Synergy Effect of Nitrogen and Molybdenum on Activated Carbon Matrix for Selective Adsorptive Desulfurization: Insights into Surface Chemistry Modification

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Abstract

This study reports the synthesis of mesoporous metal-modified nitrogen doped activated carbon (AC-N-Mo) from date seeds by ZnCl_2 activation and its applicability for selective adsorptive desulfurization of dibenzothiophene (DBT). The AC-N-Mo exhibits higher adsorption capacity for DBT at 100 mg-S/L with the maximum value of 99.7% corresponding to 19.94 mg-S/g at room temperature than the unmodified carbon with 17.96 mg-S/g despite its highest surface area and pore volume of $1027 \text{ m}^2\text{g}^{-1}$ and $0.55 \text{ cm}^3\text{g}^{-1}$ respectively. The adsorption capacity breakthrough follows the order $\text{AC-N-Mo} > \text{AC-Mo} > \text{AC} > \text{AC-N}$. AC-N-Mo also displayed excellent selectivity in the presence of aromatics (toluene, naphthalene and 1-methylisoquinoline). The enhancement in the DBT uptake capacities of AC-N-Mo is attributed to synergy effect of nitrogen heteroatom that aid well dispersion of molybdenum nanoparticles on carbon surface thereby improving its surface chemistry and promising textural characteristics. The kinetic studies showed that the DBT adsorption proceeds via pseudo-second order kinetics while the isotherm revealed that both Freundlich and Langmuir fit the data but Freundlich fit the data more accurately for the best performing adsorbent. The physico-chemical properties (surface area, pore volume, carbon content, particle size etc.) of as-prepared adsorbents namely; AC, AC-N, AC-N-Mo and AC-Mo were characterized by N_2 - physisorption, X-ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Spectroscopy/Energy Dispersive Spectroscopy (SEM/EDS), Raman Spectroscopy (RS), Fourier Transform Infrared Spectroscopy (FTIR) and Ammonia-Temperature-Programmed Desorption (NH_3 -TPD).

Introduction

In fuel, sulfur compounds present combust to produce SO_x resulting in acid rain and contribute to the occurrence of photochemical smog, two severe threat to the flora and fauna (Hanif et al. 2020), poisons catalytic converters used to reduce CO_x and NO_x in automotive engines and also causing numerous corrosion problems in pumping, pipeline, refinery equipment (Muzic et al. 2008). Owing to the deleterious impact of sulfur compounds, the concern authorities in a number of countries set stringent regulations to limit the concentration of sulfur present in industrial and transportation fuels, which becomes stricter with time. The highest permissible sulfur content has been set to 10 ppm and 15 ppm for gasoline and diesel oil respectively in countries like US, EU and Japan (de Lima et al. 2018).

The conventional hydrodesulfurization (HDS) technology, developed in 1930s, is largely utilized in the refineries to remove compounds of sulfur available in crude oil distillates (Song 2007). Although, HDS is an excellent desulfurization technology especially for disulfides, sulfides, thiols, and mercaptans, its activity towards thiophene and its alkylated derivatives is energy and cost intensive, especially towards achieving ultra-deep desulfurization (Sadare and Daramola 2019). HDS limitations also include severe operation conditions such as working at higher pressure and elevated temperature of 3-7 MPa and 300-400°C respectively, thereby resulting in excessive energy consumption. These drawbacks are unavoidable and involve significant capital investment, thus increasing fuels cost (Ghahramaninezhad and Ahmadpour 2020). A number of desulfurization technologies such as ionic liquids (ILs) desulfurization,

adsorptive desulfurization (ADS), bio-desulfurization and oxidative desulfurization (ODS) have been adapted as an alternative and complementary process towards traditional HDS technology (Bhatia and Sharma 2012; Guo et al. 2019; Ghahramaninezhad and Ahmadpour 2020; Haghighi and Gooneh-farahani 2020; Rekos et al. 2020; Tireli et al. 2020). Meanwhile, ADS using porous adsorbents is gaining increasing attention as an alternative to achieve ultra-deep desulfurization owing to its promising characteristics that include easy accessibility of adsorbents, renewability of spent adsorbents, workability at moderate temperature and pressure, low-energy consumption, thermal stability, and satisfying textural features like elevated surface area, desirable micropores volume as well as thoroughly developed pore size (Wang et al. 2009b). Varieties of sorbent materials used in adsorptive desulfurization studies have been reported. Among others, metal organic framework (MOF), zeolites, amorphous silica-alumina, activated carbon (AC), silica gel, metal oxides, sorbents were studied for desulfurization of fluid catalytic cracking feedstock, model oils, coker naphtha and distillates (Shi et al. 2010; Ahmed and Jung 2016; Namchot and Jitkarnka 2016).

AC are carbonaceous materials specially treated to give a highly-developed internal pore structure and a large surface area (Al-Qodah Z, Shawabkah 2009). Oxidation of the carbon atoms present on the interior and exterior surfaces distinguished AC from the elemental carbon. The usage of non-renewable, high cost precursors namely; peat, petroleum residue, lignite, bituminous coal and wood make commercial AC expensive (Yahya et al. 2015). Thus, reasonably cheap, environmental friendly and desirable adsorbents have been investigated using agricultural by-products and waste as precursors for AC production. There is a number of reported articles that show how activated carbon surfaces were oxidized with the incorporation of metals to positively enhanced adsorption efficiency of DBTs (Ganiyu et al. 2016; Danmaliki and Saleh 2017; Olajire et al. 2017). It should be mentioned that surface chemistry modification and special treatments of AC that include both the physical and chemical modification of carbon surfaces and the treatments such as oxidation, steaming, sulfidation, acidification, metal loading and metal-oxides incorporation play essential role in adsorption capacity breakthrough as well as in the enhancement of carbon selectivity towards sulfur containing compounds (Ganiyu et al. 2016).

Xiong et al. synthesized zirconium dioxide modified activated carbon (ZrO_2/AC) adsorbent and applied it for adsorptive removal of refractory sulfur compound DBT from a simulated diesel oil. The adsorption capacity of ZrO_2/AC was found to outperform bare AC by a magnitude of 17% and the spent ZrO_2/AC was found displaying a higher adsorptive capacity breakthrough than unmodified AC after recycling three times. The improved adsorption efficiency was ascribed to the surface acidic sites impregnated ZrO_2 (Xiong et al. 2010). Cerium-loaded activated carbon was prepared and its applicability was studied for refractory sulfur compound removal from model fuel (dissolution of DBT in petroleum ether). The study confirmed that the cerium-loaded activated carbon showed higher adsorption selectivity and capacity for DBT compared to a virgin carbon attributed primarily to the enhanced active site created through surface chemistry modification (Xiong et al. 2012). Saleh et al. prepared four composites named as AC, AC/Ce, AC/Fe, and AC/Ce/Fe and were examined closely for the removal of organosulfur compounds of DBT, benzothiophene (BT) and thiophene (TP) in a simulated fuel. The research confirmed that AC/Ce/Fe

exhibited improved adsorption efficiency with the sorbent performance in the order of $AC < AC/Fe < AC/Ce < AC/Ce/Fe$, despite the highest pore volume and surface area of $0.71 \text{ cm}^3/\text{g}$ and $460.27 \text{ m}^2/\text{g}$ respectively recorded for bare AC. This excellent performance of AC/Ce/Fe was attributed to the crystalline nature of iron and acidic nature of cerium (Danmaliki and Saleh 2017).

