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**ORIGINAL ARTICLE**

Adsorptive desulfurization of model oil using untreated, acid activated and magnetite nanoparticle loaded bentonite as adsorbent



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Abstract The present research work focuses on a novel ultraclean desulfurization process of model oil by the adsorption method using untreated, acid activated and magnetite nanoparticle loaded bentonite as adsorbent. The parameters investigated are effect of contact time, adsorbent dose, initial dibenzothiophene (DBT) concentration and temperature. Experimental tests were conducted in batch process. Pseudo first and second order kinetic equations were used to examine the experimental data. It was found that pseudo second order kinetic equation described the data of the DBT adsorption onto all types of adsorbents very well. The isotherm data were analyzed using Langmuir and Freundlich isotherm models. The Langmuir isotherm model fits the data very well for the adsorption of DBT onto all three forms of adsorbents. The adsorption of DBT was also investigated at different adsorbent doses and was found that the percentage adsorption of DBT was increased with increasing the adsorbent dose, while the adsorption in mg/g was decreased with increasing the adsorbent dose. The prepared adsorbents were analyzed by scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDX) and X-ray diffraction (XRD).

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1. Introduction

Production of energy is one of the most imperative issues of modern era. Energy usage and economic activity are intimately associated, because useful goods production, services and more inclusive economic output need high energy usage. From 1980 to 2013 the annual energy usage in the world increased by an average of 404 quadrillion BTUs. Although over the same period, the percent energy attained from fossil fuels declined, still the share of energy from fossil fuel is

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about 82%, and about half of which emanates from petroleum. Thus in the world petroleum is considered one of the main sources of energy, but major problems from petroleum are due to its sulfur compounds. Sulfur compounds are present in petroleum in the form of free sulfur, sulfides, disulfides, mercaptan, thiophene, benzothiophene and dibenzothiophene [1]. During combustion of petroleum these sulfur compounds are converted into obnoxious Sulfur oxides (SO_x). SO_x resulting from combustion of sulfur rich fuels have become one of the serious environmental issues in the world as they are a major root of atmospheric pollution, global warming and acid rains.

Since last decade considerable attention has been paid to the desulfurization of diesel fuel oil and gasoline due to increasingly rigorous environmental protocols being imposed to decrease the sulfur content of fuel to minimum levels. Industrially the removal of sulfur compounds from liquid fuel is carried out by catalytic hydrodesulfurization process (HDS) [2]. Although, HDS is more effective for the removal of sulfur compounds such as: sulfide, disulfide, thiol, thiophene, benzothiophene, but dibenzothiophene most objectionable sulfur components present in the petroleum fractions are fewer reactive to this process [2]. Further enhancement of the catalytic HDS process for ultra-deep desulfurization is limited due to increasingly severe working conditions at high cost. Moreover, the deep HDS processes entailed substantial hydrogen consumptions, huge energy and significantly improved selectivity and reactivity of the required catalysts. Presently most of the catalysts used in the HDS process are very expensive and also cause unwanted sideways reactions, which lead to a decrease in the required octane number of gasoline [3]. Thus, from both economic and environmental considerations, recently other alternative ultra-deep desulfurization processes have been explored, such as: bio-desulfurization, oxidative desulfurization (ODS) using various catalysts, extractive desulfurization with different ionic liquids [4].

Presently new approach for the sulfur removal from liquid fuels is adsorptive desulfurization (ADS), which seems to be very promising and economical methods with regard to energy consumption, because the adsorption process can be achieved at ambient pressure, temperature and without use of any expensive hydrogen as well as catalyst. Moreover, some types of adsorbents have high adsorption capacity which can remove more refractory aromatic sulfur compounds very effectively [5,6]. In this regard, great deal of research on the desulfurization of liquid fuel has been diverted to adsorption process in order to develop new type of adsorbents with enhanced adsorption capacity, high regenerability and selectivity [7].

Sulfur compounds present in fuel affect its quality as well as the environment. Therefore, it is necessary to carry out more and more work in order to remove or decrease their concentration in petroleum fraction into formidable level by cheaper and easily operating method. In order to remove one of sulfur compound from petroleum cuts, the study was carried out on the removal of DBT from model oil by the adsorption method. In this study bentonite was used as an adsorbent. Bentonite; activated with acid and loaded with magnetite nanoparticles was also used as an adsorbent for the effective removal of DBT from model oil.

2. Experimental

2.1. Reagents and solutions

Dibenzothiophene (DBT) was purchased from Merck Company, and was used without further purification. Stock solutions of 1000 mg/L DBT were prepared in 1000 mL n-heptane and working solutions were then prepared from stock solutions by using the dilution formula.

