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Adsorptive desulfurization and denitrogenation by nickel impregnated activated carbon

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Nickel impregnated granular activated carbon (Ni-GAC) has been synthesized and characterized by various techniques like BET, FTIR, SEM, EDX and TGA. It is later employed for the individual adsorption of dibenzothiophene (DBT) and quinoline (QN). The influence of various factors such as percentage of Ni loading, initial concentration, time, adsorbent dose and temperature on the individual adsorption of DBT and QN from model fuel by Ni-GAC have been investigated. On the basis of the present study, 1%Ni-GAC is found to be the best among various wt.% Ni-GAC. Equilibrium time for DBT and QN adsorption is found to be 6 hr and 9 hr, respectively. The optimum adsorbent dose is found to be 20 g/L. Adsorption kinetics of the both DBT and QN are represented by pseudo-second-order kinetic model. For single component systems, the experimental equilibrium data is well matched with R-P isotherm. Values of change in enthalpy and entropy for DBT and QN were found to be 2.04, 1.55 kJ/mol and 10 and 20 J/mol K, respectively. Isosteric heat of adsorption is modeled in terms of surface heterogeneity.

Keywords: Desulfurization, Denitrogenation, Activated carbon, Adsorption kinetics, Thermodynamic modeling.

Energy production has become a crucial issue these days. About 82% of the energy required for the production of goods and services comes from fossil fuels and half of it comes from petroleum. Gasoline, diesel and jet fuel are used as transportation fuel[1]. Diesel fuel is derived from crude oil and sulfur forms a part of crude oil which causes emission of particulates and soot. Soot results in the emission of black fumes which contribute to air pollution. Sulfur compounds present in diesel produce SO_x and in addition to the catalysts used in catalytic convertors[2]. Ultra deep desulfurization inherently has lot of technical issues. Factors which affect the degree of desulfurization include presence of nitrogen and other aromatic compounds, process parameters, source and quality of feed, type of sulfur compound, etc. Some sulfur containing molecules like dibenzethiophene (DBT), 4, 6-dimethyl DBT (DMDBT), etc. are difficult to remove by hydrodesulfurization (HDS). Various techniques that are used for desulfurization are oxidative desulfurization, adsorptive desulfurization, reactive adsorption, and biodesulfurization[3-13].

Nitrogenous compounds in the refinery streams inhibit the removal of DBT and other sulfur compounds. This is because sulfur and nitrogen compounds both compete for the same catalyst sites, however, nitrogen compounds generally show strong adsorptive removal. Therefore, it becomes necessary to remove the nitrogen compounds[14]. Degree of inhibition depends on the concentration and type of nitrogen compounds. It has been reported that the HDS reactivity increases with decrease in the nitrogen content[15].

Hydrodenitrogenation (HDN) has been used for the removal of nitrogen compounds, but it is very costly and energy intensive process[16]. Various other methods are used for the denitrogenation of fuels like solvent extraction using ionic liquid such as 1-butyl-3-methylimidazolium chloroaluminate (III), 1-butyl-3-methyl-imidazolium chloride. Extraction by membranes and adsorption have benefit of not using H_2 gas and can be carried out at ambient temperature and pressure, thus reducing the cost of the process as compared to HDS[11,17-19]. Adsorption is also extensively used to remove the sulfur and nitrogen compounds and a lot of work has been done using various adsorbents and their performances are given in Table 1[20-27]. It may be seen that no work is reported on utilization of nickel impregnated activated carbon

Table 1 — Comparison of different adsorbents for the adsorption of DBT and QN compounds

Sulfur	Adsorbent	System	Model oil	T (˚C)	C_o (mg/L)	% Removal/q_e	Reference
DBT	Activated alumina	Batch	n-Hexane	30	500 (S)	58 (S)	[20]
Total sulfur	Activated carbon Norit SXRO PLUS	Batch	Diesel	-	250 (S)	67.4 (S)	[21]
BT	WMC	Batch	n-Octane	-	1000 (S)	80.5 (S)	[22]
DBT	WMC	Batch	n-Octane	-	1000 (S)	78.5 (S)	[23]
4,6-DMDBT	WMC	Batch	n-Octane	-	1000 (S)	36 (S)	[23]
BT	CACs	Batch	n-Octane	-	1000 (S)	39.5 (S)	[23]
DBT	CACs	Batch	n-Octane	-	1000 (S)	36.9 (S)	[23]
4,6-DMDBT	CACs	Batch	n-Octane	-	1000 (S)	19 (S)	[23]
DBT	CAC	Batch	n-Octane	30	100 (S)	53 (S)	[24]
DBT	CAC	Batch	n-Octane	30	300 (S)	48 (S)	[24]
Carbazole, Indole, Quinoline, DBT	Activated carbon	Batch	Do-decane		990 (N), 760 (S)	1.19 (mmol N/g), 1.12 (mmol S/g)	[25]
DBT	Zirconia	Batch	Iso-octane	30	1000 (S)	-	[26]
Carbazole, Indole, Quinoline, DBT	Ni_2P/ SBA15	Batch	Paraffin		999.9 (N), 761.60 (S)	q_e=9.1mg/g (N)	[27]
DBT Quinoline	Ni-GAC	Batch	Iso-octane		500 (S) 500 (N)	64 (S) 73 (N)	Present work

(NIGAC) for desulfurization or denitrogenation of liquid fuels.

