Desulfurization studies of liquid fuels through nickel-modified porous materials from *Pongamia pinnata*

Zakiullah Zaidi¹ · Laxmi Gayatri Sorokhaibam¹

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Abstract

A new biomass-based carbonaceous adsorbent has been developed from *Pongamia pinnata* and its effect upon nickel modification- and adsorption-coupled ultrasonication was investigated. Adsorption experiment of the model oil constituting 50 ppm dibenzothiophene in cyclohexane showed the maximum capacity as 8.11, 13.36, and 17.15 mg·g⁻¹ for the commercial carbon DARCO, virgin bio-adsorbent PP, and nickel-modified adsorbent Ni@PP, respectively, with the time required for attaining equilibrium being the fastest in Ni@PP (120 min). The significant effect of ultrasonication was in attaining faster kinetics where ~96–98% removal was achieved in only 30 min. Also, the developed adsorbents had a very good specific surface area of 915 and 677 m²·g⁻¹, respectively, for PP and Ni@PP. Investigation of the effect of higher initial sulfur concentration (200 ppm) indicated the significance of Ni modification, where a very high capacity of 66.18 mg·g⁻¹ for Ni@PP was attained against 30.90 mg·g⁻¹ for PP and 13.18 mg·g⁻¹ for DARCO. Ni@PP was also effective for the simultaneous removal of more refractory sulfur fractions from multicomponent model fuel systems and exhibited good regeneration ability till the fourth cycles or more. Cost estimation showed that the developed adsorbents are relatively ten times cheaper than commercial carbon, while the fixed-bed study indicated a breakthrough time of 250 min and 270 min for PP and Ni@PP, respectively.

Keywords Desulfurization · Liquid fuels · Adsorption · Pollution · Sonication

Introduction

Desulfurization of liquid fuels is an important step in the petroleum refining process, as sulfur in liquid fuels contributes to the emission of SO_x and other particulate matters as air pollutants. In the atmosphere, SO_x may further react with water (H₂O) to form sulfurous (H₂SO₃) and sulfuric acid (H₂SO₄), leading to acid rain, causing harmful effects such as corrosion of metallic parts, damage to woodland and river water, etc. [1]. SO_x in air is also associated with various health issues, such as irritation of the nose, throat and eyes, and cough, while a higher level is linked with asthma, bronchitis, and heart disease [2]. According to the

US Environmental Protection Agency (EPA), and governments worldwide, the concentration of sulfur is limited to less than 30 ppm for gasoline and 15 ppm for diesel [3]. New regulations demand further limiting of these figures. Fuel cell applications also demand stricter regulations on sulfur levels (≤ 1 ppm), to avoid poisoning of the catalyst [4]. Also, sulfur compounds in liquid fuels are known to affect the functioning and efficiency of catalytic converters in automobiles [5]. It is therefore imperative to achieve an ultralow level of sulfur for cleaner fuels and a cleaner environment.

Most widely used liquid fuels such as gasoline and diesel contain aliphatic as well as aromatic hydrocarbon fractions with different sulfur fractions such as mercaptans (thiol), sulfides, disulfides, thiophene (T), benzothiophene (BT), dibenzothiophene (DBT), 4-methyl dibenzothiophene (MDBT), 4,6-dimethyldibenzothiophene (4,6-DMDBT), and alkyl-substituted benzothiophene [6]. Existing methods for reducing sulfur content from liquid fuels include hydrodesulfurization (HDS) [7], oxidative desulfurization [8], bio-desulfurization [9], extractive desulfurization [10], integration of such technologies, etc., where HDS is the most conventional method. However, due to the requirement of

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✉ Laxmi Gayatri Sorokhaibam
laxmigayatri1@gmail.com; laxmigayatri@chm.vnit.ac.in

¹ Environmental Remediation Laboratory, Department of Chemistry, Visvesvaraya National Institute of Technology Nagpur, Maharashtra 440010, India

high pressure (~20 MPa), high temperature (~500 °C) [11] and highly selective catalyst with a continuous supply of hydrogen, the cost of operation of the HDS process is quite high to meet the new environmental norms [12]. It also faces limitations for removing thiophenic derivatives such as BT, DBT and their alkyl substituents which are quite persistent and form a major sulfur component in liquid fuels [13].

Adsorptive desulfurization is one of the alternative energy-efficient methods which can be operated under ambient temperature and pressure conditions without consuming any catalyst or hydrogen gas. Common adsorbents such as zeolite, alumina, silica, activated carbon [14], and some metal–organic frameworks have also been explored for the removal of thiophenic sulfur compound [15]. In this regard, activated carbon is known to possess desirable physical properties like high surface area, large pore volume and chemical properties with the potential for a tunable surface with various metals/functional groups for selective sulfur removal. To improve its desulfurization capability, there are attempts to improve the pore structure/porosity and surface functionality or surface area through various modifications and wise choice of adsorbent source. In this regard, biomass-based material may offer an easy source with its rich functional groups. The present work involves the development of a new bio-adsorbent from the shells/pods of *Pongamia pinnata* fruit (Karanja Tree), its modification, and application in desulfurization studies. The raw material, *Pongamia pinnata*, is widely available in Asian regions and its utilization as a biomass source for environmental remediation is a good option. *Pongamia pinnata* (PP) tree grows in semi-arid regions of Asia and South Asian regions [16], and 9–90 kg of fruit shells can be obtained from a single tree in one season. Different parts of the plant can be used to prepare adsorbents for metal (Cu, Cr, Pb, etc.) adsorption [17–19] and wastewater treatment, particularly dyes such as methylene blue rhodamine B [20]. However, no studies have been reported yet on the desulfurization of liquid fuels using this plant material as an adsorbent. The need for the development of highly efficient adsorbents for desulfurization demands further modification or fabrication. Immobilization with nickel metal may enhance desulfurization performance through the formation of π -complexation between surface-deposited Ni metal and π -electron of the organosulfur compound or direct binding of metal to thiophenic sulfur compound [21–23]. Besides providing active sites, the incorporation of Ni metal may provide textural/structural changes on the biomass matrix, which is already rich in various chemical constituents like flavonoids and fatty acids [24].

