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Research Octane Number Improvement of Iraqi Gasoline by Adsorption of n-Paraffins Using Zeolite Molecular Sieves

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Abstract

This study focused on the improvement of the quality of gasoline and enhancing its octane number by the reduction of n-paraffins using zeolite 5A. This study was made using batch and continuous mode. The parameters which affected the n-paraffin removal efficiency for each mode were studied. Temperature (30 and 40 ˚C) and mixing time up to 120 min for different amounts of zeolite ranging (10-60 g) were investigated in a batch mode. A maximum removal efficiency of 64% was obtained using 60 g of zeolite at 30 ˚C after a mixing time 120 min. The effect of feed flow rate (0.3-0.8 l/hr) and bed height (10-20 cm) were also studied in a continuous mode. The equilibrium isotherm study was made using different amounts of zeolite (2-20 g) and then simulated for n-hexane and n- heptane using Langmuir, Freundlich isotherms. Kinetic of the adsorption of n-hexane and n-heptane was investigated using pseudo first order, pseudo second order and intra particle model. The Research octane number (RON) for some selected samples was measured to show the effect of the removal on the quality improvement of gasoline. Results showed an increase of 5.5 units in RON using 40 g zeolite at 40 ˚C and after 120 ˚C min. also an increase in 7 units was obtained in the continuous mode after 30 min using flow rate of o.3 l/hr and bed height of 10cm. Experimental data for n-hexane and n-heptane was found to fit Langmuir isotherm with correlation coefficient of 92.7% and 88.8% for n-C7 and n-C6, respectively. Adsorption of n-hexane and n-heptane was found to follow second order kinetics with correlation coefficient of 99.9% and 99.8% for n-C7and n-C6 respectively. This study revealed a favorable adsorption of n-paraffins on zeolite 5A as indicated by the separating factor of 0.6 and 0.44 for n-C7and n-C6, respectively.

Keywords: Octane number upgrading, Adsorption, Zeolite 5A.

Introduction

Separation and purification of mixtures by selective adsorption of one or more of its components on a micro- or meso-porous solid adsorbent is a major unit operation in the chemical, petrochemical, environmental, medical, and electronic gas industries. The main reasons are as follows: Commercial availability of a spectrum of porous adsorbents (zeolites, activated carbons, silica and alumina gels, polymeric sorbents, etc.) which offer many different choices of core adsorptive properties (equilibria, kinetics, and heats) for a given gas separation or purification application. Zeolite 5A is used in two major separation processes. The first is the separation of linear and iso- paraffins by allowing the former to pass through the channels and the latter is not. The second process is air separation where the equilibrium loading of Nitrogen on the 5A zeolite is much greater than that of Oxygen and Argon [1].

In spite of the potential advantages of adsorptive separation, it did not achieve wide commercial acceptance until the introduction of the UOP Sorbex process in the early 1960s Invented by UOP in the 1960s, the Sorbex technique was the first large-scale commercial application of continuous adsorptive separation. The first commercial Sorbex unit, a Molex unit for the separation of linear paraffins, came on-stream in 1964. Most applications of the Sorbex process deliver high-purity products that can be sold or used in downstream technologies. This process offered a truly continuous adsorptive separation process that produced products with essentially constant compositions [2].

Octane rating or Octane number is a standard measure of the performance of a motor or aviation fuel. The higher the Octane number, the more compression the fuel can withstand before detonating. In broad terms, fuels with a higher octane rating are used in high-compression engines that generally have higher performance. In contrast, fuels with low octane numbers are ideal for diesel engines. Use of gasoline with low octane numbers may lead to the problem of engine knocking [3].

The most common type of octane rating worldwide is the Research Octane Number (RON). RON is determined by running the fuel in a test engine with a variable compression ratio under controlled conditions, and comparing the results with those for mixtures of iso-octane and n-heptane. Modern automobile engines require high octane gasoline for efficient operation. Previously lead had been added to gasoline to increase the octane number. However, with the removal of lead from the gasoline pool due to environmental concerns, other methods for increasing the octane number are needed. However, MTBE, while generally less toxic than lead, has been linked to ground water contamination. At the same time, some of the high octane components normally present in gasoline, such as benzene, aromatics, and olefins, must also be reduced. The coking gasoline is usually used as the blending components of automobile gasoline [4] or the feed of the catalytic reforming process after being hydrogenated. Obviously, a process which will increase the Octane of gasoline without the addition of toxic or environmentally adverse substances will be preferable [5-7].