In the present study, nickel impregnated granular activated carbon (Ni-GAC) was synthesized and used for the individual removal of DBT and QN, from the model oil (DBT or QN dissolved in iso-octane). Textual properties of the adsorbent were revealed by Brunauer–Emmett–Teller (BET) surface area analysis. Physico–chemical properties were found by other techniques such as X-ray and energy dispersive diffractogram, scanning electron micrograph (SEM), thermo-gravimetric analysis (TGA) and Fourier transform infra-red (FTIR) spectroscopy. Present research also studied the effects of different factors such as initial concentration of DBT (C_o), percentage of doping, contact time (t), adsorbent dose (m) and temperature (T). Adsorption kinetics was studied by using various kinetic models. Equilibrium adsorption data was also studied with help of different isotherm models and thermodynamic parameters including isosteric heats of adsorption have been estimated.

Experimental Section

Materials and model oil

Analytical grade chemicals were used in the present study. Model fuel, a mixture of DBT and QN dissolved in iso-octane was used for adsorptive desulfurization and denitrogenation study. QN and iso-octane (99.8%) were purchased from S.D. fine Chemicals, Mumbai, India. DBT was procured from Spectrochem Pvt. Ltd. Mumbai, India. Adsorbent used was nickel loaded granular activated carbon (Ni-GAC). GAC was furnished by G.S. Chemical testing lab and allied industries, India.

Adsorbent preparation and its characterization

GAC, as received, was made free from ash by washing with distilled water. Further its moisture was removed by as it was kept at 100°C for 6 h. Later it was subjected to 30% HNO_3 and made *p*H neutral by again washing with large amount of distilled water. Finally the GAC was kept in the oven for 6h to completely remove the moisture. The dried GAC was thereafter stirred in aqueous solution containing different concentration of Ni $(NO_3)_2.6H_2O$ so as to obtain a Ni loading of approximately 1%, 2.5%, 5% and 10%. The volume of the solution used was 10% excess with respect to the pore volume of the GAC. After Ni loading, samples were again dried and calcined at 200, 400 and 600°C for 3 hr. The hot adsorbent was taken in a dessicator under vacuum to lose its temperature and utilized further for removal of DBT and QN. To confirm the Ni loading, 1 g of the samples were soaked in 10 ml 65% nitric acid for 24 h at room temperature. Thereafter, the samples were filtered and atomic absorption spectrophotometer was used to find out loading of Ni in the filtrate[28]. Ni impregnation in GAC samples was found to be in the range of 0.85–0.94 times of that desired.

X-ray diffraction (XRD) analysis was carried out for the adsorbent by using Phillips (Holland) diffraction unit (Model PW1140/90) with Ni as the filter media and Cu as the target. Goniometric speed and Radiation was maintained at 10°/min and at 1.542 Å, respectively. Surface area and porosity analyzer (ASAP 2020, Micromeritics) was employed to determine the Brunauer-Emmett-Teller (BET) surface area. N_2 adsorption and desorption isotherms were obtained at -196°C which helped in determining the surface area. Fourier transform infrared (FTIR) spectrometer (Thermo Nicolet, USA), spectral range of 4000-400 cm^{-1}, was helpful in knowing type of functional groups present and chemical nature of the adsorbent. The sample pellet was prepared using KBr. Quanta 200 F (FEI Netherlands) with gold splutter coater of Baltech was employed to obtain the energy-dispersed X-ray (EDX) spectra/field emission scanning electron microscope (FE-SEM). Setting the temperature range of 25-1000°C and with a heating rate 10°C/min, Differential thermal analysis (DTA) and Thermal gravimetric analysis (TGA) were carried out in presence of air.

Experimental procedure

Model fuel for the experimental study was prepared by taking 31.25 and 71.42 mmol/L of DBT and QN individually. Thus prepared 10 mL sample of known DBT or QN solution was taken into a 25 mL test tube with glass stopper and the loaded test tube was subjected to a constant stirring rate (500 rpm) in a temperature controlled chamber (Aqualytic, Germany) at 30°C, however, experiments for isotherm study were carried out at three different temperatures i.e. at 15, 30 and 45°C. After sufficient contact time is provided, the samples were withdrawn from the chamber and the remaining concentration of DBT and QN were analyzed by gas chromatograph (GC) provided with flame-ionization detector (FID) and having capillary column (length 30 m, internal diameter 0.53 mm, film 0.88 μm), obtained from Netel India Ltd. The detector temperature was maintained at 300°C and the injector temperature was set to 280°C and the. The temperature of column was initially at 150°C for 3 min and was heated to 200°C at a rate of 10°C/min and held at 200°C for 2 min. The carrier gas (N_2) flow was 15 mL/min. For every GC-FID run, 1 μL sample volume was injected and the sensibility (limit detection) is 2 mg/L. Thus the DBT and QN concentration in the solution was identified and analyzed with standard samples.