2.2. Adsorbent preparation

2.2.1. Preparation of bentonite as adsorbent

Bentonite was obtained from soil sciences laboratory, Pakistan Council of Science and Industrial Research (PCSIR), Peshawar. The bentonite was grinded into powder form and was sieved by sieve size of 120 μm. The sieved bentonite was washed with distilled water for the removal of dust and other water soluble particles. The washed bentonite was dried in oven and was stored for further use.

2.2.2. Acid treatment of bentonite

25 g of cleaned and dried bentonite was taken in a round bottom flask and 150 mL of 0.1 N HNO₃ solutions was added to it. The bentonite and acid solutions in flask were refluxed with continuous stirring and heating (70 °C) for 3 h. After 3 h the bentonite slurry was filtered by Buchner funnel, then washed with distilled water, dried in oven and stored for further use.

2.2.3. Loading of magnetite nanoparticles on bentonite

Magnetite nanoparticles were loaded on bentonite by the following procedures: FeCl₂·4H₂O and FeCl₃·6H₂O were dissolved in 80 mL double distilled water in 1:2 ratio respectively; and were then shaken at 85 °C in a water bath shaker for 30 min. Then 30% ammonium hydroxide solutions of 20 mL were added to the mixture solutions and with ammonium addition the solutions color changed to black from orange immediately. Then 6 g of the pretreated bentonite was added to the mixture, and was then shaken for 2 h in a water bath shaker at 85 °C. After 2 h, the bentonite loaded with magnetite nanoparticles (MNLB) was filtered, then washed with water in order to remove extra chloride ions, and dried. The dried MNLB were checked through magnet. It was found that the magnet attracts all the MNLB because of its magnetic nature. The MNLB were then stored in a bottle for further experiments and characterization.

2.3. Batch adsorption program

Adsorption of dibenzothiophene (DBT) from model oil onto untreated bentonite (UB), acid activated bentonite (AAB) and magnetite impregnate bentonite (MNLB) was conducted at different adsorption parameters like: different contact time, adsorbent dose, initial DBT concentration, temperature. For each experimental set up, known volume, DBT concentration, and mass of the adsorbent were taken in a 100 mL Erlenmeyer flask, and were shaken for the respective time in temperature control water bath shaker. After the respective time, the Erlenmeyer flask was taken from the shaker and the mixture

was filter by whatman filter paper. The residual concentration of the DBT in model oil was then analyzed for the absorbance by using UV Visible spectrophotometer at wavelength of 325 nm. The residual concentration of the DBT in model was calculated from the absorbance using the calibration curve. The DBT adsorbed per unit mass of the adsorbent (mg/g), and their percentage adsorption was calculated using Eqs. (1) and (2)

$$q_e = \frac{C_i - C_e}{W} \times V \quad (1)$$

$$R\% = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

where, q_e is the adsorption capacity in mg/g, C_i (mg/L) is the initial concentration of DBT in model oil, C_e is the equilibrium concentration of DBT in model oil, V is the volume of model oil in liter and W is the mass of adsorbent in gram.

3. Results and discussion

3.1. Adsorbent characterization

3.1.1. Surface morphological study of the prepared adsorbents

The morphological study of the prepared adsorbents was carried out with scanning electron microscopy (SEM) in order to check its surface and porosity. Pores present in the adsorbent surface have high role in the adsorbate adsorption. Generally the adsorbent with porous and rough morphology has high adsorption capacity [8,9]. Fig. 1A–C shows the SEM images of UB, AAB and MNLB. From the figures it can be seen that the acid treatment has increased the porosity of the bentonite, which has a positive effect on its adsorption capacity. Because, pores present on the adsorbent surface reduce resistance to adsorbed molecules and also facilitate their diffusion from solutions to adsorbent surface. The surface of bentonite loaded with magnetite nanoparticles is also porous, but along with porous structure its surface also seems very rough, due to rough and porous structure, its adsorption capacity will be more than the UB and AAB. Thus the SEM images of UB, AAB and MNLB strongly supported the experimental results.

3.1.2. EDX analysis of the prepared adsorbents

EDX analyses of the prepared adsorbents were carried out in order to determine their elemental compositions. Fig. 2A–C

shows the EDX spectrum and elemental compositions of UB, AAB and MNLB respectively. EDX spectrum of UB and AAB shows the highest percentage of oxygen, silicon and aluminum, while other elements like: sodium, calcium, sulfur, chlorine, potassium, calcium and tellurium are present in minute quantities. The EDX spectra of MNLB show the highest percentage of oxygen, silicon, aluminum and iron along with minute quantities of calcium, potassium and magnesium. The highest percentage of iron in the EDX spectra of MNLB is from the magnetic (Fe_3O_4) nanoparticles. Thus the EDX spectra of MNLB conform that the bentonite was successfully loaded by magnetite nanoparticles.