Another possibility of enhancing the desulfurization capacity may be through coupling with the ultrasonication process. Adsorption under the ultrasonication process introduces waves that agitate the adsorbent quickly and may aid

in achieving adsorption equilibrium in a very short period [25]. High-frequency sonication is known to improve the pores of adsorbent, whereas extremely high reaction conditions may break the pore structure. It is therefore worthy to investigate the effect of ultrasonication on the adsorption process. The present study involves the development of a new bio-adsorbent and modification with Ni as active species to investigate its desulfurization performance using a model oil consisting of DBT in cyclohexane and the effect of ultrasonication. Desulfurization performance of the synthesized bio-adsorbent (PP), nickel-modified bio-adsorbent (Ni@PP), and commercially activated carbon (DARCO) were studied and compared. The kinetics and thermodynamics study, of the prepared adsorbents, was also investigated.

The present work is a complete study on the effect of Ni modification and covers the investigation of various adsorption parameters, which is essential to understand the adsorption mechanism rather than a mere determination of batch adsorption capacity. Further, to understand the possibility of scaling up, industrial application and reusability of the adsorbent, adsorption study of the multicomponent model fuel system, fixed-bed study, and regeneration studies were also investigated. In a nutshell, the present work is a complete study to understand the different aspects of adsorptive desulfurization.

Experimental section

Materials

All chemicals used in the present study were of analytical grade and used without further purification. The detailed information of these chemicals is given in Table 1, and consists of nickel (II) nitrate hexahydrate (Central Drug House 99%), sodium lauryl sulfate (SLS, Fisher Scientific $\geq 99\%$), sodium borohydride ($\geq 97\%$ Fisher Scientific), sodium hydroxide ($\geq 97\%$ Merck), orthophosphoric acid (Fisher Scientific 98%), activated charcoal (DARCO, 4–12 mesh), dibenzothiophene (Sigma-Aldrich 98%), 4,6-dimethyldibenzothiophene (Sigma-Aldrich 97%), and cyclohexane (RANKEM HPLC grade 99.7%). Millipore water used in the experiment was obtained from Merck Millipore (Progard TS2).

Preparation of PP and Ni@PP adsorbent

The pods of *Pongamia pinnata* were collected from the local area of Nagpur, India, and washed thoroughly with tap water to remove all the impurities and sun-dried for 12 h. The dried shells were ground to fine powder of uniform size through sieving (60/ASTM 30, the width of aperture: 0.592 mm). The next step consisted of chemically activating the samples

Table 1 Chemical compounds and CAS registry details

Chemical name	Molecular formula	CAS number	Model/Company	Assay
Nickel (II) nitrate hexahydrate	Ni(NO ₃) ₂ ·6H ₂ O	13478-00-7	Central Drug House	99%
Sodium lauryl sulphate	C ₁₂ H ₂₅ NaO ₄ S	151-21-3	Thermo Fisher Scientific	≥ 99%
Sodium borohydride	NaBH ₄	16940-66-2	Thermo Fisher Scientific	≥ 97%
Sodium hydroxide	NaOH	1310-73-2	Merck	≥ 97%
Orthophosphoric acid	H ₃ PO ₄	7664-38-2	Thermo Fisher Scientific	≥ 88%
Activated charcoal, DARCO, Acros organics	C	7440-44-0	Thermo Fisher Scientific	4–12 mesh
Dibenzothiophene	C ₁₂ H ₈ S	132-65-0	Sigma-Aldrich	98%
4,6-Dimethyldibenzothiophene	C ₁₄ H ₁₂ S	1207-12-1	Sigma-Aldrich	97%
Cyclohexane	C ₆ H ₁₂	110-82-7	RANKEM (HPLC)	99.8%
Millipore water	H ₂ O	PROG0T0S2	Merck, Progard TS2	–

with orthophosphoric acid (1:1; w/v) at 60 °C for 1 h [26]. Acid-treated paste was then placed inside a muffle furnace maintained at 500 °C for 1 h at a heating rate of 10 °C per hour. The black-colored powder so obtained was crushed into a fine powder and washed several times with distilled water to nearly neutral pH. The sample was then dried overnight at 85 °C for complete dryness and finally activated carbon, and the thereby obtained product was referred to as PP.

PP was further modified through Ni impregnation. Briefly, 40 mL of 0.3 M solution of nickel nitrate and 2 g of PP were mixed in a 100 mL beaker and stirred at room temperature. To this mixture, 15 mL of 0.05 M NaBH₄ in ethanol as a reducing agent and 10 mL of 3.0 M NaOH (aq) were added dropwise. The resulting mixture was stirred continuously at 80 °C for 3 h with simultaneous addition of 0.2 g of SLS as a binding agent. The resultant carbon was collected by centrifugation at 4000 rpm and washed several times to remove any unbound metal as well as the surfactant. The collected powder was dried overnight in an oven at 85 °C and calcined at 350 °C for 1 h in a silica crucible; finally, ~7% Ni-impregnated carbon was obtained and is designated as Ni@PP hereafter.

Desulfurization of model oil and analysis method

Desulfurization of model oil was studied through batch adsorption using 50 ppm DBT in cyclohexane. Pre-determined load of adsorbents in 10 mL DBT solutions in several conical flasks were placed inside an orbital shaker incubator (EIE Instruments Pvt. Ltd, India), maintained at 100 rpm and a constant temperature (30 °C) for a total time of 5 h. The flasks were kept for different time intervals under similar experimental conditions for the kinetic study. After performing adsorption experiments, these solutions were filtered with filter discs (Sartorius) of diameter 125 mm. The final concentration of DBT present in the reaction mixture was analyzed through UV–Vis

double beam spectrophotometer (UV 1800, Shimadzu) at a maximum wavelength ($\lambda_{\max}$) of 326 nm. The equilibrium adsorption capacity q_e (mg·g⁻¹) and percentage removal of DBT from prepared model oil were calculated from Eqs. (1) and (2), respectively, where C_0 is the initial concentration in mg·L⁻¹, C_e is the concentration at equilibrium, also in mg·L⁻¹, ' m ' is the weight of adsorbent in g and ' V ' is the volume of the model oil in L.

$$q_e = \frac{(C_0 - C_e)}{m} \times V \quad (1)$$

$$\% \text{ removal} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

The effect of initial sulfur concentration was studied at three different concentrations, 50, 100, and 200 ppm under optimum experimental conditions, and the different concentrations of DBT were prepared by appropriate dilution of the stock solution (1000 ppm DBT in cyclohexane as hydrocarbon stream). Multicomponent model fuel (MMF) system was studied using a binary mixture of DBT and 4,6-DMDBT in cyclohexane with a total sulfur concentration of 50 ppm. Batch adsorption experiments of MMF were performed with DARCO, PP, and Ni@PP under the optimized reaction conditions, i.e., 8 g·L⁻¹ for 3 h at room temperature. The initial and final concentrations of MMF were analyzed through GC-FPD (Chromatec-Crystal 9000) with GS BP-1 capillary column (30 m × 0.32 mm × 4 μm) using helium as carrier gas with capillary flow 3 mL·min⁻¹, with continuous hydrogen flow (140 mL·min⁻¹) and airflow (40 mL·min⁻¹). The oven temperature of FPD was 250 °C (50;0, 200;15, 250;25) with a sample injection of 0.1 μL and the total analysis time was 36 min with 0.9 min hold time. The instrument was first calibrated with DBT and 4,6-DMDBT to know their retention period peaks which were obtained at 24 and 31 min.