Some versions of UOP's hydroisomerization processes use highly active zeolite-based, Pt containing hydroisomerization catalysts, such as UOP I-7, which contains modified synthetic (large-port) mordenite. In the presence of hydrogen at moderate conditions, such catalysts optimize isomerization and minimize hydro cracking [8]. To further increase octane level, products from a hydroisomerization unit can be sent to the Molex process, where the remaining lower-octane, linear paraffins are separated from the other compounds by using a zeolite adsorbent and a liquid desorbent; the Molex process is an example of UOP's Sorbex simulated- moving-bed technology [9]. The extracted linear paraffins are recycled to the hydro isomerization unit, and the remaining higher-octane fraction is recovered for gasoline blending. The combination of the hydroisomerization and Molex processes boosts the research octane number of a typical feed from 68–70 to 89–92. Shell and Union Carbide are commercially using zeolite CaA (¼4.6A°, also referred to as zeolite 5A) in the separation of linear paraffins from iso-paraffins in their TIP process (Total Isomerization Process). In this process, the linear C5 and C6 paraffins were first isomerized to the thermodynamic equilibrium where after the linear paraffins are selectively adsorbed on zeolite CaA and recycled to the isomerization reactor [10]. The isomerization catalyst of the TIP process is zeolite Pt-H-Mordenite, showing the catalytic potential of Zeolites. In this case, the zeolite not only serves as a support for the platinum particles but also as a solid-acid catalyst [11]. The TIP process (>100 plants worldwide) is an excellent example of the versatile nature of zeolites in industrial processes. The demand for new zeolite is, however, modest because of the long service life of the separating and the isomerizing zeolites. To achieve higher octane levels, UOP’s TIP total isomerization process uses the once-through isomerization process combined with UOP’s Iso Siv process, which uses size-selective zeolite adsorption of the unreacted linear paraffins so that they can be recycled and converted to extinction. Both the TIP and Iso Siv processes originally were developed at Union Carbide’s Molecular Sieve Department, now part of UOP. [12].

This study represents a first unique study of commercial light naphtha obtained from Al Dora refinery as an a attempt to upgrade the quality of gasoline by improving its research octane number. The objective of the present work is to study the removal of n-paraffins from Iraqi light naphtha using zeolite 5A in batch mode and continuous mode adsorption experiments. In the batch mode, the influence of temperature, zeolite dosage and agitation time were studied while in the continuous mode, the influence of bed height and feed flow rate on the removal of n-alkanes were studied in a fixed bed adsorber. For both modes, the effect of removal efficiency on RON was tested for selected samples. The equilibrium adsorption isotherms using the most common models and the kinetics for the adsorption of n-hexane and n-heptane using pseudo-first- order, pseudo- second-order and intra-particle diffusion were also investigated.

Experimental Work

Hydrogenated light naphtha, consisting 35.134 wt. % of total n-paraffins, was supplied by Al-Durra Refinery. Zeolite 5A was supplied by Arab company for detergent chemicals (0.833 mm white spherical, pore volume 11.1% (V)). The zeolite samples were activated by heating for 2 hours in a stepwise manner from room temperature to 200 ˚C.

Equilibrium Study

The procedure involved filling five flasks with 50 ml of hydrogenated light naphtha. Amounts of zeolite 5A (2, 5, 10, 15, and 20 gm) were added into the flasks, sealed and shaken for 24 hours at speed 200 rpm. The supernatant after filtration by Buchner funnel was analyzed for the remaining amount of n-paraffins (pentane, hexane and heptane) by gas chromatography. The equilibrium amounts of n-paraffins sorbed by zeolite qe (g/g zeolite.) in the sorption system were calculated using the mass balance:

$$qe = V\,(C_o - C_e)\,/m \qquad \ldots(1)$$

Where V is the solution volume (l), m is the amount of sorbent (g), and C_o and C_e (g/l) are the initial and equilibrium concentration, respectively.

