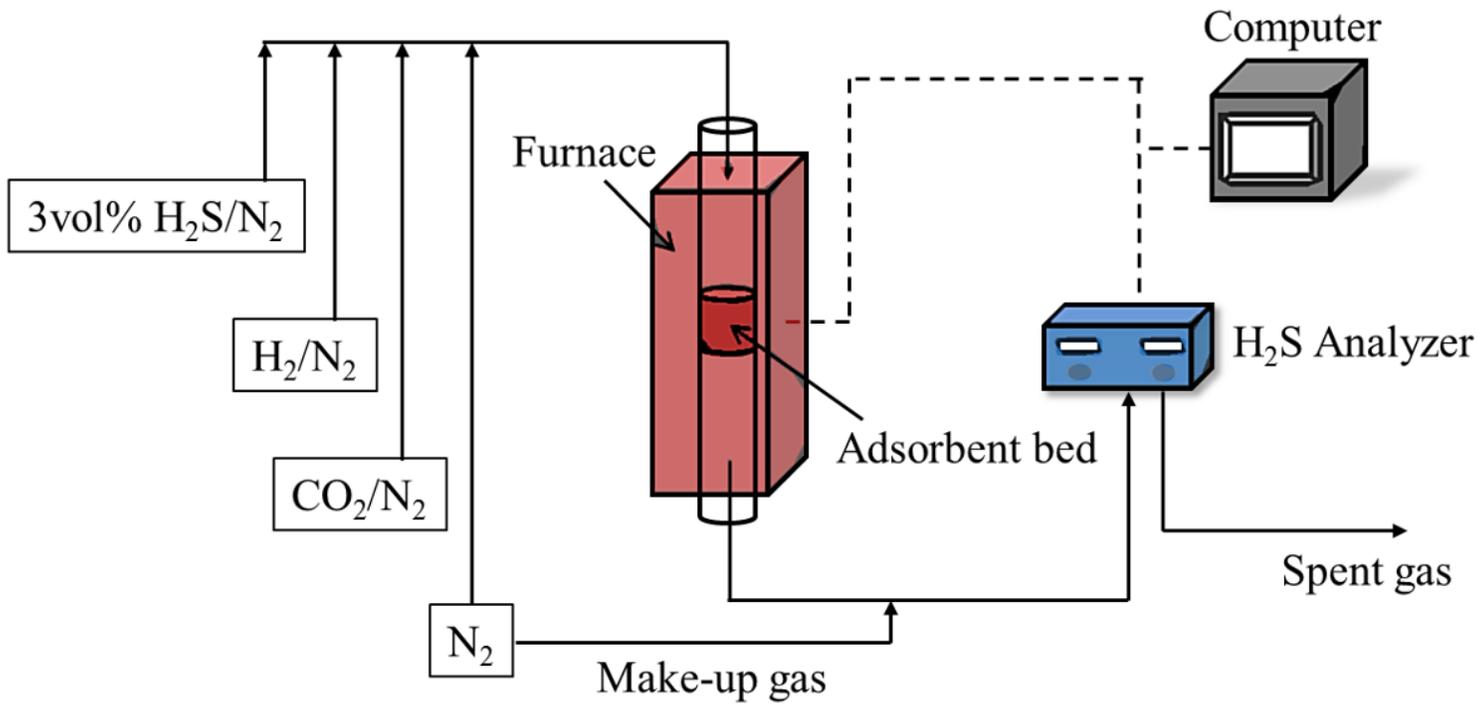


Figure 1

H₂S adsorption setup [14].