Adsorption-coupled ultrasonication

The sonication process is known to increase the porosity of sorbents which also affects the adsorption results. The adsorption behavior of DBT over DARCO, PP, and Ni@PP, followed by adsorption-coupled sonication treatment under the batch-optimized condition was studied using a sonicator, ultrasonic cleaner Fs4 of Dharmale Lab Instruments (volume 2.5 L, frequency 40 kHz, power 50 W) filled with Millipore water. The experimental flasks were placed in the center of the bath and the intensity of sonication was maximum [27] with a breakage of 5 min every 30 min. The experiment was performed for a total time of 3 h. During sonication, the temperature of the water bath was maintained with a variation of about ± 2 °C to achieve ideal reaction conditions.

Fixed-bed column studies and cost estimation

The column experiment was carried out by using a glass column of 20 cm height and 1 cm inner diameter with the optimized equilibrium data from the batch study. The experiment was performed with 1 g each of DARCO, PP, and Ni@PP filled with a bed height of 3 cm, supported with cotton and glass wool at both the ends. Model oil of 50 ppm sulfur was passed as influent and collected at different time intervals of 15 min each up to 5 h time duration for analyzing the DBT concentration. The column study was investigated at two different flow rates: 0.75 mL·min⁻¹ and 1.5 mL·min⁻¹. The column experiment parameters were obtained from the breakthrough curve and with the help of the linearized Thomas model.

Characterization techniques

Powdered X-ray diffraction (PXRD) data of virgin activated carbon (PP) and Ni@PP were collected from Xpert Pro PAN analytical diffractometer with a Xenon proportional detector employing Cu K α radiation ($\lambda = 1.5418$ Å) over a 2θ range of 10–70 °C with 0.04 degree per 6 s of scanning rate. The Fourier transform infrared (FTIR) spectra of PP, Ni@PP, and DARCO were recorded on IR Affinity-1, Shimadzu, using KBr in the frequency range of 400–4000 cm⁻¹. The texture and the morphology of the adsorbents were analyzed using field emission-scanning electron microscopy (FESEM-JEOL) with platinum coating on carbon tape and the distribution of various hetero atoms and Ni species on the surface of the adsorbent was examined using INCA Oxford energy-dispersive X-ray (Japan) for elemental composition. Thermal gravimetric analysis (TGA) with EXSTAR HITACHI A7200 was conducted under nitrogen flow at a heating rate of 10 °C per min up to 900 °C to understand the thermal stability of the prepared adsorbents. The surface area of the prepared adsorbents was studied using nitrogen adsorption

and desorption isotherm with prior degassing at 200 °C for 4 h through Brunner–Emmett–Teller surface analysis (BET-Quanta Chrome model Q2: Florida, USA) at liquid nitrogen temperature 77.35 K, where BJH (Barrett–Joyner–Halenda) method was used to calculate the values for pore size distribution curves.

Results and discussion

Characterization of the adsorbents

The XRD patterns of PP and Ni@PP are given in Fig. 1a; appearances of broad peaks at 24° and 44° indicate the amorphous nature of PP, as it is a carbonaceous material. Ni@PP exhibited some major peaks at 29.54°, 35.78°, 39.06°, 42.91°, and 53.42°. associated with the d value of (220), (222), (400), (331), and (511), respectively, which could be matched with #PDF 021,216 as nickel oxide, whereas the appearance of low-intensity peaks at 53.42°, 60.33°, and 67.66° indicate that nickel was highly dispersed on the surface rather than forming any crystal structure of nickel in pure phase. The synthetic reaction for the reduction of nickel nitrate (Ni(NO₃)₂) with sodium borohydride (NaBH₄) occurs to form metallic nickel (in zero oxidation state), which upon extended exposure to high temperature leads to the formation of nickel oxide (NiO). The X-ray diffraction analysis of Ni@PP was observed to be of NiO formation, whose corresponding JCPDS number is provided. On the other hand, the peak corresponding to Ni(0) was not significant for validating with JCPDS.

FTIR spectra of DARCO, PP, and Ni@PP (Fig. 1b) revealed an almost similar pattern between 4000 cm⁻¹ and 3000 cm⁻¹. In DARCO, a broad band was observed at 3325 cm⁻¹ due to O–H stretching vibration, whereas in PP and Ni@PP the same band may have disappeared due to calcination. In the case of PP and Ni@PP, the band at 2954 cm⁻¹ may be ascribed to aliphatic C–H stretching vibrations of CH₃, CH₂, and CH in carbonaceous material, whereas the bands near 1750 cm⁻¹ and 2200–2400 cm⁻¹ can be ascribed to the C=O axial deformation and at 1600 cm⁻¹ can refer to C=C stretching vibration [28, 29]. FTIR spectra of PP and Ni@PP showed bands at 1375 cm⁻¹ due to –CH₃ bending vibration; however, C–O stretching of ethers, phenols, esters, acids, and carboxylate are mostly identified in oxidized carbon material at 1415 cm⁻¹ and 1010 cm⁻¹ and also the O–H bending vibrations attributed at 1110 [30, 31]. Various weaker bands present between 500 and 800 cm⁻¹ (fingerprint region) illustrate the presence of aromatic groups on the surface of DARCO, PP, and Ni@PP. Nevertheless, in the case of Ni@PP, some bands such as 2360 cm⁻¹ and 1600 cm⁻¹ have disappeared after impregnation of nickel metal which may be due to the increasing the

Fig. 1 Characterization of adsorbents: **a** XRD, **b** FTIR and **c** TGA pattern

crystallinity of the sample behavior that may also be correlated to the successful loading of metal onto activated PP.