Adsorption Kinetic Experiments
Batch Mode

A specified amounts of the zeolite (10, 40, 50 and 60 g) were added in a 500 ml conical flask containing a 300 ml of light naphtha and temperature was set as 30 or 40 ˚C. Samples were withdrawn at different agitation time (15, 30, 60, 90, 120 and180 min). Each samples was filtered using Whatman-31 filter paper and analyzed for total n-paraffins concentration. A schematic representation of the batch adsorption unit is shown in Fig. 1.

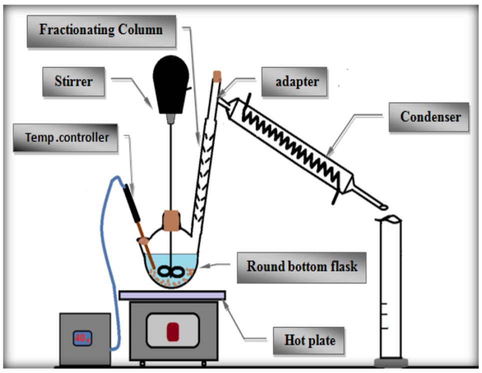

Fig. 1: Schematic diagram of laboratory batch adsorption unit

Continuous Mode

A 2.54 cm quartz column and 35cm long, packed with zeolite 5A was used as the adsorption column. About 41.2 and 82.4 g of the 5A zeolite were packed in the vertical column having a bed length of 10 and 20 cm, respectively. Down flow conditions were used in the experiment. The feed of light naphtha was pumped into the fixed-bed reactor through a distributer at a flow rate of 0.3 and 0.8 liter hr^{-1} as measured by a rotameter N-paraffin content of the effluent was sampled at different operating intervals up to 120min and analyzed by GC. Fig .2 shows a diagram of the fixed bed adsorption unit.

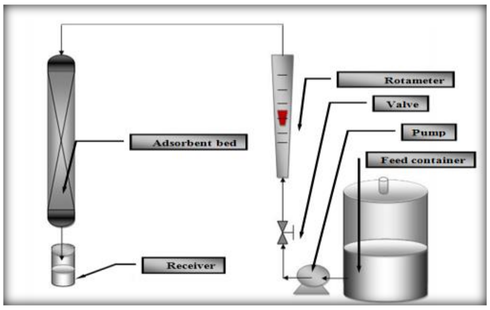

Fig. 2: Schematic diagram of laboratory fixed bed adsorption unit

Results and Discussions
Batch Mode

Effect of Contact Time

The total removal efficiency of n-paraffins is presented in Figs. 3 to 6. It can be seen that the removal by adsorption process proceeded in two stages. An initial rapid increase in the first 15 minutes of contact time is very sharp, and becomes slower and the uptake rate gradually decreases with the increase of contact time. This is due to the continuous filling of the adsorption sites as the time proceeds and to continuous uptake of these materials until reaching equilibrium. Some fluctuations are seen around equilibrium due to the adsorption desorption phenomena. Moller et al. [13] had obtained such results by studying the sorption uptake of n-butane and n-hexane on zeolite 5A and ZSM-5.

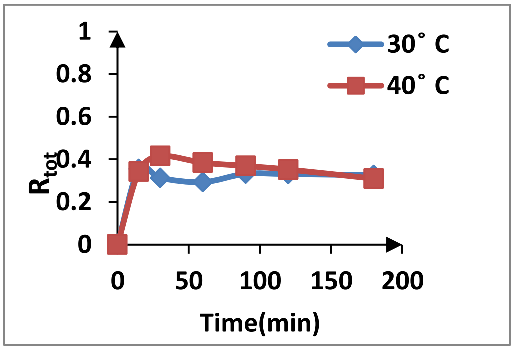

Fig. 3: The relation between the removal efficiency of total n-paraffins with temperature using 10 g of zeolite in 300ml of Light naphtha