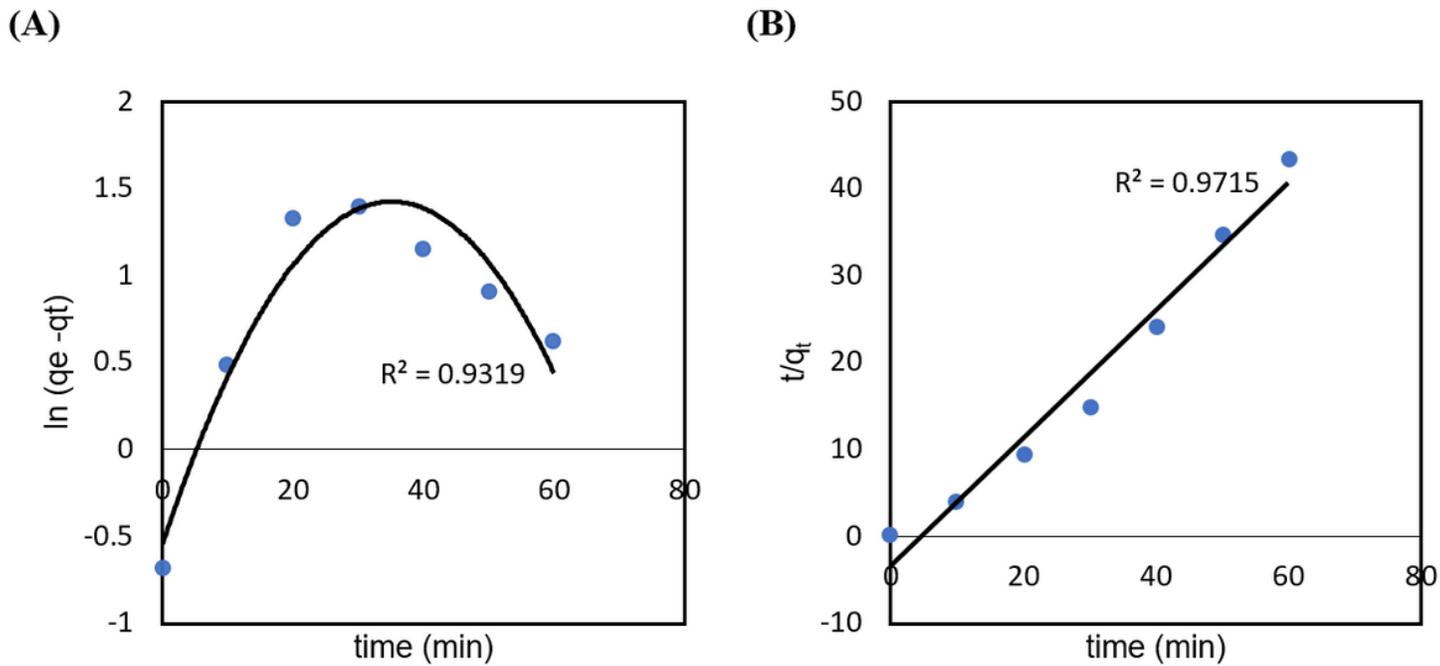


Figure 2

(A) Pseudo First order and (B) Pseudo Second Kinetic for adsorption of Sulphur using 20 wt.% PAC.