3.1.3. X-ray diffraction (XRD) analysis of the prepared adsorbents

Fig. 3 represents the XRD spectra of UB and MNLB. The XRD spectra of UB show four strongest peaks at 2θ values of 26.65° , 29.5° , 13.9° and 16.9° . The peaks at 26.65° and 29.5° can be assigned to silica (SiO_2), while the peaks at 13.9° and 16.9° can be assigned to alumina (Al_2O_3). Thus the major chemical constituent of UB is silica and alumina. The XRD spectra of MNLB show the dominant peaks at 2θ values of 35.6° and 57.2° which can be assigned to magnetite (Fe_3O_4). The XRD spectra of MNLB also show some peaks at 2θ values of 30° that can be assigned to hematite (Fe_2O_3) rather than magnetite [10]. The presence of hematite may be an impurity phase in magnetite. The XRD spectra of MNLB confirm that the bentonite surface was successfully loaded by magnetite (Fe_3O_4) nanoparticles.

3.2. Effect of contact time

To find the equilibrium contact time for the adsorption of DBT from model oil onto UB, AAB and MNLB adsorbents, the adsorption study was carried out at different time intervals ranging from 20 to 200 min, while other experimental conditions such as: initial DBT concentration (100 mg/L), model oil volume (20 mL), adsorbent dose (0.02 g) and temperature (25°C) were kept constant. The adsorption of DBT from model oil onto all forms of adsorbents is shown in Fig. 4. From the figure it can be seen that adsorption of DBT onto all three forms of adsorbents increases with increasing contact time up to 160 min and then becomes almost constant after 160 min on each type of adsorbent. The maximum adsorption capacity of UB, AAB and MNLB for DBT from model oil at

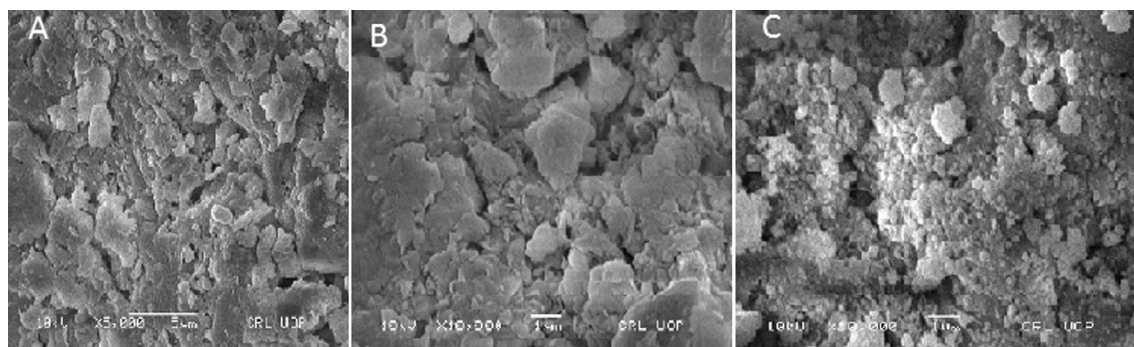


Figure 1 SEM images of (A) UAS, (B) AAB and (C) MNLB.