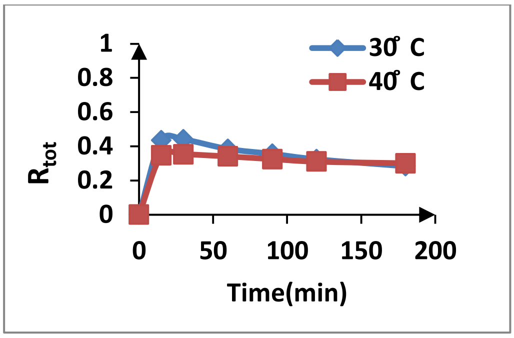

Fig. 4: The relation between the removal efficiency of total n-paraffins with temperature using 40g of zeolite in 300ml of Light naphtha

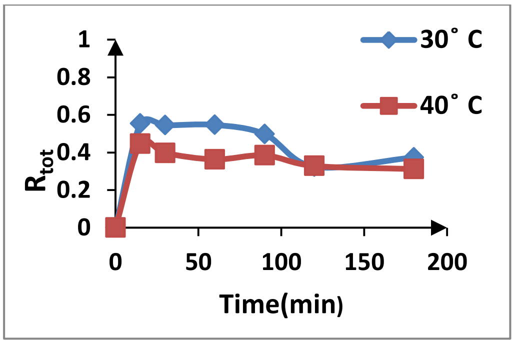

Fig. 5: The relation between the removal efficiency of total n-paraffins with temperature using 50g of zeolite in 300ml of Light naphtha

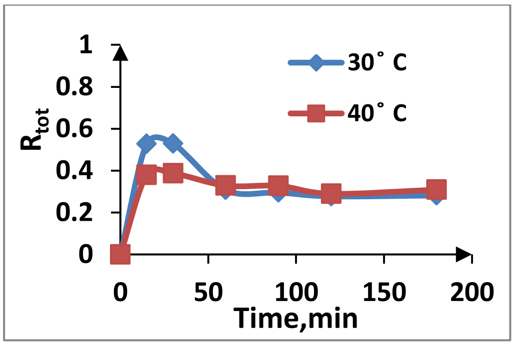

Fig. 6: The relation between the removal efficiency of total n-paraffins with temperature using 60g of zeolite in 300ml of Light naphtha

Effect of Temperature

The effect of temperature on reduction of n- paraffins was studied at 30 ˚C and 40 ˚C and at different amounts of zeolite of 10, 40, 50 and 60 g. As a general trend, increasing the temperature had a negative effect on the reduction of n- paraffins; i.e. increasing the temperature decreases the adsorption of the solute; therefor, desorption or regeneration of the adsorbent is normally achieved by raising the bed temperature [1]. This result is in agreement with *Wender et al* [14] as they found a decrease in the adsorption capacity for individual system of n-hexane up to n-dodecane with increasing temperature. In our study on the cut of light naphtha which is very heat sensitive for it contains different compounds of aromatics, naphthenes, iso-paraffins and n-paraffins with different vapor pressures, so it is expected that high interference on the uptake of adsorbent to linear paraffin and a continuous adsorption/desorption process occurred.

This result agrees well with the result of Nahdhir et al [15] who studied the adsorption of methane in the presence of ethane or ethylene and concluded that the model was better fit for paraffin system and not for others and a separation can be achieved easily at any conditions but was the best at low temperature and pressure.

Effect of Amount of Zeolite

Fig. 7 shows the results of adsorption study carried out with different adsorbent dose. It was found that with increasing dosage of adsorbent the rate of removal of adsorbate ($n-C_7$) increases. The data obtained reveals that there is a substantial increase in adsorption when amount of adsorbent is increased from 2 to 20 g. Increasing the amount of the adsorbent offers more adsorption sites available and ready for higher uptake [16].