Thermal gravimetric analysis of all the three adsorbents (Fig. 1c) shows the process of dehydration from 50 $^{\circ}\text{C}$ onward. Commercial activated carbon (DARCO) and prepared bio-adsorbent (PP) showed almost similar weight loss in the range of 50–500 $^{\circ}\text{C}$. Since the developed biomass PP has a relatively higher surface area and greater porosity than DARCO, the rate of desorption of adsorbed species was higher with greater weight loss in the region of 500–900 $^{\circ}\text{C}$. Above 270 $^{\circ}\text{C}$, PP exhibited an extensive loss in weight percentage (up to 26%) as compared to DARCO, which indicates the possible loss of oxygenated groups. In the aqueous medium, SLS (used in the synthesis of Ni@PP) may be oxidized to their corresponding alcohols and may produce gasses at 270 $^{\circ}\text{C}$ [32]. Continuous heating at higher temperature yielded their fractions such as dodecene, tetradecene, hexadecene mixtures, and pyrolyzed form, such as alcohols and ethers derivatives. The TGA curve of Ni@PP

shows the weight loss percentage reached up to 37% in heating from 500–900 $^{\circ}\text{C}$. SLS is used in the synthesis process only to develop negatively charged sites on PP. Since SLS is an anionic surfactant, it is expected to deliver a higher deposition of electropositive metals. It is therefore plausible that SLS present on the PP surface may be holding the Ni atoms. Thus, the TGA curve shows the high weight loss due to SLS itself which may correspond to the liberation of various fractions such as dodecene, tetradecene, and hexadecene mixtures.

The specific surface area and pore size distribution of DARCO, PP, and Ni@PP were calculated by BET and BJH methods, respectively, at 77.35 K. Figure 2 shows the nitrogen adsorption–desorption isotherm of all the three adsorbents. The pore radius obtained from the pore size distribution curve is between 0.71 and 0.72 nm for all the three adsorbents, indicating microporous nature with less external face shows one of good adsorption potential. According to IUPAC, all three adsorbents approaches

Fig. 2 N_2 adsorption–desorption isotherm and pore size distribution curve of adsorbents

Table 2 Structural properties of the adsorbents

	Adsorbents		
Physical property	DARCO	PP	Ni@PP
Surface area ($m^2 \cdot g^{-1}$)	458	915	677
Pore volume ($cm^3 \cdot g^{-1}$)	0.23	0.61	0.51
Pore radius (nm)	0.720	0.719	0.717
Micropore surface area ($m^2 \cdot g^{-1}$)	288	787	597

Type II isotherm, and in DARCO the inflection point/knee point ‘B’ is almost linear and resembles Type I isotherm showing monolayer adsorption. In PP and Ni@PP, some multilayer adsorption also occurs at relatively low pressure due to adsorption at available pores and surface sites in a stepwise manner. Hysteresis loop at relatively low pressure associated with H4 in all three cases may also be attributed mainly to microporous carbon [33]. The BET surface area of DARCO and PP is 458 and 915 $m^2 \cdot g^{-1}$ whereas, upon Ni loading onto PP, the surface area decreased to 677 $m^2 \cdot g^{-1}$ along with reductions in pore volume. Acid treatment and calcination process may be responsible for higher surface area and greater pore volume of the as-synthesized adsorbents. A closer look at the shape of the adsorption–desorption isotherms, particularly the existence of clear knee point inflection in PP and Ni@PP, hints toward complete monolayer adsorption, followed by multilayer adsorption. This is not so prominent in the case of DARCO, indicating the overlapping of monolayer and multilayer adsorption. The information on the porosity and surface area of all the three adsorbents are given in Table 2. The surface area of PP and Ni-modified PP was relatively high as compared to the commercial activated carbon, which indicates that the synthesized bio-adsorbent

and the modification of the same may find suitable application with good potential.

Surface morphological characteristics of commercial activated carbon (DARCO) and prepared adsorbents PP and Ni@PP were analyzed by field emission scanning electron microscopy (FE-SEM) technique. Figure 3a indicates a smooth surface of the commercial adsorbent, while Fig. 3b demonstrates that synthesized PP having numerous pores and heterogenous rough surfaces. Figure 3c indicates successful impregnation of Ni on the PP surface, also supported by the color mapping of successful Ni impregnation as shown in the inset image (within Fig. 3c), revealing fine dispersion of Ni species in the pore channels of the carbon matrix. EDX pattern of Ni@PP (Fig. 3d) shows the occurrence of carbon, oxygen, and nickel of weight percent 75.3, 17, and 7.8%, respectively. Since Ni@PP showed favorably higher performance for DBT in comparison to the remaining two adsorbents, detailed characterization using EDX was conducted for Ni@PP.

Adsorption equilibrium study

An adsorption equilibrium study was conducted with different quantities of adsorbents, in the range 0.5–8 $g \cdot L^{-1}$ at ambient temperature (30 °C) for an optimized reaction time of 5 h. The samples were kept in contact with the model oil of 50 ppm concentration under continuous agitation inside a thermostat orbital shaker at 100 rpm as described previously. It was observed that the removal of DBT increased with the increase in adsorbent doses which may be attributed to the availability of a greater number of vacant sites or due to π complexation sites as with Ni@PP. The maximum adsorption capacity was 8.11 $mg \cdot g^{-1}$ for DARCO, 13.36 $mg \cdot g^{-1}$ for PP, and 17.15 $mg \cdot g^{-1}$ for Ni@PP respectively (Fig. 4).

Fig. 3 FE-SEM images of **a** DARCO, **b** PP, **c** Ni@PP (color mapping of Ni metal is shown in the inset image) and **d** EDX of Ni@PP

Fig. 4 Equilibrium adsorption isotherm plot for **a** DARCO, **b** PP, and **c** Ni@PP

The optimum dose selected for adsorption was 8 g.L⁻¹ for further kinetic and thermodynamic studies. Ni modification also shortened the equilibrium time needed for adsorption from 3 to 2 h in the case of PP and Ni@PP, while the commercial DARCO had a longer equilibrium time of 5 h for DBT adsorption, the detailed information for which is given in supplementary file (Fig. S1).