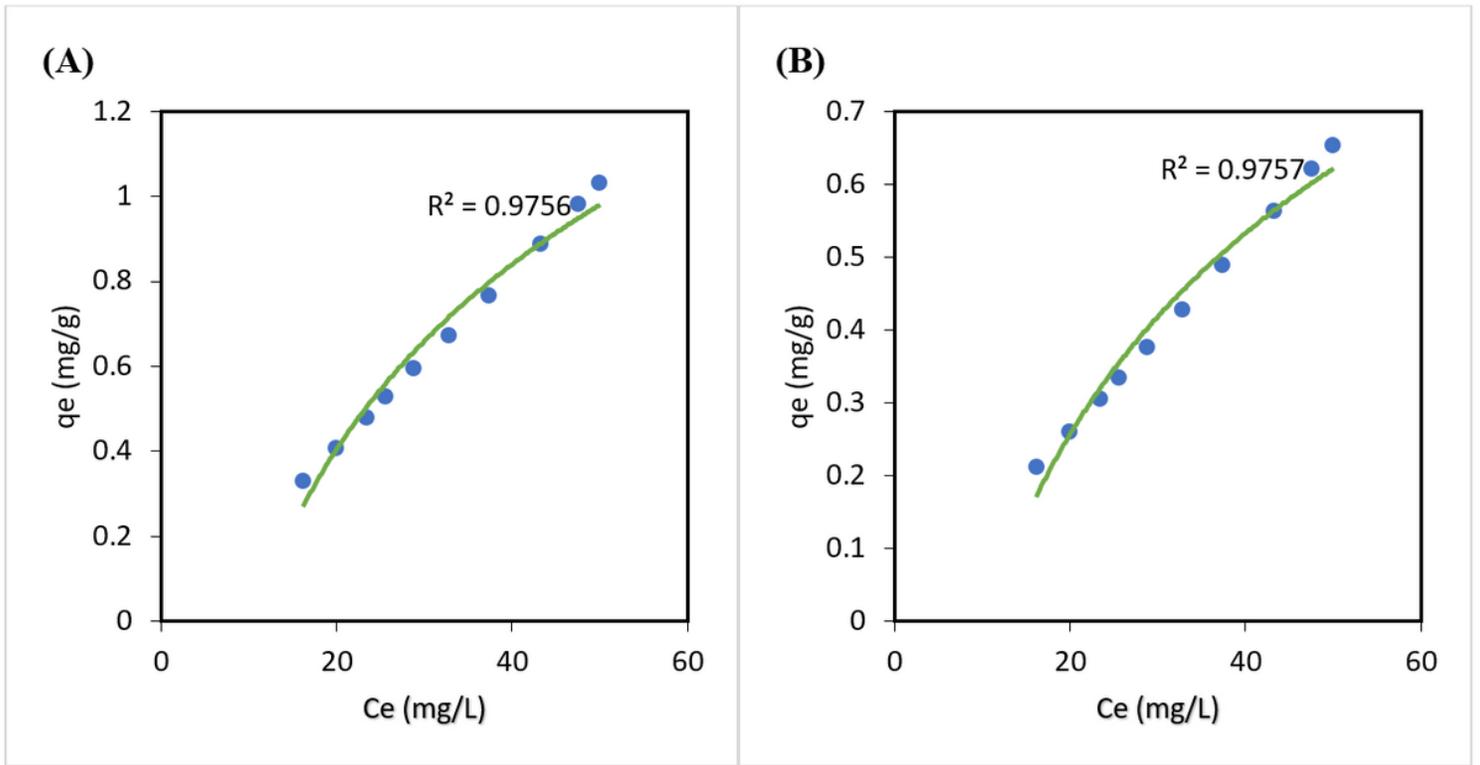


Figure 3

(A) Fitting of Langmuir Adsorption Isotherms on GO and (B) Fitting of Langmuir Adsorption Isotherms on GAC at Room Temperature.