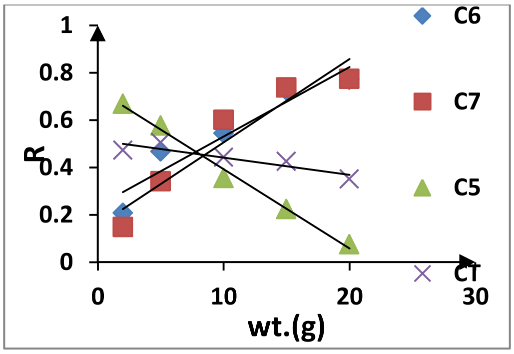

Fig. 7: Effect of amount of adsorbent for the removal of $n-C_6$,$n-C_7$and $n-C_T$ using 5A zeolite:ambient temperature; time = 24 h

Competitive Adsorption of n-Paraffins

By observing Fig. 8, it can be seen that the uptake of n-C_7 on 5A zeolite was higher than n-pentane and n-hexane. This is due to the fact that long Chain hydrocarbons are favorably adsorbed on 5A zeolite [1]. The removal efficiency of n-$C_7$was 53% after 30 minutes while 45% of n-C_6 and 27% of n-C_5 at the same time. After 180 minutes, the adsorption of n-C_7 reached a maximum value where 61% was removed. The removal efficiency of n-C_6 was 46% while for n-C_5 a continuous decrease of the removal efficiency until reaching 14%. The decrease for n-C_5 can be attributed to the desorption occurring in the zeolite structure and replacement by other compounds of higher affinity; i.e. n-C_6 and n-C7.

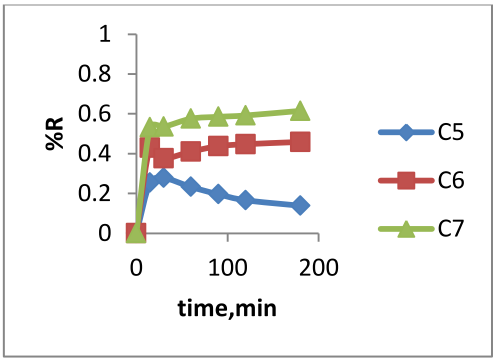

Fig. 8: The removal of n-hexane, n-heptane and n-pentane using 5A zeolite: temperature = 40℃; wt. = 40g

Effect Removal of n-Paraffins on RON

From Table 1, it can be seen that the removal of n- paraffins and specifically n-heptane improves the RON for cut of light naphtha which is studied in the present work. The RON of n-heptane is zero so the reduction in this constituent greatly enhance the fuel property. Removing about 56% of n-heptane increases the RON of light naphtha .This table indicates that the amount of n-C_7 adsorbed is higher than n-C_6 using 40 g of zeolite so that the RON increases 5.5 units from (64.5 to70).

Table 1: Research octane number for light naphtha in the batch mode

Wt	%R_{tot}	%RC_7	RON	Increase in RON
10	31.	56.26	66	1.5
40	30.1	61.49	70	5.5

Continuous Mode

Effect of Flow Rate

The effect of flow rate 0.8 and 0.3 l/h on the adsorption of n-paraffins is shown by breakthrough curves drawn in Figure 9.The adsorbent bed height was fixed at 10 cm and inlet concentration of n-paraffins of 35.134%. It can be seen that the saturationtime decreases for n-paraffin with flow increase.This can be explained by that incearsing the rate of adsorption and the saturation of bed occurs at a shorter time. Besides, the effluent concentration for higher flow rate is higher as compared to low flow rate at constant time because the adsorbate will not have enough time to diffuse into the pores of adsorbent.

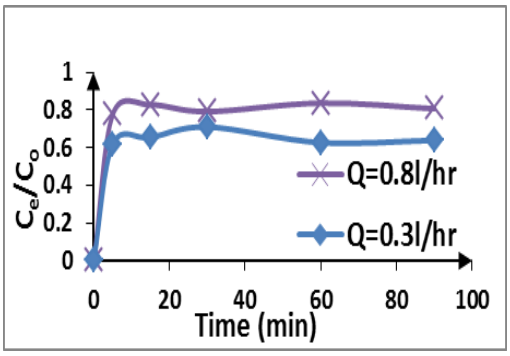

Fig. 9: breakthrough curves for adsorption n- paraffins at Z=10 cm

Effect of Bed Height

Two bed heights had been studied as 10 and 20 cm which represent a weight of 41.2 and 82.4 g, respectively. The flow rate was fixed on 0.3 l/hr. Fig. 10 shows the breakthrough curves for the two bed heights at constant flow rate of 0.3 l/hr.