Results and Discussion

Adsorbent characterization

X-ray diffraction for Ni-GAC shows broad peaks at $2\theta=24^o$ and 44^o indicative of amorphous nature of the adsorbent. In accordance with the IUPAC classification, pore sizes are categorized into micro pores (d < 20 Å); mesopores (20 Å < d < 500 Å); macro pores (d > 500 Å).

BET surface area of the blank GAC and Ni-GAC were found to be 591 and 553.2 m^2/g, respectively. This decrease could be due to the loading of 1%Ni onto GAC which blocked some of the pores[29]. Single point total pore volume for blank-Ni-GAC was 0.312 cm^3/g. BJH adsorption/desorption area of pores (17 Å < d < 3000 Å) was 48.3 m^2/g and 37.6 m^2/g, respectively. BJH cumulative adsorption/desorption pore volume (17 Å < d < 3000 Å) was 0.0337 cm^3/g and 0.0216 cm^3/g, respectively.

EDX of blank GAC and Ni-GAC was conducted. EDX analysis showed the presence of 86.83% C and 13.17% O in blank GAC. While blank Ni-GAC contained 88.22% C, 9.92% O and 1.87% Ni.

TGA and DTA curves of the Ni-GAC at a heating rate of 10 K/min were plotted. Up to 400°C, there is 18% loss of light volatile molecules and moisture. Due to loss of the surface tension bound water of the particles, higher temperature drying (> 100°C) occurs. Blank Ni-GAC did not show any endothermic transition, between room temperature and 400°C, infers that there was no phase change while heating process[30].

Blank Ni-GAC showed 80.5% weight loss between 400°C and 585°C. The exothermic peak between 400–625°C, represents oxidation degradation of the samples. DTA analysis shows two peaks for blank Ni-GAC. This study shows that Ni-GAC is fully stable up to 400°C and that the spent Ni-GAC can be fully oxidized in oxidative environment with sufficient recovery of energy.

FTIR of blank Ni-GAC (Fig. 1) showed a broad band at 3430.81 cm^{-1} which indicated the presence of free and hydrogen bonded OH group on its surface. At 1570 cm^{-1}, the spectrum showed a broad band which witnessed the presence of CO group due to aldehyde and ketone. The band around 1461 cm^{-1}

might be due to carbonyl group which may be conjugated hydrocarbon bonded. At 1200 cm^{-1}, the spectra showed transmittance which may be due to –CO and Si-O-Si stretching or due to CC group vibration in lactones and also due to deformation of –OH group. The peak at around 750 cm^{-1} signified SiH bond. Some of these broad and weak bands are likely to help in adsorption of DBT and QN.

Effect of parameters

In this part of the study, effect of parameters on individual adsorption of DBT and QN onto Ni-GAC was assessed Table 1. First, blank GAC and different percentage Ni loaded GAC calcined at different temperatures were tested for their efficacy in DBT removal (Fig. 2) from solutions containing 500 mg/L of DBT (i.e. $C_{o,S}$=15.62 mmol/L). It may be seen that 1%Ni-GAC calcined at 400°C gave maximum DBT removal**.** Removal efficiency decreased with an increase in Ni loading. This may be due to decrease in BET surface area of the adsorbents. Further experiments were conducted with 1%Ni-GAC only calcined at 400°C.

The effect of m on the individual adsorption of DBT and QN onto 1%Ni-GAC was studied at T=303 K and $C_{o,S}$=15.62 mmol/L, $C_{o,N}$=35.71 mmol/L, which is shown in Fig. 3a. The removal of DBT and QN increased with an increase in m from 1 to 20 g/L. The removal was constant for m > 20 g/L. When 1% Ni-GAC dose was further increased, surface area was increased because the availability of more adsorption sites[27]. At about *m*=20 g/L, the removal efficiency remained almost unchanged for DBT and QN removal using 1%Ni-GAC. It is seen from Fig. 3b that the rate removal rate of DBT and QN was so rapid i.e. at initial 60 min after that removal rate was decreased.

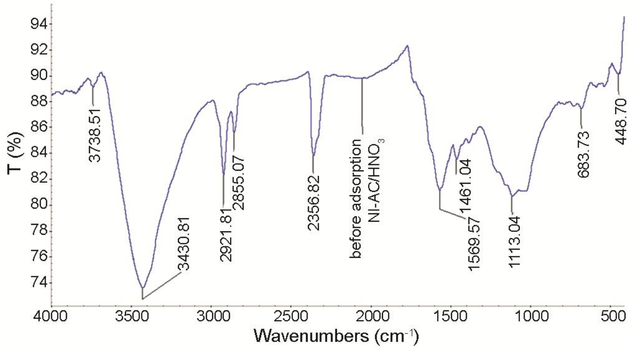

Fig. 1 — FTIR of 1%Ni-GAC before and after adsorption.