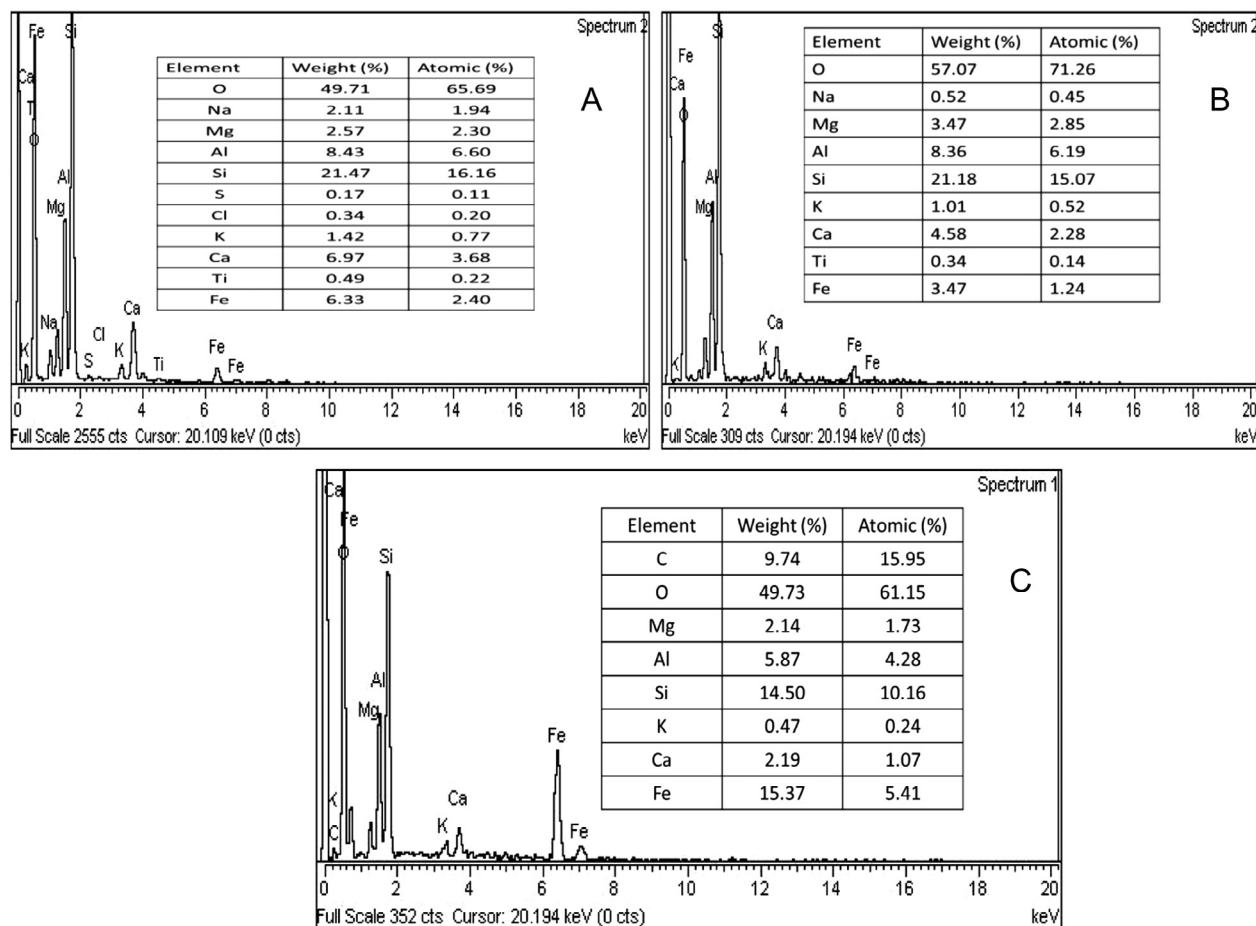


Figure 2 EDX spectra of (A) UB, (B) AAB and (C) MNLB.

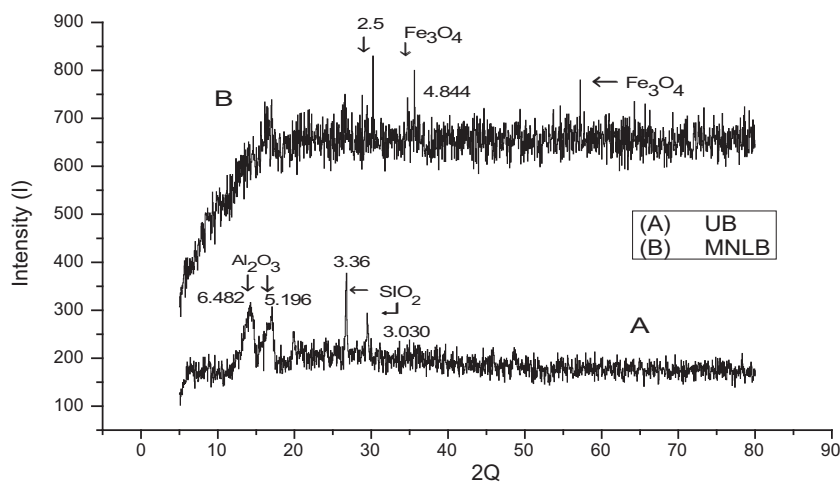


Figure 3 XRD spectra of UB and MNLB.

160 min was 77.4 mg/g, 84.4 mg/g and 99.5 mg/g respectively. From the present discussion it can be concluded that 160 min is the equilibrium time for the removal of 100 mg/L of DBT from model oil using UB, AAB and MNLB as adsorbents. For further study 160 min was selected as equilibrium time.

3.3. Kinetics study

To find a suitable mechanism for the DBT adsorption from model oil on to UB, AAB and MNLB, kinetic data were checked through pseudo first, second order kinetic and the intraparticle diffusion models.

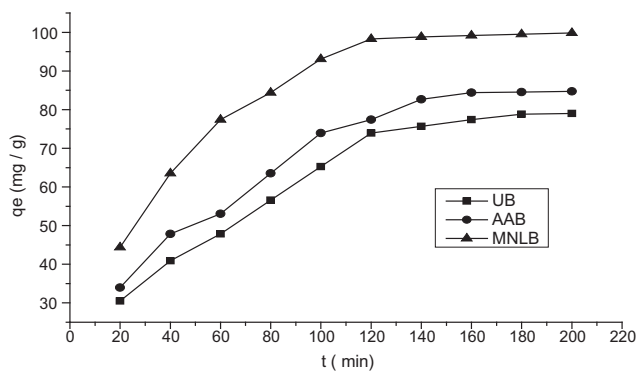


Figure 4 Effect of contact time on the adsorption of DBT from model oil onto UB, AAB and MNLB.