It can be observed that, as the bed height increased the time needed for breakpoint increases. This shows that for a value of C_e/C_0=0.6, the time is (5min) and (17min) for 10 and 20 cm respectively. The increase of bed height means an increase in the mass of the adsorbent packed in the column which offers more available adsorption sites for adsorbate to be adsorbed. Furthermore, the bed would be saturated in less time for smaller bed height.

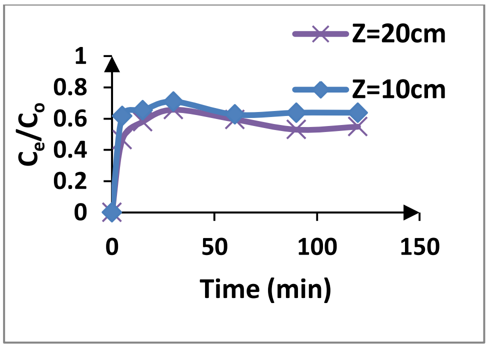

Fig. 10: Breakthrough curves for adsorption n-Paraffins at Q=0.3l/h

Effect of Removal of n-Paraffins on RON

The effect of the reduction of n-Paraffins is clarified by the measurement of RON for selected samples. Records are shown in Table 2. The time for a specified volume of (300 ml) of the effluent from the start of operation is shown along with feed flow rate and bed height. In these experiments, the feed RON was 66.2. Values of the increase can be attributed to the reduction of n-Paraffins present in the fuel. For bed height of 10 cm and 0.3 l/h, an increase of 7 units is obtained, and the quality of the fuel is enhanced.

Table 2: RON for the continuous mode

Time, min	Feed flow rate l/h	Bed height (Z) cm	RON	Increase
20	0.8	10	67.1	0.9
30	0.3	10	73.2	7
35	0.3	20	71.3	5.1

Adsorption Isotherm

The profile obtained from the study of concentration at room temperature was used to obtain Langmuir and Freundlich adsorption isotherms by using well-known adsorption isotherm equations [17]. In both the cases, linear plots were obtained, which reveal the applicability of these isotherms on the ongoing adsorption process. Figs. 11 and 12 exhibit Langmuir and Freundlich plots respectively for the adsorption n-hexane and n-heptane on feathers and different Freundlich and Langmuir constants derived from these plots are presented in Table 3.

To examine the progression of adsorption dimensionless constant, separation factor r was calculated by the following equation:

$$r = \frac{1}{1+bC_o} \qquad \ldots(2)$$

Where b and C_o values were derived from Langmuir isotherm. The parameters indicate the shape of isotherm accordingly.

Table 3: Relationship between separation factor and type of isotherm

r value	Type of isotherm
r > 1 *r* = 1 0<*r* < 1	Unfavorable Linear Favorable

The separation factor, as calculated from Equation 2, indicates a favorable adsorption. Values given in Table 4 confirm the higher affinity of zeolite 5A to n-heptane as compared to n-hexane.

The adsorption data of n-hexane and n-heptane were described equally well by Langmuir and by Freundlich. The exponent (n) in the Freundlich isotherm indicates favorable adsorption. These isotherms are shown in Fig. 12.