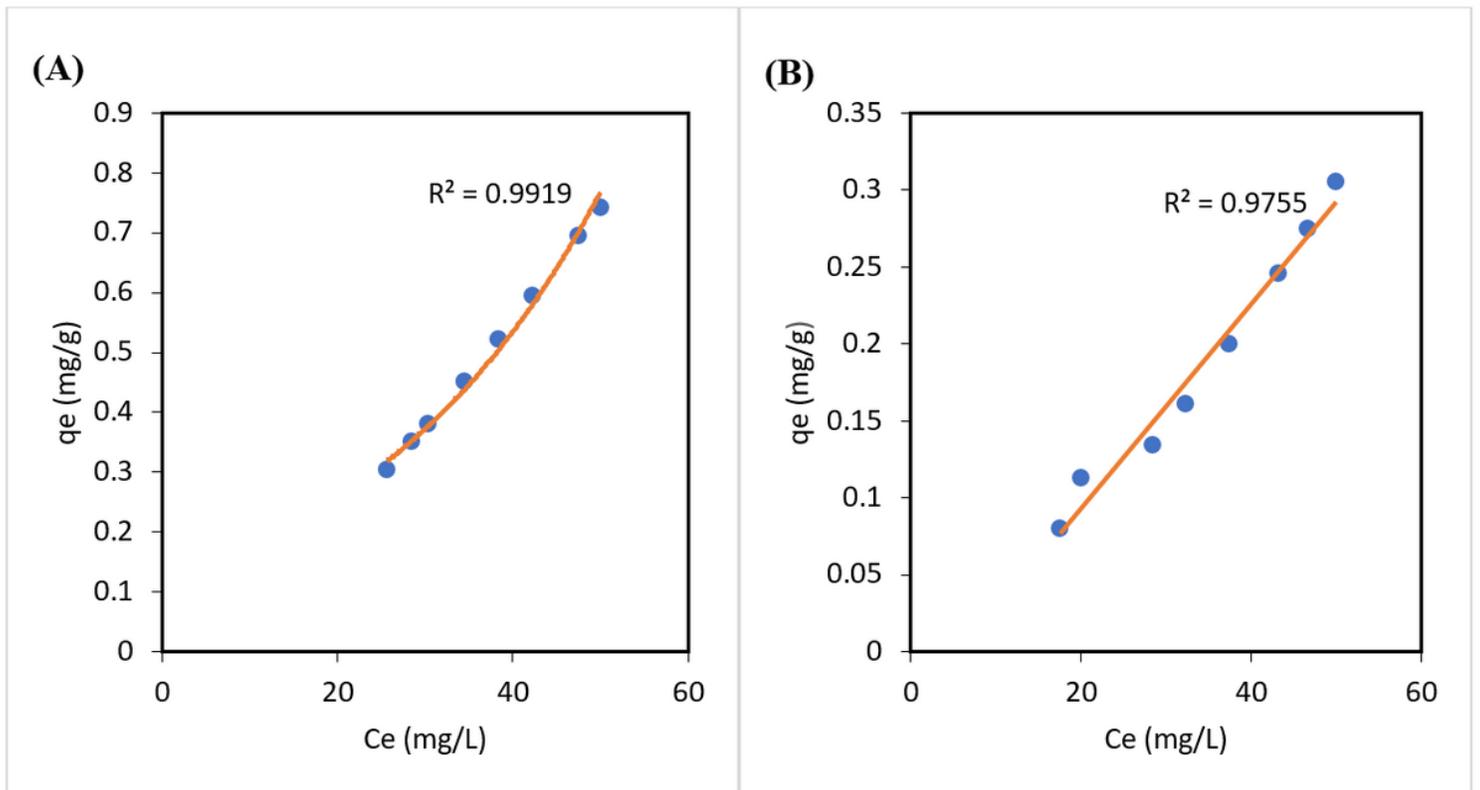


Figure 4

(A) Fitting of Freundlich Adsorption Isotherms on GO and (B) Freundlich Adsorption Isotherms GAC at Room Temperature.