Lagergren proposed pseudo first order kinetic model [11] is given as:

$$\text{Log}(q_e - q_t) = \text{Log} q_e - K_1 t / 2.303 \quad (3)$$

where q_e and q_t are the amount of DBT adsorbed in mg/g at equilibrium and at respective time, and K_1 is the rate constant of pseudo first order kinetic model which can be calculated from the linear plot of $\text{Log}(q_e - q_t)$ versus time.

The pseudo second order kinetic model [12] is given as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

Plotting t/q_t versus t gives a straight line from which K_2 (mg/L) and q_e (mg/g) can be calculated.

The intraparticle diffusion model [13,14] is given as:

$$q_t = K_{id} t^{1/2} + C \quad (5)$$

In Eq. (5) q_t is the amount of DBT adsorbed at the surface of adsorbent at respective time, K_{id} is the intraparticle diffusion rate constant and C is the intercept, which explain the thickness of boundary layer, i.e. the greater the C value, the larger will be the effect of boundary layer. If the kinetic study followed the intraparticle diffusion model, the graph of q_t versus $t^{1/2}$ will be passed from origin [15].

The plot of pseudo first, second and intraparticle diffusion models is shown in Figs. 5(a-c) and their parameters are listed in Table 1. From the parameter comparison of pseudo first and pseudo second order kinetic models it can be concluded that the kinetic study followed pseudo second order kinetic model because of its high regression coefficient (R^2) value, and also calculated q_e value from pseudo second order kinetic model was very close to experimental q_e value. From Fig. 5c it can be seen that the plot of the intraparticle diffusion model of both adsorbents consists of three different linear plots. The first linear plot represents the rapid adsorption of DBT