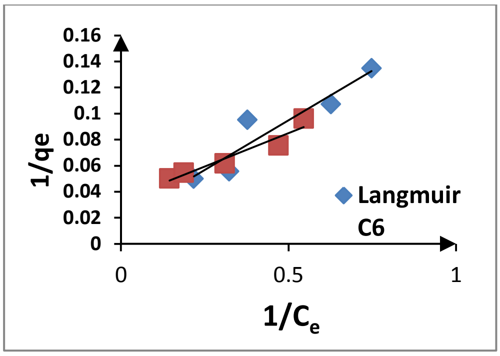

Fig. 11: Langmuir isotherm at room temperature for n-hexane and n-heptane adsorbing to zeolite 5A

Results show that the adsorption capacity for n-heptane on 5A zeolite was higher than that of n-hexane, which can be attributed to the higher molecular weight or higher carbon atoms. Liu and shan [18] concluded also that the low-carbon-number normal paraffins occupying the microchannels of 5A zeolite can be partly replaced by normal paraffins with more carbon numbers. This is a basic phenomenon for adsorption that was reported by the earlier studies [1]. Silva et al. [19] also concluded that zeolite 5A has more favorable nature of n-hexane compared to n-pentane.

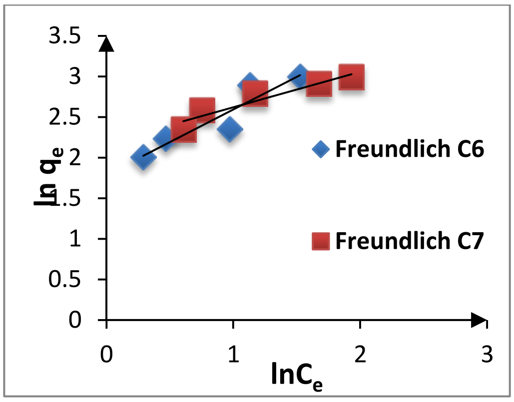

Fig. 12: Freundlich isotherm at room temperature for n-hexane and n-heptane adsorbing to zeolite 5A

Table 4: The Separation factor

Component	r	Type of isotherm
n-C_6	0.441939	Favourable
n-C_7	0.601999	Favourable

Table 5: Constants for the isotherm models

	Langmuir			Freundlich		
	Q^0 ($g/g_{zeolite}$)	b (l/g)	Q^0 ($g/g_{zeolite}$)	b (l/g)	Q^0 ($g/g_{zeolite}$)	b (l/g)
n-C_6	29.762	0.327	0.888	2.228	0.558	0.8770
n-C_7	53.47	0.123	0.927	1.547	0.457	0.9087

Kinetic Study

The Pseudo first-order and second-order kinetic models are the most popular models. In order to investigate the mechanism of sorption and potential rate controlling steps, the pseudo first and second order models were used.

The first-order rate expression is:

$$\text{Ln}\ (qe - qt) = \ln qe - K_1 t \qquad \ldots(3)$$

To investigate the fitness of pseudo first-order equation for n-hexane and n-heptane adsorption, ln(qe −qt) versus t is plotted as shown in Fig. 13. The low R^2 value gives poor correlation of this model.

The pseudo second order kinetic model is expressed as:

$$t/q_t = 1/K_2 q_e^2 + t/q_e \qquad \ldots(4)$$

If the pseudo second-order kinetics is applicable, the plot of t/q_t versus t should give a linear relationship. The linearized form of this model is presented in Fig. 14.

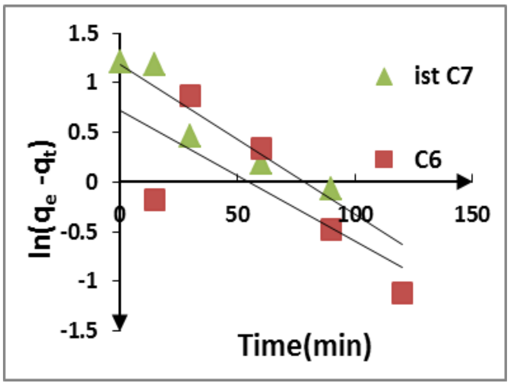

Fig. 13: Pseudo first-order equation for n-hexane and n-heptane adsorption

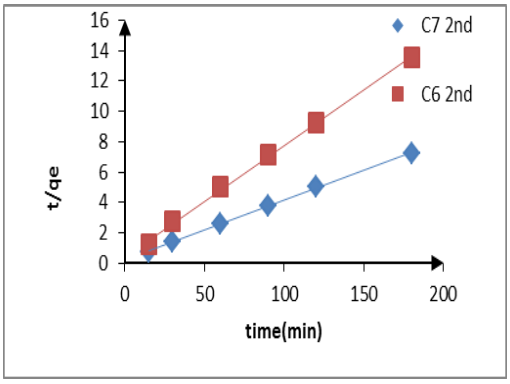

Fig. 14: Pseudo-second-order equation for n-hexane and n-heptane adsorption, at temp.=40℃; t.=40g andvolume=0.3liter