DBT data on each trial

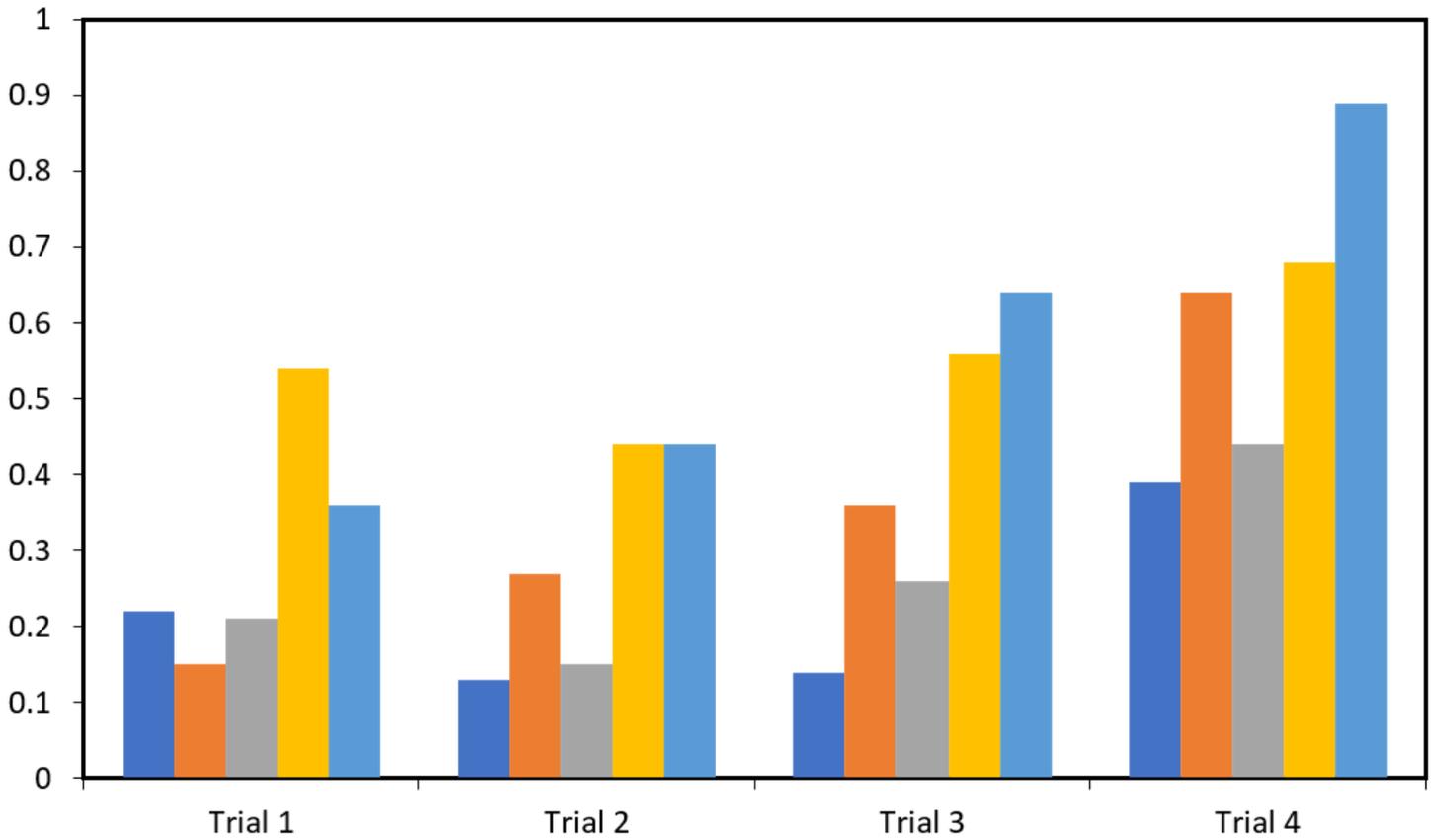


Figure 5

Trial of DBT test

Sulphur content vs temperature at each wet percentage

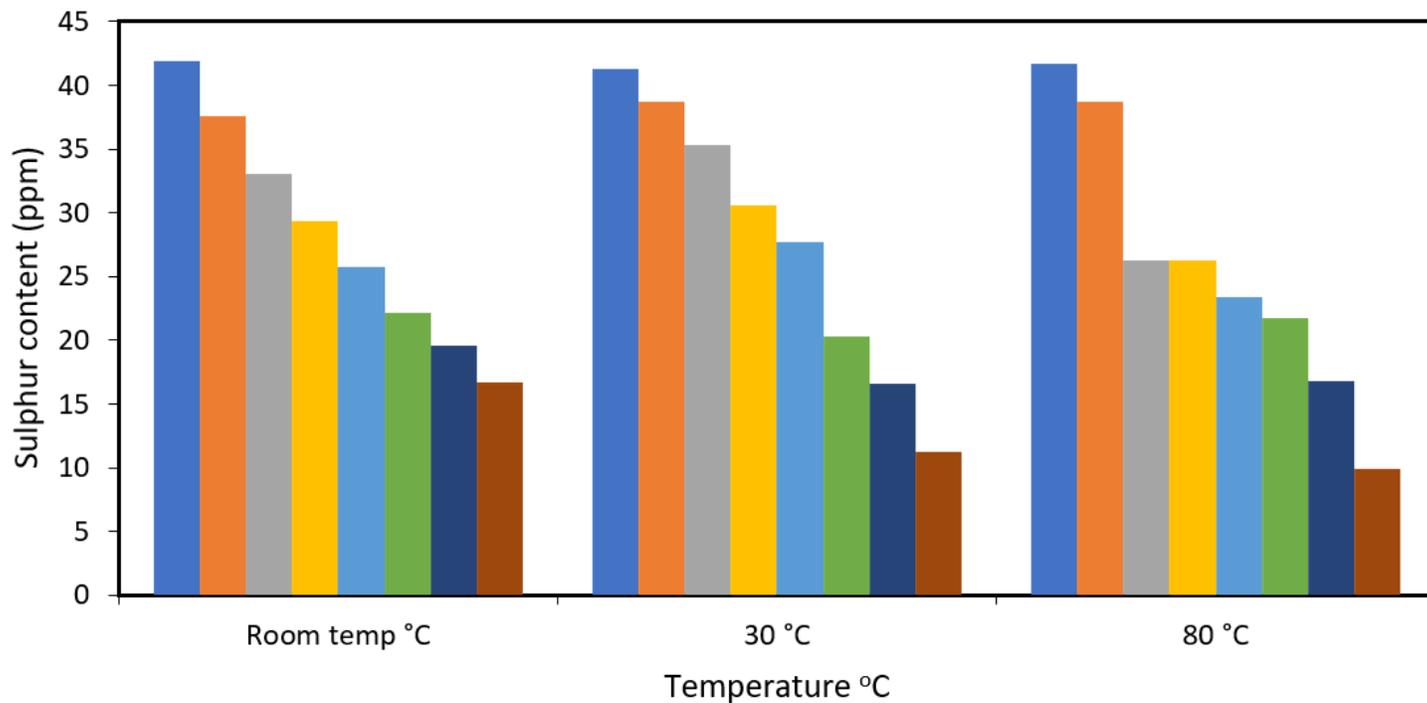