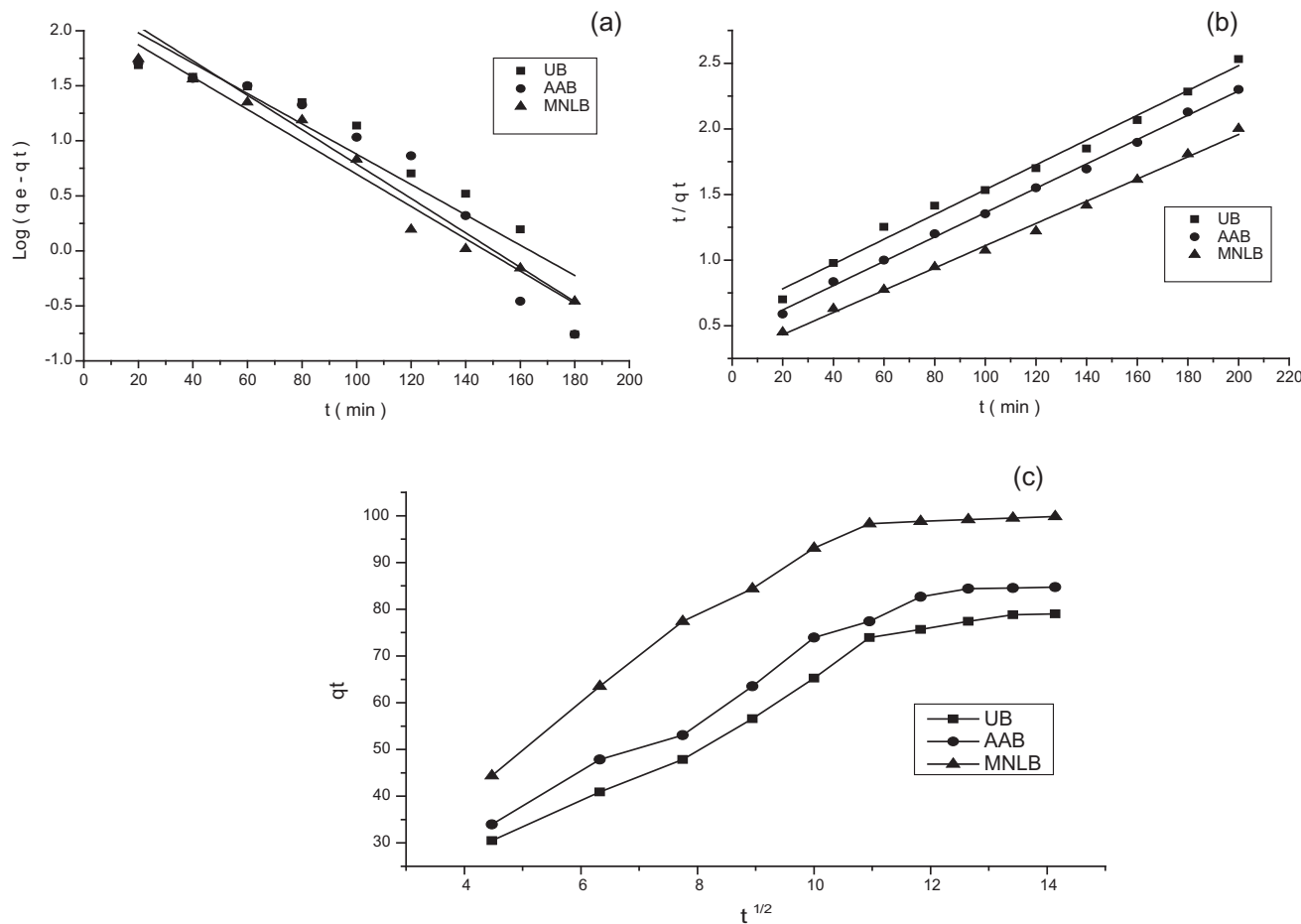


Figure 5 (a) Pseudo first, (b) second orders and (c) intraparticle diffusion model for the adsorption of DBT onto UB, AAB and MNLB.

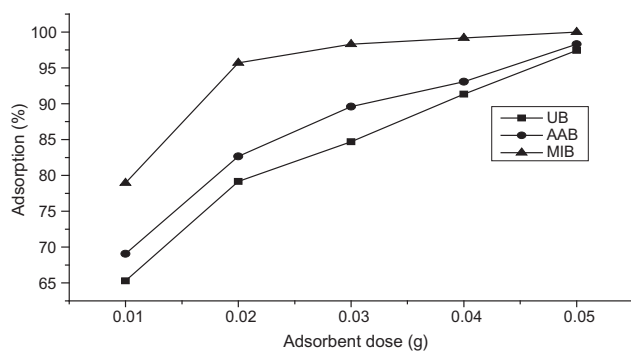
Table 1 Parameters of pseudo first, second and intraparticle diffusion models.

Pseudo first order			Pseudo second order			Intraparticle diffusion model	
q_e (mg/g)	K_1 (min) ⁻²	R^2	q_e (mg/g)	K_2 (g/mg min)	R^2	K_{id} (mg/g min) ^{1/2}	C (mg/g)
<i>DBT on UB</i>							
59.9	0.032	0.975	82.5	0.021	0.991	5.5	7.6
<i>DBT on AAB</i>							
74.6	0.036	0.905	86.7	0.044	0.998	5.7	12.5
<i>DBT on MNLB</i>							
50	0.034	0.889	102.1	0.023	0.996	5.9	29.4

molecules on the adsorbent surface through boundary layer diffusion process, in which molecules of DBT move from solutions to the surface of the adsorbent with a very fast rate and tend to cover the pores of the adsorbent. The second line is the gradual adsorption stage where the intraparticle diffusion is the rate limiting step and third straight line represents the establishment of the equilibrium stage. The line in the intraparticle diffusion model does not pass from the origin which indicated that the intra particle diffusion was not controlling mechanism in the adsorption process [16].

3.4. Effect of adsorbent quantity

The availability and accessibility of adsorption sites depend on the quantity of adsorbent [17]. Therefore the adsorption of DBT from model oil onto selected adsorbents was carried out at different adsorbent doses ranging from 0.01 to 0.05 g, and other experimental conditions such as: DBT concentration (100 mg/L), model oil volume (20 mL), shaking time (160 min) and temperature (25 °C), were kept constant. Results obtained for the adsorption of DBT from model oil on different adsorbent doses in percentage are shown in Fig. 6, from which it can be seen that the percentage adsorption of DBT from model oil onto all types of adsorbent increases with increases in adsorbent dose, which may be contributed to the availability of larger surface area and adsorbent sites for the adsorption of DBT at higher adsorbent dose [18]. Adsorption of DBT per unit mass of the adsorbent not mentioned here, decreases with increasing adsorbent dose, this trend may be attributed to the aggregation of adsorbent particles due to which some active sites of the adsorbent remain unexposed for the adsorption of DBT molecules [19].

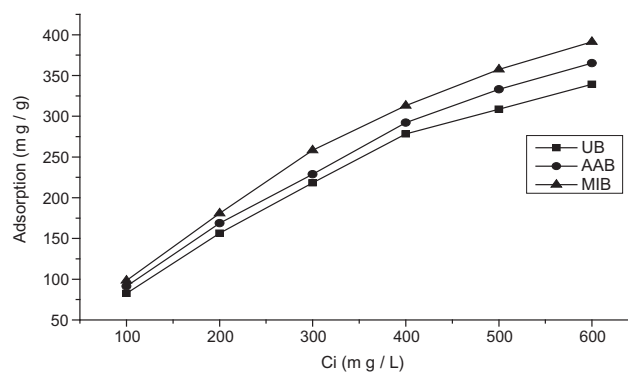
**Figure 6** Effect of adsorbent dose on the adsorption (%) of DBT from model oil onto UB, AAB and MNLB.