Adsorption isotherm analysis helps to understand the possible interactions between adsorbate and adsorbent. The adsorption data were analyzed using three different models, Freundlich, Langmuir, and Temkin isotherm, whose expressions are given in Eqs. (3), (4), and (5), respectively.

$$\ln(q_e) = \ln K_F + \frac{1}{n} \times \ln C_e, \quad (3)$$

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}}, \quad (4)$$

$$q_e = \left(\frac{RT}{b_T} \right) \times \ln A_T + \left(\frac{RT}{b_T} \right) \times \ln C_e, \quad (5)$$

where C_e ($\text{mg}\cdot\text{L}^{-1}$) is the equilibrium concentration of DBT, q_e is the maximum adsorption capacity obtained experimentally, K_f ($\text{mg}\cdot\text{g}^{-1}$) is the Freundlich constant representing the quantity of DBT adsorbed onto adsorbents, and $1/n$ denotes the adsorption intensity [28]. A lower value of $1/n$ shows the greater possibility of a heterogeneous reaction.

Langmuir adsorption isotherm assumes that each site of the adsorbent surface can hold a maximum of one molecule, indicating monolayer adsorption on a homogeneous adsorbent surface without interaction between the adsorbed DBT species [34]. q_{max} is the maximum theoretical monolayer adsorption capacity and K_L is the Langmuir equilibrium constant or the affinity of the adsorbate molecule to bind with the adsorbent. An essential characteristic of Langmuir isotherm is the separation factor, R_L , whose expression is given in Eq. (6). If $R_L = 0$, then the adsorption process would be irreversible; for favorable reaction condition, it should be $0 < R_L < 1$, and if $R_L = 1$ then the reaction would be completely unfavorable [35]. The obtained separation factor for DARCO, PP, and Ni@PP are 0.49, 0.56, and 0.58, respectively, with values less than unity indicating favorable DBT adsorption.

Temkin isotherm is an extension of Langmuir isotherm where A_T represents the Temkin equilibrium binding constant ($\text{L}\cdot\text{g}^{-1}$), b_T ($\text{kJ}\cdot\text{mol}^{-1}$) is the Temkin isotherm constant, $T(\text{K})$ denotes the temperature, and R is the universal gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) and $(RT\cdot b_T^{-1})$ is constant, i.e., B ($\text{J}\cdot\text{mol}^{-1}$) which is related to the heat of sorption. A higher value of b_T favored a strong interaction between DBT and the adsorbent. The obtained values for all three isotherm parameters are given in the supplementary file (Fig. S2 and Table S1) from where we can differentiate the most fitting curve. Based on the correlation factor, Langmuir isotherm could best describe the adsorption of DBT onto the three adsorbents. Furthermore, b_T values for all the three adsorbents indicate the adsorption of DBT as physisorption via an exothermic process [36].

$$R_L = \frac{1}{(1 + KC_0)} \quad (6)$$

Effect of initial sulfur concentration

Determination of the effect of initial sulfur concentration may help us to give an idea behind the applicability of the adsorbent under higher S conditions. Hence, adsorption of DBT was carried out with three different initial concentrations of sulfur, viz., 50 ppm, 100 ppm, and 200 ppm. The equilibrium adsorption capacities are 8.11, 11.9, and 13.18 $\text{mg}\cdot\text{g}^{-1}$ for DARCO, 13.36, 22.59, and 30.90 $\text{mg}\cdot\text{g}^{-1}$ for PP, and 17.15, 43.18, and 66.18 $\text{mg}\cdot\text{g}^{-1}$ for Ni@PP, respectively, for three different increasing sulfur concentrations as given in Table 3.

It is seen that an increasing DBT concentration increases the adsorption capacity, and the difference between commercial activated carbon and synthesized adsorbent PP and Ni@PP is very wide (Fig. S2). This is due to the presence of larger surface area and pore volume of the synthesized adsorbent PP which provides more space/volume to capture DBT. Increasing initial concentration also increased the probability of greater solid–liquid contact, allowing more DBT molecules to diffuse on the adsorbent surface. The role of active Ni species and the possibility of some chemical interaction or π interaction may be attributed to the significantly higher adsorption of Ni@PP as compared to PP. This is evident from the significantly higher capacity of Ni@PP at a higher initial S concentration of 200 ppm.

Adsorption kinetics

Investigation for determination of equilibrium time was carried using the model fuel (50 ppm DBT solution) with an optimized dose of $8 \text{ g}\cdot\text{L}^{-1}$ at different time intervals and up to a maximum of 300 min. It was observed that the adsorption efficiency consistently increases and reaches equilibrium at 120 min for Ni@PP, 180 min for PP, and 300 min for DARCO. This may be due to the saturation of active sites and decreasing concentration gradient for a fixed initial concentration of DBT [37, 38]. Ni modification could therefore effectively decrease the equilibrium time needed for maximum adsorption.

To investigate the kinetic mechanism, three different kinetic models, viz., pseudo-first order, pseudo-second order, and intraparticle diffusion model were employed whose linear expressions are given in Eqs. (7), (8), and (9), respectively.

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_1}{2.303} \right) \times t \quad (7)$$

$$\left(\frac{t}{q_t} \right) = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} \times t \quad (8)$$

$$q_t = K_d t^{0.5} + c \quad (9)$$

Table 3 Effect of initial S concentration and adsorption capacity

Initial S concentration (ppm)	DARCO ($\text{mg}\cdot\text{g}^{-1}$)	PP ($\text{mg}\cdot\text{g}^{-1}$)	Ni@PP ($\text{mg}\cdot\text{g}^{-1}$)
50	8.11	13.36	17.15
100	11.9	22.59	43.18
200	13.18	30.90	66.18

$$K_{fd}t = -\ln \left(1 - \frac{q_t}{q_e} \right) \quad (10)$$

where K_1 is the pseudo-first-order rate constant which can be calculated from the plot of $\log (q_e - q_t)$ against t , and q_t refers to the amount of DBT adsorbed at the time, ' t '. In pseudo-second-order kinetics K_2 represents the pseudo-second-order rate constant which can be obtained from the linear plot of t/q_t versus t . The value of the different kinetic parameters of the three models is given in the table (Table S2). The intraparticle diffusion plot for the adsorption study is given in Fig. 5a, while Fig S4 indicates the pseudo-first- and -second-order plots. The correlation coefficient (R^2) approaches unity with pseudo-second-order model, proving that it is the best fit model to explain the kinetics of the adsorption process. The rate constant values from kinetics study also proved that Ni@PP had the fastest kinetics for DBT ($0.34 \text{ g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$) removal, followed by PP ($0.21 \text{ g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$) and DARCO ($0.004 \text{ g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$).