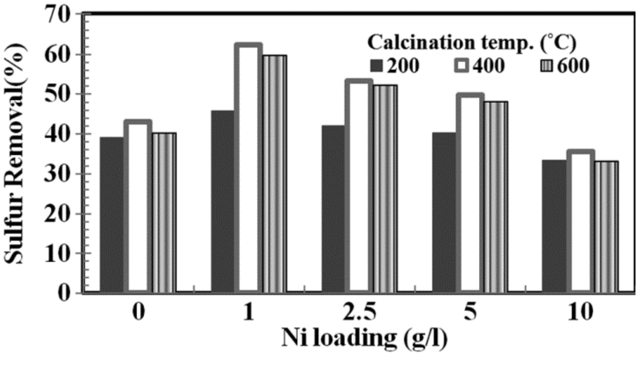

Fig. 2 — Percentage removal of sulfur versus blank and various percentage loadings of Ni on GAC at various calcination temperatures. $C_{0,\,DBT}$=15.62 mmol/L, T=303 K, t=9 h.

It was found that the removal of both DBT and QN decreased after 9 h and 6 h of residence time with the adsorbent i.e., 1%Ni-GAC. This is because during initial stage, large number of sites were vacant where solute molecules could be adsorbed and after a lapse of time repulsive forces come into play between bulk phase and the solute molecules and the solid surface as a result of which adsorption becomes difficult[20]. Initially the pores of the adsorbent got saturated with solute molecules and in the later stage the adsorbate molecules had to penetrate into the micro-pores and faced high resistance. As a result of this adsorption process slowed down after sometime.

The adsorption of organo-sulfur compound and basic organo-nitrogen compound such as DBT and QN respectively on to Ni-GAC, is dominated by Bronsted base (through lone pair of electrons on DBT and QN atom in DBT and QN respectively) and acid (Ni^{2+} on GAC)[31].

Adsorption kinetics

Pseudo-first-order model and pseudo-second-order model were applied to the adsorption of DBT and QN adsorption onto 1%Ni-GAC. The best fit values of kinetic parameters such as k_f, h, q_e and k_s with the correlation coefficients, sum of square of error (SSE) for both the models were shown in Table 2. The R^2 value for pseudo second order is higher than pseudo first order and hence, pseudo-second-order model best-fits the adsorption kinetic data for 1%Ni-GAC. Figure 3b shows the fitting of the experimental value to the pseudo 2nd order kinetic model for both DBT and QN. It is clear that the adsorption of DBT and QN onto 1%Ni-GAC follows the second- order – kinetics.

Transfer of adsorbate molecule from the solution to the surface of the adsorbent is controlled either by surface diffusion, film diffusion, pore diffusion or adsorption. Weber-Morris intraparticle diffusion model is given as:

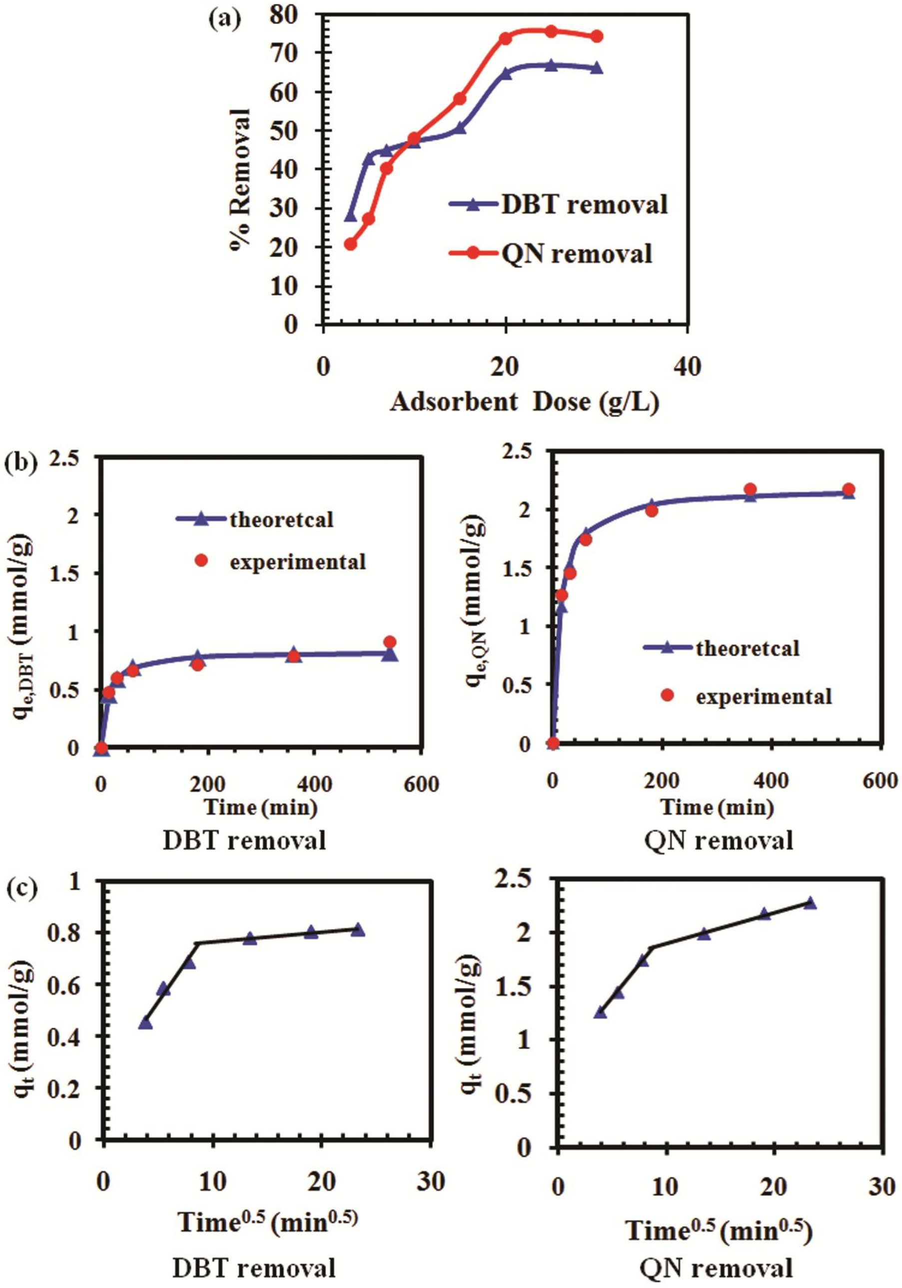

Fig. 3 — (a) Effect of adsorbent dose on the removal of DBT and QN ($C_{o,DBT}$=15.62 mmol/L, $C_{o,QN}$=35.71 mmol/L, T=303 K, t=6 hr (QN), t=9 hr (DBT)); (b) Effect of contact time on the removal of DBT and QN (t=9 hr, $C_{o,DBT}$=15.625 mmol/L, t=6 hr, $C_{o,QN}$=35.71 mmol/L, m=10 g/L). (c) Weber and Morris plot for intraparticle diffusion of DBT and QN onto 1%Ni-GAC.

$$q_t = K_{td} t^{1/2} + I \quad \text{... (1)}$$

It can be seen in the Fig. 3c that the plots for DBT and QN are not linear over the whole range of time which implies that more than one process is involved in adsorption. Slope of the two linear portions ($K_{id,1}$ and $K_{id,2}$) indicate the rates of adsorption during surface and pore diffusion. As the value of $K_{id,1}$ is higher than $K_{id,2}$ (Table 2), it suggests that the second linear portion is pore diffusion i.e., rate limiting step. The intercept, I, indicates boundary layer thickness.

Adsorption equilibrium and thermodynamics study

The plots of adsorption isotherms, q_e versus C_e, at three different temperatures (288, 303 and 318 K) are shown in Fig. 4. From Fig. 4, it is clear that with an increase in temperature up to 303 K, the adsorption first increased and thereafter decreased. It means that

Table 2 — Kinetic parameters for the removal of DBT and QN by 1%Ni-GAC. (t=9 hr, $C_{0,\,DBT}$=15.625 mmol/L, $C_{0,\,QN}$=35.71 mmol/L, m=10 g/L, T=30°C).

	Pseudo 1st order	$q_t = q_e[1 - \exp(-k_f t)]$				
	q_e (mg/g)	k_f (min^{-1})		SSE	RMSE	R^2
Sulfur	0.77	0.05		0.03	0.02	0.94
Nitrogen	2.05	0.05		0.12	0.05	0.96
	Pseudo 2nd order	$q_t = \frac{tk_S q_e^2}{1+tk_S q_e}$				
	q_e (mg/g)	k_s (g/mg min)		SSE	RMSE	R^2
Sulfur	0.83	0.09		0.01	0.02	0.97
Nitrogen	2.19	0.03		0.02	0.02	0.99
	Weber-Morris	$q_t = K_{td} t^{1/2} + I$				
	$K_{id,1}$	I_1	R^2	$K_{id,2}$	I_2	R^2
Sulfur	0.05	0.31	0.97	0.02	0.56	0.96
Nitrogen	0.12	0.77	0.99	0.03	1.60	0.99

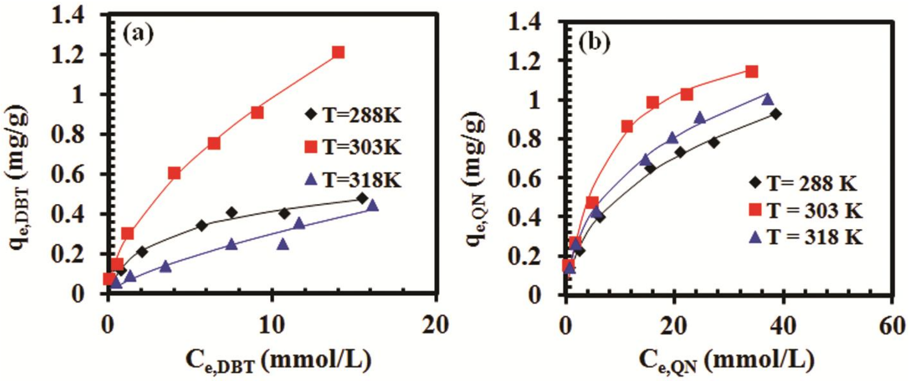

Fig. 4 — Adsorption isotherms for (a) DBT and (b) QN at different temperatures. $C_{o,DBT}$=1.56 mmol/L to 25 mmol/L, $C_{o,QN}$=3.57 mmol/L to 57.14 mmol/L, t=6 h, m=20 g/L.