Figure 6

Sulphur content (ppm) against temperature at each wet percentage of sorbent.

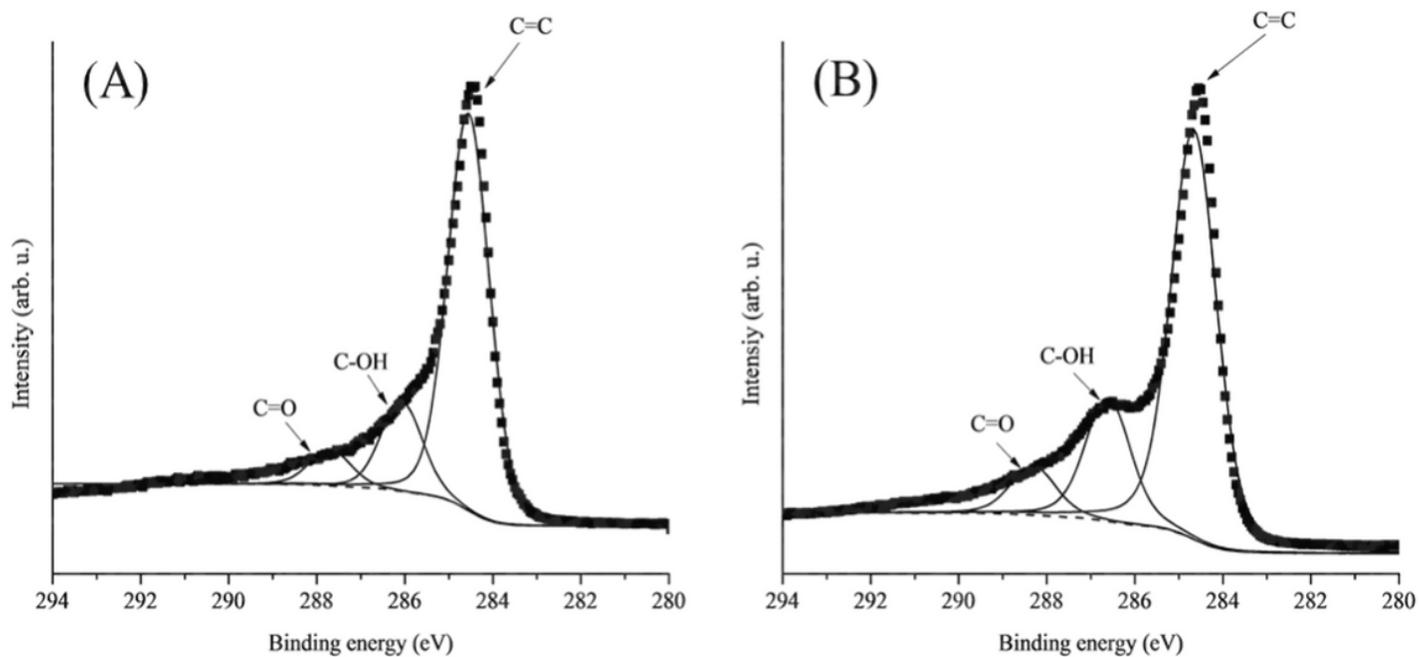


Figure 7

XRD analysis for (A) ZnO/rGO-R and (B) ZnO/GO.