It is established that the electronic and surface features of carbon materials can be changed via introduction of heteroatom like phosphorus, oxygen, boron and nitrogen (Fagury et al. 2014). Specifically, modification of carbon with nitrogen to form porous nitrogen-doped carbon and embedding of other heteroatoms have gained significant attention in the electrochemistry related applications (supercapacitors fuel cell, batteries, photocatalysis, etc.), as well as in catalysis, separation and water purification (Fan 2013).

Carbon-doped porous boron nitride (C-BN) was investigated for the removal of sulfur compound by Xiong and co-workers (Xiong et al. 2015). The porous C-BN showed higher adsorption efficiency for DBT as compared to boron nitride materials attributed to the stronger Lewis acid–base interactions between C-BN and DBT molecule as well as the significant exposure of more atoms along the pores edges.

This study report the usage of synthesized metal-modified nitrogen doped AC adsorbent and its applicability for selective adsorptive desulfurization of model fuel containing the solution of dibenzothiophene in isooctane. The AC was prepared from agricultural waste material date seeds via ZnCl_2 activation and subsequently treated with melamine to obtain nitrogen doped carbon. Molybdenum nanoparticle is explored owing to its acidic nature and its tendency to form direct sulfur-metal interaction with the electron donor groups containing sulfur such as DBT. Selective performance of as-developed adsorbents was also investigated on DBT in the presence of other aromatics, namely: toluene, naphthalene, and 1-methylisoquinoline. The adsorbents were extensively characterized to obtain structure-activity performance with respect to adsorbate-adsorbent interaction.

Experimental

2.1 Materials

Grinded Ajwa Al-Madina date seed was procured from a packaging factory in Saudi Arabia. Dibenzothiophene (99%), 1-methylisoquinoline, toluene were all purchased from Sigma Aldrich, while isooctane and melamine were from Fluka AG. Ammonium heptamolybdate tetrahydrate (molybdenum precursor) and zinc chloride were supplied by ACROS organics and BDH Ltd Poole England, respectively. Naphthalene was obtained from Fisher Scientific Company. Ultrapure distilled water was obtained in-house using ThermoScientific Barnstead NANOPURE, after initial distillation through Labstrong FiSTREEMTMII 2S Glass Still distiller.

2.2 Methods

2.2.1 Activated carbon (AC) preparation from date seeds

Grinded Ajwa Al-Madina date seeds was procured from a packaging factory in Saudi Arabia and subsequently used as a precursor for AC production by chemical activation. Equal grams of ZnCl_2 (activator) and precursor (pulverized date seeds) were measured and mixed together in a beaker. 25 ml of distilled water was introduced into the mixture of date seeds and ZnCl_2 , thoroughly agitated at room temperature (RT) for 2 h at 600 rpm. The temperature was increased to boiling point until dryness and the stirring was reduced to 400 rpm to allow homogeneity and prevent aggregation. The resultant mixture was transferred to an oven for further drying at 80 °C and left overnight. The resulting sample was pyrolyzed in a horizontal silica quartz-tube of diameter 60mmx1000mm length and inserted in an electric 1200 °C compact split tube furnace MTI (OTF-1200X-S) set at 950 °C using heating rate of 5 °C/min, flow rate of 300 mL/min and maintained at this temperature for 3 h to allow the complete carbonization. Ultimately, the sample was cooled to room temperature under N_2 (99.95%) at the same flow rate before it was removed from the furnace. The as-prepared pristine activated carbon was therefore denoted as AC.

2.2.2 Preparation of nitrogen-doped activated carbon (AC-N)

As-developed activated carbon and melamine were subjected to solid state impregnation and thermal spreading by direct mixing of the duo in ratio of 2 to 1 by weight (melamine/AC = 2). The sample mixture was heated up to 900 °C at 10 °C/min under N_2 (99.95%) for a hold time of 2 h. The resulting sample was cool to RT under N_2 at the same flow rate before it was removed from the furnace.

2.2.3 Synthesis of Mo-modified nitrogen-doped carbon (AC-N-Mo) and Mo-loaded activated carbon (AC-Mo)

2.5 wt% molybdenum was loaded into nitrogen-doped AC via solid state impregnation and thermal spreading. This is achieved by direct mixing of 0.023 g of molybdenum ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$) with 1.0 g of AC-N and the resultant mixture was treated under the continuous flow of N_2 (99.95%) and was heated up to 600 °C at 10 °C/min for a hold time of 1 h. To obtain Mo-loaded activated carbon (AC-Mo), the above procedure was repeated using virgin AC.

2.3 Characterization of as-synthesized adsorbents

2.3.1 BET analysis

Surface area and pore volume analysis of the adsorbent were determined by N_2 adsorption-desorption isotherms by employing BET and BJH-adsorption methods respectively. Samples were analyzed at boiling point of liquid nitrogen (-196 °C), on a Micrometrics ASAP 2020 equipped with chemisorption set (Micrometrics, USA) after degassing at 300 °C for 3 h (ramping at 10 °C/min) to remove impurities and moisture under vacuum.

2.3.2 X-ray diffraction (XRD)

X-ray Diffraction analysis was done on Rigaku Ultima IV X-ray diffractometer using K α radiation of Cu by recording the adsorbents diffraction pattern at 2 θ angle between 10 ° to 60 °, and stepwise of 0.03. The operation was conducted at 40 kv and 40 mA with a scan rates of 3 °/min.

2.3.3 Fourier transform infrared spectroscopy (FT-IR)

Surface functional groups of the prepared adsorbents was investigated by FTIR using **Thermo Scientific Nicolet™ 6700** FT-IR spectrometer model equipped with deuterated triglycine sulfate detector and OMNIC program. Samples were pelletized with the aid of KBr in right proportion (2: 100 of sample to KBr) in an agate mortar, and spectra was obtained while correcting for the background noise and recorded by adding 64 scans with a resolution of 2 cm⁻¹ at scanning range of 400- 4000 cm⁻¹.