The intraparticle diffusion model was first examined by Weber–Morris, the linearized form of which is expressed in Eq. (9), where K_d is the intraparticle diffusion rate ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-0.5}$), t is the time and the intercept ' c ' is a parametric constant that reflects the thickness of the diffusion layer ($\text{mg}\cdot\text{g}^{-1}$). If the straight-line plot between q_t vs $t^{0.5}$ passes through the origin, then the obtained intercept (c) and the regression coefficient (R^2) identify the rate-determining step of the adsorption process. As observed from Fig. 5, all the three adsorbents are expected to follow multilinear paths with an initial sharp inclined path. In the case of DARCO, the first linear path indicates the instantaneous adsorption

process, whereas the second one pertains to intraparticle diffusion on the surface of the adsorbent due to the presence of micropores [3]. However, in the case of PP and Ni@PP following three-stage adsorption processes, the first straight line shows immediate adsorption which is due to the presence of active surface sites and the high concentrations of DBT. The second stage is fairly slow, as the active surface sites decrease, which may be ascribed to intraparticle diffusion. The final stage of the adsorption process approaches an equilibrium where the intraparticle diffusion slowed, as all the active sites were occupied by the DBT molecule. The overall rate of adsorption depends on the slowest of these steps. The higher deviation from the origin in PP and Ni@PP may occur due to the high agitation rate during kinetics or due to the difference in mass transfer rate during the initial and final adsorption process.[39]. Thus, the multilinear path suggested that intraparticle diffusion may not be a rate-controlling step and the film diffusion model [40] was as such investigated, whose linearized expression is given in Eq. (10), where K_d is the intraparticle diffusion rate ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-0.5}$), K_{fd} is the film diffusion rate (min^{-1}), ' t ' is the time and the intercept ' c ' is a parametric constant reflecting the thickness of the diffusion layer ($\text{mg}\cdot\text{g}^{-1}$). The plot for the same is given in Fig. 5b. The higher the K_d value, the higher is the rate of DBT deposition on the surface of the adsorbent. Consequently, the values obtained for DARCO is $0.31 \text{ g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$, which suggests that the DBT adsorption is still an ongoing process, while for PP and Ni@PP the rates are 0.014 and $0.016 \text{ g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$, respectively, corresponding to reaching the equilibrium state. The overall result shows that the rate of mass transfer for DARCO is fairly controlled by intraparticle diffusion; however, for PP

Fig. 5 Kinetic study through diffusion model, **a** Intraparticle diffusion and **b** film diffusion model

and Ni@PP, it was controlled by film diffusion or chemical reaction.

Adsorption thermodynamics studies

The adsorption of DBT on DARCO, PP, and Ni@PP was carried out at three different temperatures (303 K, 313 K, and 323 K) for thermodynamic studies. The parameters ΔG° (Gibbs free energy), ΔH° (Enthalpy change), and ΔS° (Entropy change) are the keys to explain the adsorption behavior. The values of ΔH° and ΔS° were determined from the slope and intercept obtained from linearized van't Hoff Eq. (11) from the plot of $\log K$ versus $1/T$ (Fig. 6), where $K = q_e/C_e$. A negative value for ΔH° and ΔS° will indicate that the adsorption process is exothermic. A higher negative value of ΔS° is known to increase the randomness and disorderliness of DBT on the adsorbent surface (Khan, Nazir, & Khan, 2013). The ΔG° values were calculated from Eq. (12), where the negative values show the spontaneous nature of DBT adsorption (-0.328 , -6.003 , and $-7.909 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, respectively, for DARCO, PP, and Ni@PP). The magnitude of change in enthalpy is used to find the nature of adsorption, with a value of ΔH in the range of 2.1 – $20.9 \text{ kJ}\cdot\text{mol}^{-1}$ referring to the physisorption process and 80 – $200 \text{ kJ}\cdot\text{mol}^{-1}$ value as chemisorption process. ΔH value for DARCO is $5.75 \text{ kJ}\cdot\text{mol}^{-1}$ which suggests the removal of DBT as a physisorption process, whereas for PP and Ni@PP, the values are, respectively, 45.28 and $56.41 \text{ kJ}\cdot\text{mol}^{-1}$ reflecting the chemisorption process. Entropy change values were found to be positive in all three cases as 17.9 , 129.62 , and $160.07 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, respectively, for DARCO, PP, and Ni@PP. The detailed information of all thermodynamics parameters at different temperatures are given in the supplementary file (Table S3). Furthermore, by raising the temperature, ΔG° value increases which also indicates that the

DBT adsorption is more favorable at a lower temperature, while only desorption occurs at a higher temperature.

$$\log \left(\frac{q_e}{C_e} \right) = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad (11)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (12)$$

Adsorption studies using multicomponent S containing model liquid fuel

To check the effectiveness of the developed adsorbent toward the removal of more refractory sulfur compounds and the applicability to real fuel systems, an adsorption experiment was performed on a multicomponent model fuel (MMF) consisting of DBT (474 ppm) and refractory 4,6-DMDBT (111 ppm) in cyclohexane. With the total initial S concentration of 575 ppm, the adsorption experiments were performed with DARCO, PP, and Ni@PP under the optimized reaction condition, i.e., $8 \text{ g}\cdot\text{L}^{-1}$ for 3 h. The initial and final concentrations of MMF were analyzed through GC-FPD. Two major peaks were obtained at retention times of 24.6 and 31 min, corresponding to DBT and 4,6-DMDBT (Fig. 7). After the adsorption experiments, the response of DBT gradually decreased up to 14 ppm; however, a lesser removal of 4,6-DMDBT was observed (8.8 ppm). The results depict

Fig. 6 Thermodynamics plot $\ln K$ against $1/T$ of Ni@PP, PP, and DARCO

Fig. 7 GC-FPD chromatograms of MMF, DARCO, PP, and Ni@PP

the effectiveness of Ni@PP in reducing the concentration of both the fuel components, as the peak corresponding to both DBT and 4,6-DMDBT nearly vanished consequently after adsorption with Ni@PP, while chromatograms after adsorption with DARCO and PP still show the response due to the respective S components though with lesser intensity.