3.5. Effect of DBT concentration

Gasoline contains DBT in different concentrations; therefore, it is necessary to carry out the adsorption study of DBT at different initial concentrations. Thus the adsorption of DBT from model oil onto UB, AAB and MNLB was carried out at different initial DBT concentrations, ranging from 100 mg/L to 600 mg/L while other experimental conditions, i.e. contact time (160 min), adsorbent dose (0.02 g), model oil volume (20 mL) and temperature (25 °C) were kept constant. The results obtained for the desulfurization of model oil at different DBT concentrations are given in Fig. 7. From the figure it can be concluded that the adsorption of DBT per unit mass of the adsorbent increases with increasing initial DBT concentration. The increase of DBT adsorption with respect to its initial concentration is a result of the increase in mass transfer driving force due to concentration gradient developed between the bulk solution and surface of the adsorbent [20]. The percentage adsorption of DBT on to all forms of bentonite not mentioned here decreases with increasing initial DBT concentration from 100 mg/L to 600 mg/L. This decrease in percentage adsorption of DBT onto all forms of bentonite with increasing initial DBT concentration may be contributed to the saturation of available active sites of the adsorbent at higher DBT concentration [21].

3.6. Adsorption isotherms

In the present work Langmuir and Freundlich adsorption isotherms were used in order to interpret the isotherm data of the adsorption of DBT onto UB, AAB and MNLB.

**Figure 7** Effect of initial DBT concentration on the adsorption (mg/g) of DBT onto UB, AAB and MNLB.

The linear form of Freundlich adsorption isotherm, used for heterogeneous surface [22] is given as:

$$\text{Log } q_e = \text{Log } K_F + \frac{1}{n} \text{Log } C_e \quad (6)$$

where q_e (mg/g) is the amount of DBT adsorbed at equilibrium, C_e (mg/L) is the remaining concentration of DBT in model oil, K_F (mg/g) (L/mg) and n are constant which can be calculated from the slope and intercepts of linear plot of $\ln q_e$ versus $\ln C_e$.

The linear form Langmuir adsorption isotherm used for heterogeneous surface [23] is given as:

$$\frac{C_e}{q_e} = \frac{1}{Kq_{\max}} + \frac{C_e}{q_{\max}} \quad (7)$$

The plot of Freundlich and Langmuir adsorption isotherm is shown in Fig. 8(a and b) and there parameters are given in Table 2. From the parameters of Freundlich and Langmuir adsorption isotherms, it can be concluded that the adsorption data are best fitted to Langmuir adsorption isotherm than Freundlich adsorption isotherm, because of its close regression coefficient (R^2 0.9978, 0.9935, 0.9933) to 1, and also the experimental q_e (339.2/g, 365.3, 391.3 mg/g) value was close to calculated q_{\max} from Langmuir plot (344 mg/g, 367.5 mg/g, 393 mg/g).

3.7. Effect of temperature

In order to study the effect of temperature on the adsorption of DBT from model oil onto all forms of bentonite; the adsorption study was carried out at different temperatures ranging from 20 °C to 60 °C, while other experimental conditions such as: initial DBT concentration (100 mg/L), model oil volume (20 mL) contact time (160 min) and adsorbent dose (0.02 g) were kept constant. From the results it was found that the adsorption of DBT onto all forms of bentonite increases with increasing temperature. The increase in adsorption with an increase in temperature may be due to the widening of pores of the adsorbent and some active site formation on the surface of adsorbent due to bond cleavage at higher temperature [24]. Moreover the diffusion rate in the pore of adsorbent also increases with an increase in temperature.

Table 2 Parameters of Freundlich and Langmuir isotherm models.

Freundlich isotherm			Langmuir isotherm		
K_F (L/mg)	n	R^2	q_{\max} (mg/g)	K_L (L/mg)	R^2
<i>DBT onto UB</i>					
20.4	1.80	0.9726	344	1.6×10^{-2}	0.9978
<i>DBT onto AAB</i>					
22.8	1.95	0.9803	367.5	3.0×10^{-2}	0.9935
<i>DBT onto MNLB</i>					
24.9	1.97	0.9759	393	1.2	0.9933

3.8. Thermodynamic parameters

The temperature effect on the adsorption of DBT onto UB, AAB and MNLB was explained further by thermodynamic parameters. Thermodynamic parameters i.e. change in free energy (ΔG), change in enthalpy (ΔH) and change in entropy (ΔS) were investigated by the following equations [25]:

$$\Delta G^\circ = -RT \ln K_D \quad (8)$$

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (9)$$

$$\ln K_D = \frac{q_e}{C_e} \quad (10)$$

where K_D is the distribution coefficient, R is the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the absolute temperature in kelvin. $\ln K_D$ were plotted versus $1/T$ as given in Fig. 9. The value of ΔH° and ΔS° was calculated from the slopes and intercepts of linear plot of $\ln K_D$ versus $1/T$ while the value of ΔH° was calculated through Eq. (8). The value of ΔG° , ΔH° and ΔS° is given in Table 3. The value of ΔG° is negative which indicates that the adsorption was spontaneous. The value of ΔS° is positive which suggests that the DBT molecule was adsorbed randomly on the surface of adsorbent; while the positive value of ΔH° confirms that the adsorption process was endothermic.