2.3.4 Scanning electron microscopy coupled with energy dispersive x-ray (SEM-EDX)

SEM analysis was carried out at an accelerating voltage of 30 kV using secondary electron (SE) and back scattered electron (BSE) mode on the adsorbents to investigate porosity development with high vacuum Thermo Scientific™ Quattro ESEM equipped with electron gun and attached to EDS (Oxford, Inc.). EDS was employed for the identification of elemental composition in and on the surface of the sample for qualitative information

3.3.5 X-ray photoelectron spectroscopy (XPS)

XPS, 250Xi ESCALAB Thermo Scientific equipped with (PHI 5000 Versa Probe II, ULVAC-PHI Inc.) using Al K α as radiation source. Samples were prepared by mixing the adsorbent with ethanol in drop-wise addition of the solvent, then deposited on glass with the aid of pipette and allowed to air-dry. The samples were mounted on the carbon tape and vacuum prior to XPS analysis at 9×10^{-8} mBar as analysis chamber vacuum, and deconvolution of peaks was done by Avantage software with adventitious carbon correction at 284.8 eV.

2.3.6 Raman spectroscopy (RS)

RS analysis was conducted on the prepared adsorbents using (iHR320 with CCD detector, HORIBA) to analyze functional groups fingerprint on the adsorbents with regards to graphitization or amorphous nature by measuring the energy released from scattered photons when the adsorbents were exposed to monochromatic light from a wavelength (300 mW, green laser), laser (532 nm) observed via rotational, translational and vibrational modes produced.

2.3.7 Ammonia temperature programmed desorption (NH₃-TPD)

NH₃-TPD was conducted to understand and analyze the acidic sites that are present on the adsorbent surface. This analysis (performed on Micromeritics AutoChem II 2920, Chemisorption Analyzer) was conducted by loading roughly 100 mg of the adsorbents in a quartz tube sealed with cotton wool. Before the analysis, samples were degassed at 100 °C for 30 min in flowing helium (20 mL/min) to remove

water vapor. Thereafter, the temperature was raised to 500 °C at a ramp rate of 10 °C/min and held at that temperature for 1 h to remove strongly bound species. The samples were subsequently cooled to 100 °C under the fixed flow of helium gas. The adsorption process begins by saturating the samples with 10 wt % NH₃ gas for 30 min at 100 °C at the flowrate of 30 mL/min and the excess NH₃ was expelled by flushing with helium gas for 60 min at the same temperature. Subsequently, the temperature was raised to 900 °C at 10 °C/min and under these conditions; the amount of ammonia desorbed at the ramping temperatures was recorded using the thermal conductivity detector (TCD).

2.4 Adsorption Experiment

To evaluate adsorptive performance of the adsorbents, ADS of a simulated fuel was conducted in batch mode using DBT as the analyte. Various concentration (50 – 200 mg-S/L) of DBT in isooctane were prepared. In a typical run, 20 mL of the simulated oil of each concentration and adsorbent amounts range from 0.025 g – 0.1 g were added in a capped vial and then subjected to continuous constant shaking at the rate of 600 rpm on a magnetic stirrer (IKA RT 10) maintained at room temperature (25 °C ± 0.1 °C) for a fixed time interval of 24 h maximum. The sampling was done at 15 min interval for the first 30 min using a syringe coupled with a membrane filter for determination of residual DBT concentration evaluated by gas chromatography (Agilent 7890A) coupled with SCD (Agilent 355) within the experimental error of 2 %. To compare and study the adsorptive selectivity for organo-sulfur and nitrogen compound, a model diesel fuel containing naphthalene (5 vol %), toluene (5 and 10 vol %), and 100 mg/L of 1-methylisoquinoline were prepared in a mixture solvent of DBT and adsorption studies were carried out at the stated working condition.

The DBT adsorption (q_e , mg/g) at equilibrium was calculated with the formula stated below;

$$q_e = (C_0 - C_e) \frac{V}{W} \quad \dots \dots \dots 1$$

Where V measures in liter and represent the volume of model fuel solution, W (g) denotes weight of the adsorbent and Co (mg/L) and Ce (mg/L) are initial and equilibrium sulfur concentration respectively.

Results And Discussion

3.1 Surface area and porosity

AC are usually microporous materials thus limiting their application to studies involving small molecules such as methanol production from CO₂ and hydrogen (Abotsi and Scaroni 1989). Recent applications of activated carbon require higher percentage of mesoporosity to facilitate diffusion of larger molecules in order to attain effective adsorption efficiency (By Zhonghua Hu, Madapusi P. Srinivasan and Ni 2000). Thus, commendable efforts have been directed towards creation of mesoporosity into AC for extensive applications (Moosavi et al. 2012). The nitrogen adsorption - desorption isotherm of AC, AC-N, AC-N-Mo

and AC-Mo are shown in **Fig.1A**. The samples show typical type IV isotherms with an H4 hysteresis loop in accordance to IUPAC classification (K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquérol 1985). H4 loops are often found in micro-mesoporous carbon (K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquérol 1985). It was observed that the four samples showed a low uptake of nitrogen at relative pressures below 0.1 indicating the availability of micropores within the samples. A hysteresis loop was also seen at high relative pressure between 0.4-1, indicating mesoporosity (Min and Harris 2006; Danmaliki and Saleh 2017). **Table 1** summarizes the textural properties of all prepared adsorbents. The pure AC has the highest surface area of 1026.77 m²/g with almost 70% mesoporosity. Doping of nitrogen and loading of Mo onto AC's surface drastically lowered the pore volume and the overall surface area but increased mesoporosity to about 72%. AC-Mo gave the least pore volume and surface area as evidenced in the **Table 1**. This reduction in the surface area and pore volume was as a result of pore blockage (Ganiyu et al. 2016).