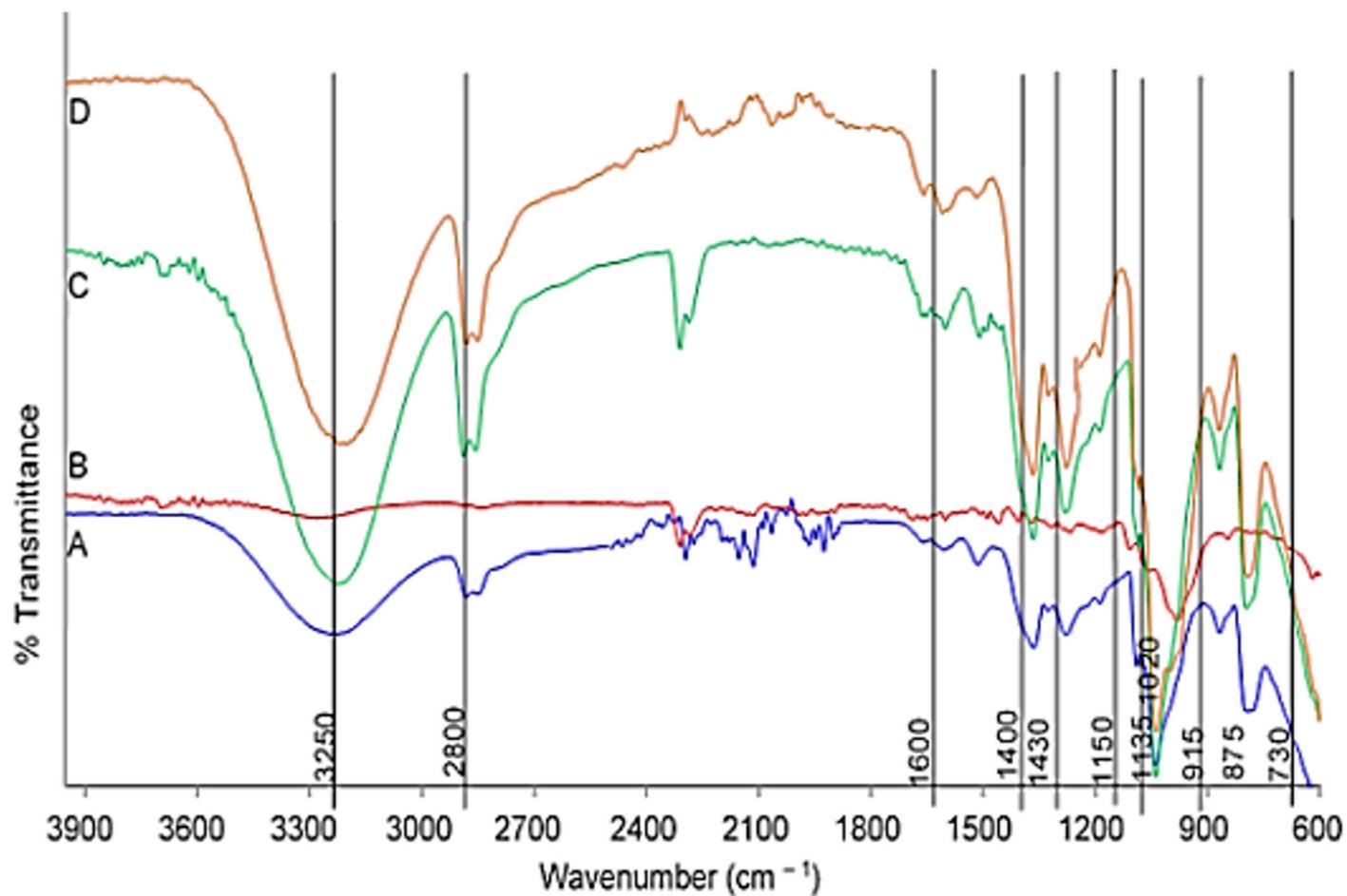


Figure 8

FTIR spectrum of pure ZnO (A), treated rGO (B), ZnO/rGO (C) and GO (D) at the frequency range of 650-3900 cm⁻¹.