intra-particle transport pore diffusion is predominant at lower temperature and therefore, when the temperature increases the adsorption capacity increases as diffusion is an endothermic process[32]. If the temperature increases then mobility of solute molecule increases and the retarding force on the molecule decreased as a result of which sorption capacity increases at higher temperature. As adsorption is an exothermic process, the adsorption capacity of the Ni-GAC decreases at higher temperature (318 K). Similar results were reported by Rakesh-Kumar and Srivastava[24].

In this study, three isotherm equations Langmuir, Freundlich and Redlich-Peterson (R-P) equations[33,34] were used for fitting the data obtained from adsorption experiments of DBT and QN onto 1%Ni-GAC. Using the SSE values, best isotherm model was found for fitting experimental data. All the isotherm parameters and R^2 values are given in the Table 3. It can be seen that the R^2 values for R-P equation are closer to 1 as compared to other isotherm models. SSE value is also minimum for R-P model. Hence R-P isotherm gives the best fit for the experimental data.

Using the classical thermodynamics,[20] the following relationship between Gibbs free energy change (ΔG°), entropy change (ΔS°), enthalpy change (ΔH°), and equilibrium adsorption constant (K_D) could be obtained.

$$\ln K_D = \frac{-\Delta G^o}{RT} = \frac{\Delta S^o}{RT} - \frac{\Delta H^o}{R}\frac{1}{T} \qquad \text{...(2)}$$

where, R the universal gas constant (8.314×10^{-3} kJ/mol K), T is the absolute temperature (K), and K_D (=q_e/C_e) the single point or linear sorption distribution coefficient. ΔH° and ΔS° values have been obtained from the van't Hoff plot of ln K_D versus 1/T. Values of ΔH°, ΔS° and ΔG° are given in Table 4. ΔS° values

Table 3 — Isotherm parameters for individual adsorption of DBT and QN onto 1%Ni-GAC. (t=9 hr, $C_{0,DBT}$=1.56-25 mmol/L, $C_{0,QN}$=3.57-57.14 mmol/L, m=20 g/L).

Freundlich $q_e = k_f c_e^{1/n}$

Sulfur				Nitrogen			
T(K)	288	303	318	T(K)	288	303	318
1/n	0.42	0.58	0.73	1/n	0.47	0.43	0.44
K_f	0.15	0.25	0.05	K_f	0.16	0.26	0.21
SSE	0.004	0.003	0.009	SSE	0.004	0.036	0.005
R^2	0.988	0.998	0.963	R^2	0.996	0.981	0.996

Langmuir $q_e = \dfrac{q_m k_l c_e}{1 + k_l c_e}$

Sulfur				Nitrogen			
T(K)	288	303	318	T(K)	288	303	318
q_m	0.55	1.85	1.18	q_m	1.15	1.41	1.24
K_l	0.31	0.11	0.03	K_l	0.08	0.13	0.10
SSE	0.002	0.017	0.008	SSE	0.007	0.013	0.012
R^2	0.992	0.994	0.973	R^2	0.996	0.995	0.994

Redlich Peterson $q_e = \dfrac{k_R c_e}{1 + a_R c_e^{\beta}}$

Sulfur				Nitrogen			
T(K)	288	303	318	T(K)	288	303	318
a_r	0.98	87.75	1144.93	a_r	0.99	0.12	1.07
B	0.78	0.42	0.29	B	0.64	1	0.66
K_R	0.29	22.92	67.30	K_R	0.27	0.18	0.35
SSE	0.001	0.002	0.006	SSE	0.002	0.013	0.003
R^2	0.993	0.998	0.976	R^2	0.997	0.994	0.997

Table 4. Thermodynamic parameters for individual adsorption of DBT and QN onto 1%Ni-GAC. t=9 h, $C_{0,DBT}$=1.56-25 mmol/L, $C_{0,QN}$=3.57-57.14 mmol/L, m=20 g/L.

	Sulfur			Nitrogen		
T(K)	288	303	318	288	303	318
K_D	5.90	6.82	5.41	5.30	5.74	5.62
ΔG^0(kJ/mol)	-4.39	-4.52	-4.64	-4.03	-4.32	-4.61
ΔH^0(kJ/mol)	2.04			1.55		
ΔS^0 (kJ/mol K)	0.01			0.02		

are positive for both DBT and QN which suggesting increased randomness on the interface. ΔH^o values are positive which indicates the endothermic nature of the reaction whereas ΔG^o values are negative which indicate the feasibility and spontaneity of DBT and QN adsorption onto 1%Ni-GAC.