Table 1 Surface area and pore characteristics

Adsorbents	BET surface area (m ² /g)	Microporous surface area (m ² /g)	Mesoporous surface area (m ² /g)	Microporous pore volume (cm ³ /g)	Total pore volume (cm ³ /g)	Average pore size (nm)	R=I _D /I _G
AC	1027	313	714	0.14	0.55	2.14	1.17
AC-N	886	300	636	0.11	0.48	2.18	1.20
AC-N-Mo	885	251	634	0.11	0.48	2.20	1.22
AC-Mo	830	236	594	0.10	0.45	2.18	1.19

3.2 XRD pattern of parent activated carbon and the treated AC

XRD is a crucial characterization tool often employed for phase identification of unknown crystalline materials (e.g. minerals, inorganic compounds). Atom has a clear-cut diffraction patterns that is seen upon exposure to X-ray beam. It is obvious from the **Fig. 1B** below, indicating XRD patterns of AC, AC-N, AC-N-Mo and AC-Mo that all the adsorbents showed a broad diffuse peaks at 2θ around 24° and 43°, assigned to the (002) and (100) reflection planes, indicating the amorphous nature of the ACs (Mahadevan et al. 2012). These peaks resulted from the pores created due to carbon decomposition in the direction of graphitic structures that proved semi-crystalline nature (Danmaliki and Saleh 2017). Also, AC crystallite structure is characterized with the interlayer spacing (d₀₀₂) (Roh 2008). The (100) reflection correlate with the honeycomb structure formed by sp² hybridized carbon (Geng et al. 2011). However, heteroatom (N) activation of activated carbon causes defect sites and modification in the carbon lattice thereby boosted the crystallinity of treated ACs and this agrees with the result of FTIR analysis as evidenced in the intensity of C-N and C=N (1640 cm⁻¹ and 1564 cm⁻¹ respectively). In addition, the corresponding peaks of Mo on the adsorbents AC-N-Mo and AC-Mo were assigned accordingly. The

intensity diffraction peaks of Mo at 2θ ($^\circ$) = 25.7 and 53.2 are typical of MoO_2 and low intensity diffraction peak at $2\theta = 37^\circ$ is typical of $\beta\text{-Mo}_2\text{C}$ in accordance with Joint Committee on Powder Diffraction Standards (JCPDS N $^\circ$ 11-0680) (Puello-polo 2014). This further showed that Mo was successfully loaded on carbon surfaces. These Mo peaks are confirmed in the XPS and NH_3 -TPD results.

3.3 Raman Spectroscopy of AC and modified sorbents

Two clear G-band and D-band peaks corresponding to E_{2g} and A_{1g} respectively are observed in the Raman spectra of untreated activated carbon (AC) and modified activated carbons AC-N, AC-N-Mo and AC-Mo with the first peaks at (1595cm^{-1}), the G-peak ascribed to the scattering peak of graphite and the D-band peak near (1340 cm^{-1}) is seen as a result of disordered arrangement, lattice defects and low symmetry carbon structure of graphite (Liu et al. 2017) (**Fig. 1C**). These two sharp peaks suggested that AC material contains of typical amorphous structures and is confirmed by the XRD results as indicated by broad diffuse peaks observed around 24° assigned to (002) seen in amorphous carbon. The degree of graphitization can be estimated with respect to D-peak intensities relative to G-peak intensities using the below expression

$$R = \frac{I_D}{I_G} \dots \dots \dots 2$$

Where I_D and I_G represent D-band and G-band intensity respectively and R denotes the degree of graphitization. The higher the degree of graphitization, the smaller the R value (Liu et al. 2017). The same pattern were observed in the Raman spectral of all the prepared samples describing an indication of qualitative existence of the disordered structure, a popular characteristics for AC materials (Roh 2008). Synthesized adsorbents AC, AC-N, AC-N-Mo and AC-Mo have R values corresponding to 1.17, 1.20, 1.22, and 1.19 respectively. This shows that AC and AC-Mo have higher degree of graphitization with little or no defects.

3.4 Fourier transform infrared spectroscopy (FTIR)

A non-destructive spectroscopy techniques such as FTIR, usually employed to show energy level of the substance, atomic or molecular structure via electromagnetic interaction effect (Aging and Munajad 2018). FTIR analysis as presented in **Fig. 1D** gave chemical identification about the characteristics functional groups using an infrared spectrum the materials absorbed. It is clear that all the spectral follow similar pattern except that slight changes were observed in the peak intensities of some functional groups that are within the expectations. The medium sharp peak at 3734 cm^{-1} is attributed to O-H stretching vibration of free alcohols (Tironi et al. 2012). The strong broad band observed at 3430 cm^{-1} in all the samples were assigned to O-H stretching vibrations of hydroxyl or carboxylic group or perhaps due to chemisorbed water (Danmaliki and Saleh 2017). Similarly, well resolved sharp peaks were seen in all

the adsorbents at 2852 cm^{-1} and 2920 cm^{-1} associated to aliphatic C-H stretching vibration of CH, CH₂ and CH₃ (Danmaliki and Saleh 2017). A characteristic sharp and strong peak of O=C=O was also observed at 2360 cm^{-1} . Broad peak observed at 1735 cm^{-1} is assigned to C=O stretching vibration of six-membered ring lactones (Coates 2006). The medium peak at 1640 cm^{-1} and 1564 cm^{-1} can be ascribed to C-N and C=N heterocycles (Lan et al. 2019). This medium peak is pronounced only in AC-N and AC-N-Mo such that it furthers support the dispersion of heteroatom (N) on carbon surfaces. The peak at 1090 cm^{-1} is a characteristics of amorphous carbon and is attributed to C-O stretching vibration (Danmaliki and Saleh 2017). This is why parent AC gave the highest intensity of this peak but upon modification with N and Mo the intensities decreased. The peak at 690 cm^{-1} corresponds to C-H bend of mono-substitution (phenyl)(Coates 2006) and these peaks only observed in all the adsorbents except in pure carbon, indicating that the modification on carbon increased the acidic sites on carbon surfaces. The last peak at the fingerprint region is centered at 468 cm^{-1} and is assigned to bending mode on Mo-O-Mo vibration entity (Bojidarka Ivanova 2011). These peaks were observed only in AC-N-Mo and AC-Mo and reflect that Mo was successfully loaded on carbon surface. This result is in close proximity with the result obtained in XRD, XPS, BET/EDS, and TPD as it confirms the presence of oxygen-containing functional groups.

3.5 SEM and EDS of as-synthesized sorbents

The porosity and elemental composition of the prepared adsorbents were examined with SEM/EDS, and micrograph of the synthesized adsorbents are presented in **Fig. 2 and Fig. SI-1**. These adsorbents show differences in the degree and nature of porosity owing to modification of surface chemistry of AC-N, AC-N-Mo and AC-Mo when compared with a pure AC derived from date seeds. AC is a diverse adsorbent containing up to 90 % carbon with a unique properties of high surface area and high degree of porosity (Yahya et al. 2015) and this fact was seen to hold in all the adsorbents, as above 90 wt% carbon were recorded in all. **Fig. 5 (a)** shows carbon and oxygen corresponding to parent AC from date seeds. It has the highest oxygen content of 5.1 wt% but slightly decreases upon nitrogen and metal loading on the surface of the adsorbent due to deposition of nanoparticles. Dispersion of heteroatom (N) and Mo on the AC surface increased the porosity as observed in the corresponding SEM micrograph and this agrees with the BET and FTIR results. It is also obvious from the EDS result that nitrogen and metal loading for AC-N-Mo have 2.8 wt% and 1.1 wt% respectively, an indication of sufficient dispersion of heteroatom (N) and successful metal loading. The EDS mapping (not shown) shows that both N and Mo are uniformly distributed yet devoid of particles agglomeration. Thus, further explained why AC-N-Mo appeared the best performing adsorbent.