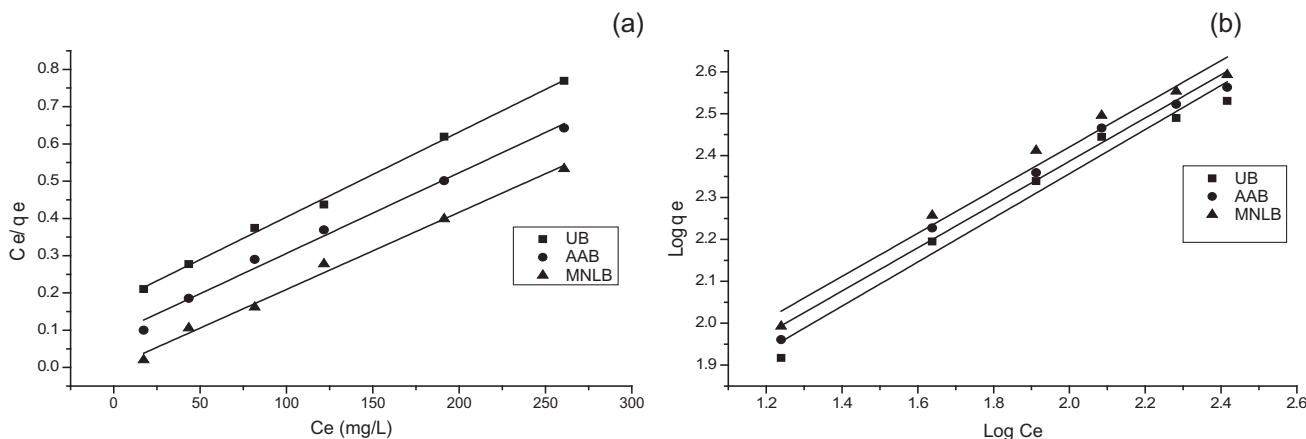


Figure 8 (a) Langmuir and (b) Freundlich isotherm of DBT adsorption on UB, AAB and MNLB.

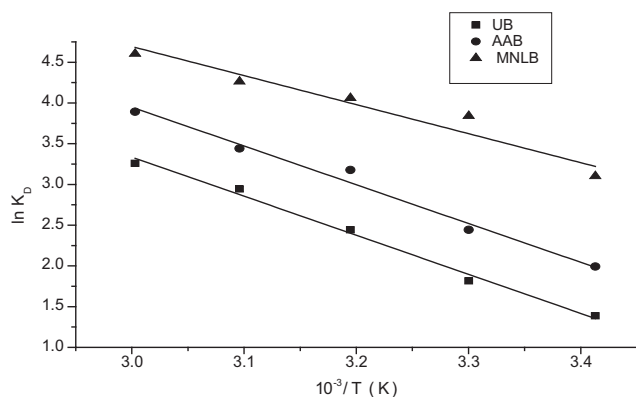


Figure 9 Van't Hoff plots for the adsorption of DBT onto UB, AAB and MNLB.

Table 3 Thermodynamic parameters for the adsorption of DBT onto UB, AAB and MNLB.

ΔH° (kJ/mol)	ΔS° (kJ/mol K)	$-\Delta G^\circ$ (kJ/mol)				
		293 K	303 K	313 K	323 K	333 K
<i>DBT on UB</i>						
39.6	146.5	3.4	4.5	6.3	7.9	9.1
<i>DBT on AAB</i>						
38	149.8	4.6	6.1	8.3	9.2	10.8
<i>DBT on MNLB</i>						
27.4	122.6	7.6	9.7	10.6	11.4	12.7

4. Conclusions

This study investigated that the bentonite impregnated with magnetite exhibits better performance in the desulfurization of fuel as compared to bentonite in untreated form as well as activated with HNO_3 . The high sulfur adsorption capacity of MNLB can be attributed to the catalytic activity of magnetite for the co-conversion or destruction of sulfur species. Moreover, magnetite can be easily recovered by the magnetic separation in the application. The study using model oil recommends that ultraclean adsorptive desulfurization of liquid fuel containing more refractory sulfur compound is possible on magnetite nanoparticle loaded bentonite.

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