By using the slope of the plot of the ln C_e versus (1/T) from Clausius-Clapeyron equation[35,36]. At constant surface coverage, apparent isosteric heat of adsorption ($\Delta H_{st,a}$) is calculated, The equation is as follows:

$$\Delta H_{st,a} = R \left.\frac{d\ln C_e}{d\left(1/T\right)}\right|_{q_e} \qquad ...(3)$$

With help of the best-fit equilibrium isotherm model, C_e values at constant amount of DBT and QN adsorbed at various temperatures were computed. For DBT adsorption onto Ni-GAC, ΔH_{st} values were calculated as -28.6, -2.49, 26.3, 42.7 and 56.7 kJ/mol for q_e values of 0.2, 0.5, 0.8, 1.0 and 1.2 mmol/g, , respectively. For QN adsorption onto Ni-GAC, respective ΔH_{st} values were calculated as 8.6, 9.2, 8.8, 8.3 and 7.6 kJ/mol, respectively.

The ΔH_{st} values can be correlated to parameters of adsorbate-adsorbent interaction and the surface heterogeneity by Do and Do model[37]:

$$\Delta H_{\theta} = \Delta H_{0,D}\left\{1-\frac{\alpha\beta\theta}{1+\left(\beta-1\right)\theta}\right\}+\mu\theta \qquad ...(4)$$

By adding the heat of adsorption of iso-octane ($\Delta H_{iso,o}$) and heat of solution (ΔH_{sol}) to $\Delta H_{st,a}$, the net isosteric heat of adsorption (ΔH_θ) is obtained. As ΔH_{sol} and $\Delta H_{iso,o}$ are not available, they were considered to be zero and ΔH_θ was assumed as $\Delta H_{st,a}$. The four parameters , $\Delta H_{o,D}$, α, β and μ, were estimated using non-linear fitting and were found to be: 2.0, -3898, 0.96 and -7601, respectively, for DBT. For QN adsorption onto Ni-GAC, respective values were found to be 1.05, -10.4, 18.50 and -5.1, respectively. Thus, DBT and QN adsorption onto Ni-GAC was endothermic in nature.

The adsorbent Ni-GAC was reused again. The used adsorbent was initially kept in hot air oven at 373 K for 4 h and at 623K in the furnace for 6 h[38]. The Ni-GAC showed about ≈95% of its adsorption capacity during reused for the first run of the experiment and it was confirmed by cycle of adsorption desorption that the used Ni-GAC could be easily regenerated.

Conclusion

In the current study, nickel loaded granular activated carbon (Ni-GAC) has been synthesized and characterized by various techniques. It is further employed for the individual adsorption of DBT and QN. Various characterization tests like BET, FTIR, EDX and TGA helped in understanding the mechanism of adsorption. EDX analysis confirms the presence of sulphur and nitrogen and N on the adsorbent surface. The thermal stability of granular activated carbon is up to 400°C as shown by TGA analysis. Various types of functional groups are found to be present on the surface of Ni-GAC. Calcination temperature is found to severely affect the adsorption capacity. The influence of various factors such as loading, time, adsorbent dose and temperature, is investigated on the individual adsorption of DBT and QN from model fuel by Ni-GAC. On the basis of the present study, 1%Ni-GAC is found to be the best amongst various wt.% Ni-GAC. Equilibrium time for DBT and QN adsorption is found to be 6 h and 9 h, respectively. The optimum adsorbent dose is found to be 20 g/L. for the both DBT and QN onto Ni-GAC, adsorption kinetics is represented by pseudo-second-order kinetics model. Also for individual component systems, R-P isotherm model is the best fit to experimental equilibrium data. Endothermic nature of the adsorption is revealed by the thermodynamic studies.

Nomenclature

a_R	R–P isotherm constant (L/mmol)
B_1	Heat of adsorption (kJ/mol)
C_e	Liquid phase concentration of the adsorbate at equilibrium (mmol/L)
h	Initial adsorption rate (mmol/g.min)
I	Thickness of the boundary layer (mmol/g)
k_f	Pseudo-first-order rate constant (min^{-1})
k_s	Pseudo second-order rate constant (g/mmol-min)
k_{id}	Intra-particle diffusion rate constant ($mmol/g.min^{0.5}$)
K_F	Freundlich constant (L/mmol)
K_L	Langmuir adsorption constant (L/mmol)
K_R	R–P isotherm constant (L/mmol)
K_T	Equilibrium binding constant (L/mol)
q_e	Uptake of the adsorbate by the adsorbent at equilibrium (mmol/g)
q_m	Adsorption capacity of the adsorbent(=K_R/a_R) (mmol/g)
R^2	Coefficient of determination (-)
SSE	Sum of square of error
T	Temperature (K)
β	R–P isotherm constant (-)
1/n	Freundlich constant (-)
ΔG^o	Gibbs free energy (kJ/mol)
ΔH^o	Enthalpy change (kJ/mol)
ΔS^o	Entropy change (J/K.mol)
$\Delta H_{0, D}$	Isosteric enthalpy at zero loading
ΔH_θ	Isosteric enthalpy of fractional loading ($\theta=q/q_m$) of DBT \and QN
α	Ratio (=$\delta H/\Delta H_{o,D} < 1$)
β_1	Pattern parameter
μ	Adsorbed-adsorbate interaction energy