3.6 X-ray photoelectron spectroscopy (XPS)

The XPS analysis of pure carbon and modified mesoporous carbon (AC, AC-N and AC-N-Mo,) presented in **Fig. 3 (a, b, and c)** respectively prove the presence of C, N, O in all the as-developed adsorbents. Additionally, Molybdenum peaks were also seen in the AC-N-Mo and AC-Mo. Two different peaks were observed in the deconvoluted spectrum of carbon in all the adsorbents with the binding energy peaks at

284.5 and 283 eV respectively. The peaks at 284.5 eV corresponds to C-C bond (sp^2) (Lo et al. 2013) but the second C1s peak at 283 eV is also sp^2 carbon but shifted to lower BE. The deconvoluted nitrogen spectrum N1s also shows one nitrogen state for AC-N at 396 eV corresponding to nitride nitrogen and three different nitrogen states were seen in the deconvoluted spectrum of AC-N-Mo adsorbent at N1s (398 eV), N1s (396 eV) and N1s (401.6 eV) which correspond to pyridinic N, nitride nitrogen and graphitic nitrogen (N-C=O) respectively (Sobol et al.; Kim et al. 2012; Fu et al. 2016). The AC, AC-N and AC-N-Mo adsorbents show O1s peak at 530.9 eV, 530.8 eV 531 eV respectively, all were attributed to the oxygen bond state in C=O in quinones, carbonyl group (Sobol et al.; Lo et al. 2013). In AC-Mo adsorbent, O1s peak was observed at 530.2 eV assigned to oxygen bond state in metal oxide Mo-O. The Mod3 deconvoluted spectrum of AC-N-Mo shows three Mo chemical states 227.8 eV, 230.8 eV and 233 eV correspond to molybdenum states in Mo_2C , MoO_3 and $(NH_4)MoO_4$ respectively. As shown in **Table SI-1** AC-N-Mo has the highest oxygen percent. This further support the reason AC-N-Mo showed the best adsorption capacity towards the DBT. This result confirmed that the adsorption capacity breakthrough of AC-N-Mo is also due to the attachment of oxygen containing functional groups onto the carbon surface.

3.7 Surface acidity by ammonia-temperature-programmed desorption (NH_3 -TPD)

Fig. SI-2 presents the NH_3 - TPD profile of as-prepared adsorbents for determination of the surface acidity. The desorbed ammonia at three temperature range of 200-300 °C, 400-600 °C and 800-1000 °C correspond to NH_3 desorption on weak, moderate and strong acid sites respectively (Glorius et al. 2018; Tanimu et al. 2019). Adsorbent bare AC exhibits two broad desorption peaks at 410 °C, and 844 °C describing two acidic sites of different strength where the former low-temperature NH_3 desorption acid site corresponds to lower strength and the later high-temperature NH_3 desorption represents strong acid sites corresponding to both Lewis and Brønsted acidic sites. Similarly, a single broad diffuse peak is observed at 485 °C for the adsorbent AC-N. This peak is attributed to moderate acid sites. In contrast, AC-N-Mo showed two peaks at 421 °C and 856 °C, the broad diffuse peak at low temperature is ascribed to moderate acid sites and the peak at narrower elevated temperature corresponds to the strongest Lewis and Brønsted acidic sites on the carbon surfaces (Ferenc Lónyi 2001; Ganiyu et al. 2017). The carbon composite AC-Mo also displayed three broad desorption maxima at 214 °C, 400 °C and 847 °C corresponding to acid sites of low, medium and strong acidic strength respectively. **Table SI-2** enumerates the calculated acidic sites where we have AC-N-Mo displayed the strongest acidic sites of 1.84 mmol/g at STP attributed to the synergy effect of nitrogen heteroatom and hence aided well dispersion of weakly acidic molybdenum nanoparticles on carbon surface (Mabena et al. 2018). This further provide a clear picture why AC-N-Mo gave higher enhancement of the DBT uptake.

3.8 Adsorption evaluation of the developed adsorbents

Adsorption efficiency of pure AC, AC-N, AC-N-Mo and AC-Mo were studied in a batch system at room temperature (RT) as a function of time for a simulated diesel fuel composed of isooctane and 100 mg-S/L as DBT. The effect of carbon surface modification with heteroatom (N) and molybdenum were also

observed for efficient DBT removal at initial concentration of 100 mg-S/L. It is obvious from **Fig. 4A** that more than 70 % of DBT is adsorbed by as-prepared adsorbents in the first 60 min of equilibration. A relatively much slower adsorption process that continues to 24 h is observed after the fast adsorption process of the first 60 min. At 24 h, DBT uptake reaches a constant value of approximately 90 % for AC, AC-N, and AC-Mo while AC-N-Mo reached a climax value of 99.7 %. Thus, 24 h was taken as equilibrium contact time. The adsorption capacity of AC, AC-N, AC-N-Mo and AC-Mo at 24 h correspond to 17.96 mg-S/g, 17.84 mg-S/g, 19.94 and 17.92 mg-S/g respectively. Adsorption efficiency of bare carbon in the first 15 min is 75 % and gradually increased to 89.8 % at 24 h. This adsorption breakthrough at the shortest possible time was ascribed to its high surface area of 1027 m²/g. On the other hand, the DBT uptake of unmodified carbon at interval of time after 360 min was relatively insignificant and was attributed to transition pores saturation with DBT molecules. AC-N-Mo adsorbent DBT uptake is 62 % in the first 15 min but increase significantly to almost 100 % at 24 h. This adsorption breakthrough capacity could be attributed to both heteroatom and metal modification in that heteroatom allowed a complete dispersion of molybdenum on carbon surfaces to facilitate sulfur-metal interaction through π -complexation and increased the attachment of oxygen containing functional group (Ganiyu et al. 2016; Danmaliki and Saleh 2017). This is confirmed in the FTIR, XPS, XRD and TPD results. The adsorption efficiency follows the order of AC-N-Mo > AC-Mo > AC > AC-N. The chemistry behind this form of adsorption is that metal ions form σ -bonds with the s-orbitals and the d-orbitals will back-donate electron density to the antibonding π - orbitals in the sulfur containing ring of dibenzothiophene (Saleh et al. 2016). It should be mentioned also that the nitrogen heteroatom (N) influenced well dispersion of metal loading on the surface of AC. **Table 2** shows the comparison of adsorption capacities of DBT from model oil on different AC adsorbents. It was discovered that molybdenum modified nitrogen doped activated carbon AC-N-Mo showed a moderately higher adsorption capacities when compared with adsorbents that were reported in a similar research papers (Ganiyu et al. 2016; Saleh and Danmaliki 2016). Whereas, some authors have reported a higher adsorption capacities for DBT as compared to this current study (Nazal et al. 2019; Yaseen et al. 2021).