Comparison of desulfurization capacity of various adsorbents

Surface modification plays an important role in the adsorption process and acid-treated activated carbon can offer effective adsorption performance over untreated carbons. Due to the high electron density in the *d*-orbital of a transition metal, it may easily form π -complexation through back π -donation to the rings of the aromatic sulfur compound. Among several transition metals, nickel has been considered as the most effective supporting element which may easily interact with sulfur [42]. Ni has been utilized to modify various substrates, but the results obtained were not convincing enough in terms of capacity achieved [43, 44]. However, the present study showed that Ni modification over suitable biomass sources like *Pongamia pinnata* has superior adsorption capacity. Literature study of some Ni-based adsorbents and their effect of DBT removal for different initial sulfur concentrations are given in Table 4. Further, it was observed that most of the modifications were done on Y zeolites as the substrate with low capacities mostly below 10 mg·g⁻¹. In the present work, we successfully developed Ni-modified bio-adsorbent referred to as Ni@PP which has a relatively higher capacity (17.15 mg·g⁻¹) than most of the zeolite types.

Effect of ultrasonication

The effect of sonication on desulfurization efficiency was investigated, which indicated that adsorption-coupled sonication could enhance the percentage removal of DBT from 42.84 to 63.53% in the first 30 min for DARCO. As the micropore surface area of DARCO is less compared to PP and Ni@PP

(DARCO, PP, & Ni@PP=288, 787, and 597 m²·g⁻¹), DARCO may have a greater scope to increase the porosity on its surface during sonication. There is a negligible improvement of less than 1% for PP and Ni@PP in the initial 30 min as DBT adsorption approaches to deep desulfurization for adsorption-coupled sonication and the surface is already saturated with no room for improvement. A graph depicting the comparison between simple adsorption and adsorption-coupled sonication is provided in Fig. 8.

Fixed-bed column studies

The fixed-bed column studies at different influent flow rates, bed height, and initial concentration determine the efficient retention time [51] of the adsorbate from the achieved breakthrough curves. The effect of batch adsorption and ultrasonication showed that Ni@PP has better efficiency for DBT adsorption. To determine the dynamic behavior of the adsorbent, the theoretical parameters of adsorption through columns were studied for DARCO, PP, and Ni@PP at different flow rates. The breakthrough curve was obtained by plotting a graph between C_t/C_0 against time (*t*), where C_t is the initial effluent concentration and C_0 is an influent concentration of DBT. The obtained breakthrough curve (Fig. 9a) demonstrates how the specified flow rate affects in achieving equilibrium. By increasing the flow rate from 0.75 to 1.5 mL·min⁻¹, a decrease in the exhaustion time was achieved at 255 min for Ni@PP and 270 min for PP.

The Thomas model [52] is mostly used to study the second-order reaction kinetics and adsorption data obeying Langmuir adsorption isotherm. The major objective for the Thomas model is to find the maximum capacity, rate constant, and deposition of adsorbate concentration during the adsorption [51]. The linearized form of the model is specified in Eq. (13) as.

$$\ln \left(\frac{C_0}{C_t} \right) - 1 = K_{TH} Q \left(\frac{W}{F} \right) - K_{TH} C_0 t \quad (13)$$

Table 4 Nickel modified adsorbents for desulfurization of liquid fuels

Adsorbent	S Compound	H–C stream	S concentration (ppm)	Adsorption capacity (mg·g ⁻¹)	References
CLP-Ni	DBT	Iso-octane	10	2.70	[45]
Ni/MMS	DBT	<i>n</i> -octane	140–572	6.53	[46]
Ce/Ni–Y zeolites	DBT	<i>n</i> -octane	500	7.80	[47]
Ni/SBA-15	DBT	Decahydronaphthalene	5 vol% arene	18.00	[48]
NiY	DBT	Toluene	500	5.40	[49]
NiCeY	DBT	Toluene	500	7.80	[49]
NiNd/Y	DBT	<i>n</i> -octane	500	12.60	[50]
Ni@PP	DBT	Cyclohexane	50	17.15	Present study

Fig. 8 Effect of sonication on adsorption of DBT for **a** DARCO, **b** PP, and **c** Ni@PP

Fig. 9 Fixed-bed desulfurization studies of the adsorbents. **a** Breakthrough curve and **b** linear Thomas model plot

where K_{TH} is the Thomas model rate constant or kinetic coefficient ($\text{mL} \cdot \text{mg}^{-1} \cdot \text{min}$), F is the flow rate ($\text{mL} \cdot \text{min}^{-1}$), Q is the maximum adsorption capacity, and W is the weight of the adsorbent. The values for Q , K_{TH} , and R^2 were obtained from the slope (Fig. 9b) of the plot between $\ln C_0/(C_t-1)$ and ' t ' by using the Thomas model. As the flow rate increased, the adsorption capacities also increased. The

achieved capacities under the flow rate $1.5 \text{ mL} \cdot \text{min}^{-1}$ were 0.81, 12.41, and $21.81 \text{ mg} \cdot \text{g}^{-1}$ for DARCO, PP, and Ni@PP, respectively, inferring that the experimental and theoretical maximum adsorption capacities lie close to each other. The different parameters of the Thomas model are given in Table 5.

Mechanism involved in adsorptive desulfurization

Investigation of all possible interactions is necessary to define the adsorption behavior. Various interactions such as van der Waals forces, chemical affinity, electrostatic attraction, and the presence of specific functionalities are responsible for the adsorption process. Adsorption of DBT onto PP and Ni@PP showed approximately 100% efficiency, whereas DARCO offered much lower efficiency, which may be due to the presence of weak van der Waals interactions and hence their results suggest physisorption process while in PP, an increase in its pore volume and high micropores surface area, i.e., $787 \text{ m}^2 \cdot \text{g}^{-1}$ yield better result. The emulous behavior of metal-modified adsorbent may be due to some additional chemical interactions such as π -complexation, hard–soft acid–base interactions, and direct sulfur metal interactions. In the case of non-modified activated carbon, many acidic groups present on its surface reveal the possible interactions with DBT. However, in nickel-modified adsorbent (Ni@PP), there is possible chemical complexation between nickel and conjugated π -bonds present in thiophenic ring, since DBT contains two benzene rings with six conjugated electrons present into each ring which could bind with the Ni^{2+} metal for complex formation, leading to the formation of strong interaction. The nickel di-cation forms σ -bonds with free s-orbitals, and the d-orbitals of nickel back donates electron density to the antibonding π -orbitals in the sulfur-containing ring of dibenzothiophene [50]. Identifying the active center is important in investigating the desulfurization mechanism of Ni@PP. Though literature hints at Ni (0) as the active form, the role of Ni^{+2} cannot be ruled out in the present study. NiO possesses +2 oxidation state with $3d^8 4s^0$ configuration, thus providing vacant d and s-orbitals available for participating in σ -bond formation via back donation of 6- π electron of the thiophenic benzene ring, whereas Ni(0) possesses $3d^8 4s^2$ electronic configuration whereby only d-orbital is available for bonding.