The intra particle diffusion model is also investigated. Then- paraffin uptake is assumed to vary almost proportionally with $t^{1/2}$ rather than with the contact time. The intra partical diffusion model is expressed in Equation 5.

$$qe = K\, t^{1/2} + C \qquad \ldots(5)$$

Where K is the intra particle diffusion rate constant (g/g $min^{1/2}$), C is the intercept (g/g) and a plot of qe versus $t^{1/2}$ gives a linear relationship as shown in Fig. 15.

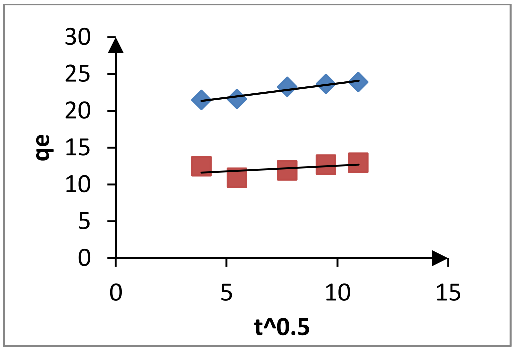

Fig. 15: Intra-particle diffusion model for n-hexane and n-heptane adsorption

Comparison of the three kinetic models revealed that the pseudo second order fits the experimental data quite well as high correlation coefficients of 0.999 and 0.998 are obtained. Values of the kinetic models parameters are listed in Table 6. Silva and Rodrigues [20] proposed that a macropore diffusion is controlling when they studied the sorption and diffusion of n-pentane on pellets of 5A (8mm). Most of the previous literature performed this study in gas phase using a pressure swing adsorption (PSA) which is highly recommended for further study.

Table 6: kinetic parameters for n-hexane and n-heptane adsorption

Kinetic models	Parameters	Compounds	
		n-Hexane	n-Heptane
Pseudo-1storder	K1 (min-1)	0.013	0.015
	qe (g/gzeolite)	2.0422	3.2772
	R2	0.555	0.895
Pseudo-2nd order	K2 (min-1)	0.01281	0.00822
	qe (g/gzeolite)	13.6986	25.641
	R2	0.998	0.999
Intra-particle diffusion	K (g/g.min0.5)	0.155	0.386
	C (g/gzeolite)	11.00	19.86
	R2	0.306	0.932

Conclusions

- Increasing the agitation time and the amount of zeolite increased the removal efficiency of n-paraffins.
- As a general trend, increasing the temperature had a negative effect on the reduction of n- paraffins but the effect of temperature needed further evaluation at different temperatures.
- The uptake of n-C7 on 5A zeolite was higher than n-pentane and n-hexane favorably adsorbed on 5A zeolite. A desorption of n-C5occursfrom the zeolite structure and replacement by other compounds of higher affinity; i.e. n-C6 and n-C7.

- The removal efficiency increased with increasing bed height and decreasing feed flow rate using continuous mode investigations. Furthermore, the bed would be saturated in less time for smaller bed height.
- The results of this study indicated that the adsorption of n-$C_6$and n-$C_7$from light naphtha followed the pseudo 2nd order kinetic.
- An increase in RON of 5.5 units was obtained using 40 g of zeolite in 300 ml light naphtha in a batch mode operation. On the other hand, an increase of 7 units was obtained after 30 min of a continuous operation using abed of 10 cm and 0.3 l/hr.
- A favorable type of the adsorption for the present case study was as presented by a Langmuir isotherm model for both n-hexane and n-heptane adsorption on zeolite 5A. The calculated value of the separation factor confirmed the great tendency of zeolite 5A to n-paraffins.

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