Table 2: Comparison of adsorption capacities of DBT from model oil on different AC adsorbents

Adsorbents	Reactor type	Adsorption capacity (mg/g adsorbent)	Model oil	References
Al-AC	Batch mode	14.19	Isooctane	(Ganiyu et al. 2016)
AC/Ce/Fe/	Batch mode	16.63	n-Hexane/toluene	(Danmaliki and Saleh 2017)
AC -Cu Y zeolite	Fixed bed	5.0	n-Decane/toluene	(Hadi 2014)
ACFH ^a	Batch mode	19.0	n-Hexane	(Moosavi et al. 2012)
ACFH-Cu(1) ^{+b}	Batch mode	14.0	n-Hexane	(Moosavi et al. 2012)
AC-MnO ₂	Batch mode	43.8	n-Heptane	(Abu Safieh et al. 2015)
AC/ γ -Fe ₂ O ₃	Batch mode	38.0	n-Hexane	(Fayazi et al. 2015)
Co/ATGAC ^c	Batch mode	37.6	Isooctane	(Sikarwar et al. 2018)
ACAL5 ^d	Batch mode	84.5	n-Hexane	(Nazal et al. 2019)
AC	Batch mode	16.63	n-Hexane/toluene	(Saleh and Danmaliki 2016)
AgNP ^{kp} /AC ^d	Batch mode	25.7	n-Heptane	(Olajire et al. 2017)
Zn/AC	Batch mode	90.09	n-Heptane	(Yaseen et al. 2021)
AC-N-Mo	Batch mode	19.94	"	This work

^aactivated carbon fiber thermally treated, ^bactivated carbon thermally treated modified with copper cation ^c1 wt % acetic-acid-treated cobalt-modified activated carbon ^dactivated carbon loaded with 5 % aluminum and ^dactivated carbon modified with silver nanoparticles synthesized from *Cola nitida* plant.

3.9 Effect on initial concentration on maximum adsorption capacity

Adsorption capacity breakthrough was studied on the prepared adsorbents where the initial concentration of DBT in a simulated fuel was varied between 50 – 200 mg-S/L as a function of time under the working condition of room temperature and fixed adsorbent dosage. **Fig. 4B** shows the equilibrium maximum sulfur adsorbed by AC-N-Mo at 24 h equilibration time. It was seen that the maximum adsorption capacity of AC-N-Mo for a varied concentration of 50 mg-S/L and 100 mg-S/L are 89.2 % and 99.7 % respectively corresponding to 8.92 mg-S/L and 19.94 mg-S/L respectively. The heteroatom–metal modified activated carbon AC-N-Mo displayed higher adsorption efficiency at the varied concentrations owing to higher amount of surface oxygen it has in combination with the enough available acidic sites that aid adsorption of basic organosulfur compounds. However, the highest adsorption capacity dropped between 150 and 200 ppm and the maximum sulfur uptake observed was almost 79 % at these concentrations corresponding to 24.78 mg-S/L and 31.94 mg-S/L respectively. This could be that the surface acidity being a favorable factor to adsorption breakthrough was consumed beyond initial concentration of 100 ppm-S. It is noteworthy to mention that the adsorbent AC-N-Mo adsorbed about 60 % DBT at the first 15 min but increases slowly to 24 h until no further removal was observed. This was attributed to the adsorbent pore size that was larger than the critical diameter of the DBT (Bu et al. 2011).

3.10 Adsorption performance as a function of sorbent dosage

The **Fig. 5 (A)** present effect of adsorbent dosage on the adsorption efficiency of organosulfur compound DBT adsorbed by AC-N-Mo at room temperature as a function of time. It is established that a positive correlation exists between sorbent amount and adsorption efficiency (Danmaliki and Saleh 2017; Olajire et al. 2017; Saleh 2018). In order to determine the optimum sorbent dosage that is an essential parameter in adsorption studies, a trend in adsorption capacity breakthrough was closely examined at room temperature as a function of dosage increment from 0.025 g to 0.1 g at fixed concentration of 100 mg-S/L. Expectedly, an increment is observed in the adsorption efficiency of DBT with dosage increment owing to more active sites introduced by the adsorbent's weight at constant process conditions (Srivastav and Srivastava 2009; Xu et al. 2014) and also due to π - π dispersive interaction between the graphene layer on AC and aromatic ring in DBT (Bu et al. 2011). It is observed that the adsorption affinity for organosulfur compound by AC-N-Mo reached climax at about 99.7% for the adsorbent dosage of 0.1 g in 24 h and no further removal is observed and that formed the basis why adsorbent dosage is restricted to 0.1 g. It is worth mentioning that 0.025 g adsorbent exhibits the highest adsorption removal performance (percentage of sulfur adsorbed per g-adsorbent dosage) of 70.95 % in 24 h contact time and in all the varied dosage, fast adsorption is seen in the first 15 min followed by slight increase till it reached equilibration time of 24 h. AC-N-Mo adsorbent dosage of 0.025 g, 0.05 g, 0.075 g and 0.1 g correspond to 56.76 mg-S/g, 32.32 mg-S/g, 23.95 mg-S/g and 19.94 mg-S/g respectively. This shows that percentage sulfur removal is inversely proportional to adsorbent dosage as shown in **Fig. 5(B)**. It goes without saying that the sorbent increment promotes higher adsorption efficiency due to multilayer adsorption being minimal, whereas, equilibrium adsorption capacity of sulfur increase with decrease in sorbent dosage as presented in **Fig. 5 (B)** (contact time up to 360 min is shown). This phenomenon is attributed to large adsorbent mass that could lead to compacting of the system, which will minimize diffusion of DBT analyte to the adsorption sites of the adsorbents (100 mg-S/L).