The plausible mechanism of DBT interaction with Ni@PP is largely based on the knowledge of all possible physical/chemical interactions between the substrate and adsorbent, substantiated by the characterization data and experimental results. The presence of hydroxyl and carboxyl groups on the Ni@PP surface has been confirmed through FTIR. The

hydroxyl (OH) groups present on the carbon surface may lead to an increase in desulfurization efficiency, accompanied by direct interactions between the thiophenic S-atom (1 lone pair) and the H-atom (δ^+) of the hydroxyl group, the O-atom (1 lone pair) and the H-atom (δ^+) of the thiophenic ring, and the O-atom (1 lone pair) and the thiophenic benzene pi-electron. The carboxyl (COOH) group on the activated carbon surface may be attributed to acid–base interaction between COOH and S-atom. Thus, the “hard–soft” acid–base interactions occurring between the acidic groups present on the surface of the carbon and sulfur of DBT enhance the capacity and selectivity of sulfur compounds. Further, the presence of negative ions on the surface of PP may cause nickel deposition, which contributes to desulfurization. The proposed scheme for DBT interaction with Ni@PP is illustrated in Fig. 10.

Regeneration and reusability of Ni@PP

Regeneration and reusability of the spent adsorbent is one of the major concern and important tool to know about their lifetime efficiency for industrial purpose. Several methods have been reported to remove the adsorbed pollutants from the surface of the used adsorbents which reduce the overall process cost. A modified procedure of the solvent washing method [53] followed by direct gasification was used to regenerate the spent adsorbents in the present study. Nearly, 2 g of the used adsorbent was dissolved in 50 mL of different solvents, viz., toluene, chloroform, and methanol under vigorous stirring in refluxed condition for 6 h at room temperature. These three solvents were chosen based on their difference in polarity and affinity for Ni-impregnated carbon. The pre-treated adsorbents were filtered and dried in an oven at 65°C for 3 h. As the boiling point of DBT is $332\text{--}333^\circ\text{C}$, the dried adsorbent was further heated at 350°C for 1 h for complete non-adherence of the adsorbed DBT from the surface and the regenerated Ni@PP was used for several cycles of regeneration studies and desulfurization under optimized conditions. The regeneration studies were performed for four different cycles. After the fourth regeneration cycle, the maximum removal of DBT gradually decreased (Fig. S3), Even after four cycles, the efficiency of Ni@PP showed a slight reduction from 97.77 to 87.53%

Table 5 Linearized Thomas modeling parameters

Thomas model	DARCO		PP		Ni@PP	
	0.75	1.50	0.75	1.50	0.75	1.50
$F(\text{mL} \cdot \text{min}^{-1}) =$						
$K_{\text{TH}}(\text{mL} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}) =$	0.4195	0.6892	0.6332	1.1850	0.6851	1.1140
$Q(\text{mg} \cdot \text{g}^{-1}) =$	0.41	0.81	3.24	12.41	3.38	21.81
$R^2 =$	0.846	0.944	0.949	0.963	0.944	0.959

Fig. 10 The proposed pathway of DBT adsorption on Ni@PP

with toluene, 92.03–85.4% with chloroform, and 90.6–81.8% with methanol. The higher removal with toluene may be due to the strong interactions between nickel metal and π electron density of toluene, whereas such interactions were not possible with chloroform and methanol, which proved to be less efficient. Thus, the regeneration efficiency of three solvents follows the order as toluene > chloroform > methanol.

Conclusions

Desulfurization efficiency of newly developed bio-adsorbent (PP) from *Pongamia pinnata* and nickel modified form (Ni@PP) were compared with commercial activated carbon (DARCO) and the capacities obtained were 13.36, 17.15, and 8.11 $\text{mg}\cdot\text{g}^{-1}$, respectively. Adsorption equilibrium data showed that Langmuir isotherm is the best fit model for adsorption of model oil, while the pseudo-second-order model could satisfactorily explain the kinetics of adsorption. Intraparticle and film diffusion models were investigated to further understand the kinetics of the desulfurization process minutely at the pore level. Ni modification of PP also enhanced the kinetics of adsorption as the equilibrium time needed for adsorption was decreased from 3 to 2 h. The surface area of PP and Ni@PP was 915 and 677 $\text{m}^2\cdot\text{g}^{-1}$, respectively, which is comparatively higher than the commercial carbon DARCO which is only 458 $\text{m}^2\cdot\text{g}^{-1}$ with their pore radius too approaching a microporous structure. Thermodynamics studies at three different temperatures proved the spontaneity and the adsorption process as more efficient at 303 K, which hints toward the physisorption process for DARCO and chemisorption process for PP and Ni@PP. The desulfurization performance of Ni@PP was also higher at

higher initial sulfur concentrations, a property desirable of being a good adsorbent. Also, adsorptive-coupled ultrasonication improved the kinetics from a period of 3 h to 30 min compared to the basic adsorption process. The fixed-bed column shows that the breakthrough curve depends on the flow rate, which is observed as 255 min for Ni@PP and 270 min in the case of PP, whereas no such breakthrough was observed for DARCO till 300 min, and the capacities achieved were 21.81, 12.41, and 0.81 $\text{mg}\cdot\text{g}^{-1}$ respectively. Regeneration and reusability experiments revealed that toluene was the best solvent for the regeneration of Ni@PP with 87.5% till the fourth cycle of regeneration studies. Cost evaluation of the prepared materials also indicating a relatively lower cost of processing and multicomponent fuel adsorption showed that Ni modification has a significant advantage toward deep desulfurization and a possibility for industrial application. Thus, the as-synthesized bio-adsorbent and its nickel modification offer good efficiency and potential for the desulfurization of liquid fuels as compared to commercial activated carbon.

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