References

1 Srivastava V C, *RSC Adv, 2* (2012) 759.
2 Kim J H, Ma X, Zhou A & Song C, *Catal Today, 111* (2006) 74.
3 Zhang B, Jiang Z, Li J, Zhang Y, Lin F, Liu Y & Li C, *J Catal, 28*7 (2012) 5.
4 Zhou Q, Fu S, Zou M, He Y, Wu Y & Wu T, *RSC Adv, 5* (2015) 69388.
5 Han X, Wisharty E & Zheng Y, *Can J Chem Eng, 92* (2014) 884.
6 Chen J, Chen C, Zhang R, Guo L, Hua L, Chen A, Xiu Y, Liu X & Hou Z, *RSC Adv, 5* (2015) 25904.
7 Taib M M & Murugesan T, *Asia Pac J Chem Eng, 7* (2012) 469.
8 Shen Y, Li P, Xu X & Liu H, *RSC Adv, 2* (2012) 1700.
9 Shah A T, Li B & Nagra S A, *Can J Chem Eng,* 89 (2011) 1288.
10 Duan F, Chen C, Wang G, Yang Y, Liu X & Qin Y, *RSC Adv, 4* (2014) 1469.
11 Nekooghadirli R, Taghizadeh M & Mahmoudi Alami F, *J Dispersion Sci Technol*, 37 (2016) 786.
12 Gao J, Chen X, Ren N, Wu W, Li C, Meng H & Lu Y, *AIChE J, 59* (2013) 2966.
13 Andaloussi S A, Lagnel C, Warzywoda M & Monot F, *Enzyme Microb Technol, 32* (2003) 446.
14 Shahriar S A, Lin H & Zheng Y, Ind Eng Chem Res, *51* (2012) 14503.
15 Yang H, Chen J W, Fairbridge C, Briker Y, Zhu Y J & Ring Z, *Fuel Process Technol, 8*5 (2004) 1415.
16 Almarri M, Ma X & Song C, *Energy Fuels* 23 (2009) 3940.
17 Gao P, Cao Z, Zhao D, Li D & Zhang S, *Pet Sci Technol,* 23 (2005) 1023.
18 Xie A L, Reguillon F, Wang X, Fu S, Rostaing G P, Toussaint C, Geantet M & Vrinat M, *Green Chem*, 10 (2008) 524.
19 Matsumoto M, Mikami M & Kondo K, *J Jpn Petro Inst,* 49 (2006) 256.

20 Srivastav A & Srivastava V C, J *Hazard Mater,* 170 (2009) 1133.

21 Larrubia M A, Gutierrez Alejandre A, Ramirez J & Busca G, *Appl Catal A,* 224 (2002) 167.

22 Ngamcharussrivichai C, Chatratananon C, Nuntang S & Prasassarakich P, *Fuel,* 87 (2008) 2347.

23 McKinley S G, PhD Thesis Iowa State University *Ames, IA* (2003).

24 Rakesh Kumar D & Srivastava V C, *Clean Soil Air Water,* 40 (2012) 545.

25 Wen J, Han X, Lin H, Zheng Y & Chu W, *Chem Eng J,* 164 (2010) 29.

26 Kumar S, Srivastava V C & Badoni R P, *Fuel,* 90 (2011) 3209.

27 Shahriar S A, Lin H & Zheng Y, *Ind Eng Chem Res,* 51 (2012) 14503.

28 Priyanka Subbaramaiah V, Srivastava V C & Mall I D, *Sep Purif Technol,* 125 (2014) 284.

29 Lataye D, Mishra I M & Mall I D, *Pract Period Hazard Toxic Radioact Waste Manage,* 13 (2009) 218.

30 Suresh S, Srivastava V C & Mishra I M, *J Chem Eng Data,* 56 (2011) 811.

31 Wu Y, Xiao J, Wu L, Chen M, Xi H, Li Z & Wang H, *J Phys Chem, C* 118 (2014) 22533.

32 Kushwaha J P, Srivastava V C & Mall I D, *Bioresour Technol,* 101 (2010) 3474.

33 Srivastava V C, Mall I D & Mishra IM, *Chem Eng Process,* 47 (2008) 1275.

34 Langmuir I, *J Am Chem Soc,* 40 (1918) 1361.

35 Young D M & Crowell A D, Physical adsorption of gases, Butterworths, London (1962).

36 Srivastava V C, Mall I D & Mishra I M, *Chem Eng J,* 132 (2007) 267.

37 Do D D & Do H D, *Chem Eng Sci,* 52 (1997) 297.

38 Rameshraja D, Srivastava V C, Kushwaha J P & Mall I D, *Chem Eng J,* 181-182 (2012) 343.