3.11 Effect of 1-methyl isoquinoline on adsorption capacity

Aromatic compounds such as pyridine and its derivatives, arenes, toluene, naphthalene, etc. are usually coexist in middle distillate oil and have significant tendency to interfere and cause depletion in the adsorption affinity of sulfur containing organic compounds. In light of this, the competitive effect of pyridine derivative (1-methylisoquinoline) on DBT solution was investigated over the best performing adsorbent AC-N-Mo as simulated diesel oil. It should be noted that heterocyclic nitrogen compounds could either be basic or non-basic on the basis of the availability of lone pair (Mathidala and Ogunlaja 2019). Pyridine and its derivatives such as quinoline, acridine are classified as basic nitrogen due to nitrogen lone pair not contributing towards the aromatic system (i.e. nitrogen lone pair is localized). This localized lone pair extends in the ring plane thus responsible for its basicity. On the contrary, non-basic/neutral heterocyclic nitrogen compounds such as pyrrole and its corresponding derivatives such as indole, carbazole have delocalized lone pair on nitrogen atom that are part of the aromatic system. This reveals the reason nitrogen atom on the basic nitrogen-containing compounds are more basic than their neutral counterparts (Liu et al. 2008). The adsorption removal efficiency of DBT (100 mg-S/L) by AC-N-Mo was evaluated in the presence of 100 ppm 1-methylisoquinoline at room temperature. The percentage removal at the equilibration time of 24 h in the presence of competitive heterocyclic nitrogen compound is reduced slightly when compared to the adsorption affinity of DBT in the absence of 1-methylisoquinoline. The **Fig. 6A** shows the removal efficiency of the adsorbent with and without the presence of nitrogen-containing heterocyclic compound. It was seen that at 24 h the highest adsorption capacity achieved is 72.25 % correspond to 14.47 mg-S/g adsorbent as compared to 19.94 mg-S/g adsorbent attained with DBT only. This impressive DBT uptake in the presence of nitrogen heterocyclic compound showed how selective AC-N-Mo adsorbent is towards the DBT. This performance was ascribed to acid-base interaction between the graphene on AC and the basic sulfur compounds. The reduction observed in adsorption capacity can be considered as a result of competition between basic heterocyclic nitrogen compounds and the sulfur compounds to be transported towards the pores on the carbon surface. This adsorption of the nitrogen compounds on carbon surface was hindered by the heteroatom nitrogen used to disperse Mo on the sorbent dosage. It is worth mentioning that melamine (67 % nitrogen) was the source of the nitrogen used to modify AC surface that is also basic and as mentioned above isoquinoline is basic and charge on nitrogen atom is more negative. Thus the principle of like charges repel might prevent the adsorption of 1-methylisoquinoline onto the carbon surface. Liu et al. used DFT theoretical approach to explain selective adsorption capacity of Cu(I)zeolite adsorbent over heterocyclic nitrogen compounds in terms of adsorption energy in that energetically preferential adsorbate adsorbed on the adsorbent surface which could also be the reason why AC-N-Mo was very selective towards DBT (energetically favorable) in the presence of competitive nitrogen-containing compound (Liu et al. 2007, 2008).

3.12 Effect of aromatics on DBT removal

Toluene and naphthalene were added to DBT dissolved in isooctane and adsorption capacity was investigated accordingly following the addition of 5 vol% each of toluene and naphthalene separately

into DBT solution and their mixture in a solution containing DBT. Additionally, 10 vol% toluene was also examined for the maximum adsorption capacity in a solution containing DBT. The adsorption experiments were carried out at the working condition of initial concentration of DBT (100 mg-S/L) at room temperature over a fixed adsorbent weight. It was observed that the adsorption capacity of the best performing adsorbent (AC-N-Mo) reduced drastically in the presence of 5 % toluene at the equilibration time of 24 h but interestingly, effect of 5% naphthalene was insignificant. The percentage removal of DBT at 24 h in the presence of the former (toluene) and later (naphthalene) are 65.52 % and 81.17 % respectively corresponding to 13.11 and 16.03 mg-S/g adsorbent respectively as compared to 19.94 mg-S/g adsorbent achieved for DBT in the absence of the two aromatic hydrocarbons. For the 10 % toluene, maximum adsorption capacity of 9.96 mg-S/g adsorbent (49.78 %) was attained at 24 h. It is quite obvious that the studied adsorbent was very selective towards both of the aromatic compounds but more selective towards DBT in the presence of naphthalene. Also, the mixture of toluene and naphthalene (each of the two compounds 5 % by volume) were introduced in DBT solution and maximum adsorption capacity was evaluated at 24 h. The adsorption efficiency attained for DBT was 9.64 mg-S/g adsorbent corresponding to 48.20 % sulfur adsorbed. The existence of drastic reduction in the adsorption capacity of the adsorbent with increased aromatic (toluene) different concentrations (vol %) was attributed to competitive adsorption between DBT and toluene, both possess similar aromatic structure (Bhandari et al. 2006; Wang et al. 2009a). The investigated adsorbent has higher affinity for DBT relative to naphthalene as shown in the **Fig. 6B**. This sulfur adsorption affinity of the adsorbent could be ascribed not only to the closer size of the DBT molecules to the size of the adsorbent's pores thereby facilitated the preferential trapping of DBT into the adsorbent but also include the fact that DBT has higher molar mass, boiling point dipole moment and aromaticity compared to naphthalene resulting to π - π interactions and stronger van der Waals with the adsorbent surface. It is also worth mentioning that the basic properties of DBT also played a crucial role in that there exist acid-base interaction between DBT and molybdenum oxide (Lewis acid) on the sorbent surface thereby resulting in elevated adsorption capacity breakthrough of DBT (Nazal et al. 2015). To further understand the inhibiting effects of aromatic on the studied adsorbent, the same vol % of toluene and naphthalene were added into DBT solution and was investigated. The result obtained as shown in **Fig. 6B** revealed that increasing aromatics negatively inhibited adsorption capacity of the adsorbent due to higher competitive adsorption between the studied aromatics and DBT (Jha et al. 2019).

3.13 Adsorption kinetics

Adsorbents AC, AC-N, AC-N-Mo and AC-Mo were examined at the concentration range of 50 – 250 mg-S/L. To understand adsorption process and pathways, different kinetic models named pseudo-first order, pseudo-second order and intraparticle diffusion were studied. The pseudo-first order is often employed to describe the initial stage of adsorption process, the pseudo-second order provide an insight of the entire adsorption process and the overall adsorption capacity (Anbia and Parvin 2010) and the intraparticle diffusion is employed to determine whether the rate-determining step for each adsorbent is only intraparticle diffusion or not (Saleh et al. 2018). The details of the equation are described in SI. The value

for and were calculated from the slope and intercept of the plot of $\ln(-)$ versus t for the pseudo-first order kinetics, the value of k_2 and were obtained from the slope and intercept of the plot of versus t for the pseudo-second order kinetics respectively as shown in **Fig. SI-3**. and C were extracted from the slope and intercept of the plot of versus (see **Fig SI-5**). **Table SI-3** showed the summary of the kinetic parameters for the adsorbents studied at the varied sulfur concentration range for both pseudo-first order and pseudo second order kinetics for easy comparison. It is obvious from **Table SI-3** that is lower than and that R^2 value for pseudo-first order are lower than the R^2 values of pseudo-second order. This implies that the pseudo-second order kinetic is well fitted by the experimental implying that that the overall sorption rate was likely controlled by the chemisorption on the adsorbent's surfaces and this indicates that the specificity of the adsorbate-adsorbent interaction was very high (see **Fig. SI-4**) (Ho and Mckay 1999). The pseudo second order kinetics model provides an insight on the rate limiting step of a reaction. This could be by chemisorption wherein valence forces are shared or electrons are exchange between the adsorbate and adsorbent (Wang and Wang 2008). The intraparticle diffusion model plot showed that the intra-particle mass transfer properties that is proportional to for the removal of DBT follows the increasing order of $AC < AC-N < AC-N-Mo < AC-Mo$ (see **Fig. SI-5**). This implies that the adsorbents AC-Mo and AC-N-Mo are more intraparticle diffusion controlled than the AC-N and AC as shown in the R^2 values in **Table SI-3**. In addition, for the fact that the intraparticle diffusion model plots for the removal of sulfur-containing compound DBT did not pass through the origin reflect that there could be possibility of combination of complex adsorption mechanisms occurring such that intraparticle diffusion is not the only rate-determining step in the adsorption process (Saleh et al. 2018). In addition, Fig. SI-6 shows the change of S concentration in model fuel over time for each adsorbent at 100 mg-S/L to give a better understanding of adsorption process.

It can be seen from the comparison **Table SI-3** that there are slight difference between both the experimental and calculated and the R^2 values are closer to unity describing that the reaction proceed via pseudo second order kinetics.

3.14 Adsorption isotherm

Adsorption isotherms of the adsorbents were studied by Langmuir (see equation in **SI**) and the results are presented in **Fig. SI-7** Langmuir isotherm is not only used to quantify and contrast adsorptive capacity of a number of sorbents material but also to describe gas-solid phase adsorption. It balances the relative rates of adsorption and desorption (dynamic equilibrium) with respect to surface coverage. Adsorption and desorption are proportional to the open and cover adsorbent surface respectively (Ayawei et al. 2017). To understand well enough if the reaction is a favorable process which is an integral part of Langmuir isotherm, the below expression in **equation 3** is used.

$$R_L = \frac{1}{1 + K_L C_0} \dots \dots \dots 3$$

Where R_L (dimensionless), K_L ($L\ mg^{-1}$) and C_0 ($mg\ L^{-1}$) represent separation factor, Langmuir constant and the initial concentration of the adsorbate respectively. The R_L value is an essential features of the Langmuir isotherm representing the shape of the isotherm such that if $R_L > 1$, it implies unfavorable process, $R_L = 1$ indicates linearity and $0 < R_L < 1$ indicates favorable process (Kenneth et al.). Adsorption isotherms of the adsorbents were studied by Freundlich and the results are presented in **Fig. SI-7**. The Freundlich explains explain the surface heterogeneity or multilayer sorption, exponential distribution of active sites as well as their energies (Ayawei et al. 2017). The Freundlich equation is given in **SI**. It is obvious from the **Table SI-4** that the data fitted more for the AC and AC-N adsorbents with better correlation coefficient for Langmuir than Freundlich isotherms, while AC-Mo and AC-N-Mo adsorbents show higher R^2 value that favors the Freundlich isotherm. The R^2 values for nitrogen modified-AC is comparable, and this sorbent has tendency for both isotherms. This implies that the adsorbent and adsorbate interaction occurred on heterogeneous surface with a well-defined active site and energy, and this is due to its multifunctional surface properties resulted from nitrogen and molybdenum (Langmuir 1916). The value of $R_L < 1$ indicates that the reaction is favorable. The inverse of $1/n$ ($g\ L^{-1}$) > 1 indicates the favorable condition of the adsorption process (V.J.P. Poots, Gordon Mckay 1978). K_F and n are both evaluated from the linear plots of $\ln q_e$ against $\ln C_e$ corresponding to slope and intercept respectively.

Conclusions

Current work researched on the selective adsorption of DBT using adsorbents synthesized from agricultural waste product by zinc chloride ($ZnCl_2$) activation. The best performing adsorbent AC-N-Mo was taken as a potential adsorbent for further evaluation of ADS process. The improved performance can be ascribed to changes in the chemical nature of the adsorbents, the acidic nature of molybdenum (as confirmed in the NH_3 -TPD) and abundance surface-containing oxygen functional groups. The kinetic studies showed that the reaction proceeded via pseudo-second order kinetics, indicating that the adsorption process was likely to proceed by chemisorption wherein specificity of adsorbate-adsorbent interaction was very high. While the isotherm revealed that both Freundlich and Langmuir fit the data but Freundlich fit the data more accurately for the best performing adsorbent. It is obvious as demonstrated in this work that preparation of activated carbon from date seeds and its applicability for ultra-deep desulfurization is feasible, promising and worth further studying.

Consent for publication

All authors have read and gave their consents to the publication of this manuscript entirety.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Authors' contribution

All authors actively participated in the research activities in both experimental and theoretical ways, data processing and manuscript writing. The manuscript is prepared and approved with all authors. **MOA** worked majorly on the experimental part and preparation of the first draft under the guidance of **SAG**, **AT** engaged in carrying out some characterizations and discussion, while **KA** and **SAG** both worked on the logistics of materials for synthesis and characterization, and also participated greatly in the preparation of the drafts.

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Ethical approval

Not applicable for this work.

Consent to participate

Not applicable for this work.

Availability of data and materials

The data that support the findings reported in this work are embedded in the manuscript.

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Figures

Figure 1

(A) N₂ sorption isotherms (B) XRD (C) Raman and (D) FTIR of adsorbents

Figure 2

SEM images of adsorbents (A) AC (B)AC-N (C) AC-N-Mo and (D) AC-Mo

Figure 3

(a): XPS spectra of C1s and O1s in pure AC. (b): XPS spectra of C1s, O1s and N1s in pure AC-N. (c): XPS spectra of C1s, O1s N1s and Mo3d in AC-N-Mo

Figure 4

(A) Adsorption capacity of DBT on adsorbents at 100 mg-S/L and (B) Effect of initial concentrations (50 – 200 mg-S/L) on the AC-N-Mo. (adsorbent dosage of 100 mg, 20 mL of model fuel and contact time of 24 h)

Figure 5

Effect of sorbent dosage as a function of (A) percentage of sulfur adsorbed and (B) equilibrium quantity of sulfur adsorbed (initial conc. = 100 mg-S/L, 20 mL of isooctane containing DBT and 360 min contact time)

Figure 6

Selectivity performance of AC-N-Mo in the presence of (A) 1-methylisoquinoline and (B) aromatics toluene and naphthalene. (C_o = 100 mg-S/L, contact time = 24 h adsorbent dosage = 100 mg, and 20 mL solution of isooctane containing DBT)

Supplementary Files

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