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Adsorption of BTX Aromatic from Reformate by 13X Molecular Sieve

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Abstract

This work deals with separation of the aromatic hydrocarbons benzene, toluene, and xylene (BTX) from reformate. The separation was examined using adsorption by molecular sieve zeolite 13X in a fixed bed process.

The concentration of aromatic hydrocarbons in the influent and effluent streams was measured using gas chromatography.

The effect of flow rate and bed length of adsorbent on the adsorption of multicomponent hydrocarbons and adsorption capacity of molecular sieve was studied.

The tendency of aromatic hydrocarbons adsorption from reformate is in the order: benzene >toluene>xylenes.

Introduction

Barrer and his associates have shown that certain natural and synthetic zeolites may be used as molecular sieve adsorbents for the separation of hydrocarbons and other compounds. A method has been developed for separating certain aromatic hydrocarbons according to shape and size of the molecules. The mixture of aromatic hydrocarbon is introduced in to a column containing the molecular sieve adsorbent. The method was tested with mixture of pure aromatic hydrocarbons and with petroleum fractions contained of mononuclear, dinuclear, and trinuclear aromatic in the C15 to C25 range [1].

Richard W.Neuzil, and Downer Grove, proposed crystalline aluminosilicate adsorbent containing barium and potassium cations for the separation of C8 aromatic components from a feed mixture containing at least two C8 aromatic hydrocarbons. A feed mixture is contacted with an adsorbent wherein one component of the feed preferentially adsorbed by the adsorbent. The preferentially adsorbed component of the feed is there after recovered utilizing a desorption step [2].

K.Al-zaid, F.Owaysi, S.Akashah and Y.A.Eltekov measured the equilibrium extent, kinetic and dynamic of adsorption of individual aromatic hydrocarbon (n-dodecylbenzene, naphthalene, and dibenzothiophene) from iso-octane solutions by molecular sieves 13X using a temperature of 343 K and at concentration of aromatic hydrocarbons 30 kg/m^3. The separation factor and number of adsorbate molecules occupied in the unit cell of the molecular sieve were calculated. The diffusion coefficients were determined using Barrer-Brook equation. The mass transfer zone has been determined using modified Shilov equation and dynamic system of adsorption [3].

According to the work of Owaysi et al, aromatic hydrocarbon impurities are removed from a liquid paraffin in the liquid phase at relatively low temperatures with an X-type zeolite molecular sieve material. The contacting is performed without recycle and purified liquid paraffin containing less than about 0.01% by weight aromatic is obtained [4].

D.Ahmetov and S.Svel-Cerovecki have performed a series of experiments in a small laboratory apparatus with fixed bed of the adsorbent to estimate the suitability of molecular sieve 13X for the preparation of low aromatic solvents from gasoline, white spirit and kerosene and also the optimal conditions for performing dearomatization in a large laboratory apparatus[5].

A refinary reformate comprised of 6 wt% benzene and 25 wt% C8 aromatics (xylenes and ethyl benzene) was passed through an adsorption column of a bed of 300 gm NaX zeolite absorbent at room temperature [6]. Samples of treated feed, as it exited the column, were analyzed in time intervals from 5 to 50 minute and the benzene reaches breakthrough time at 22 minute while the C8 aromatics at 20 min and for C8 aromatics at time 35min. This means that the adsorbent reached the saturation and no more adsorption take place until the adsorbent was regenerated or desorbed.

The adsorbent was desorbed by passing toluene through the bed of adsorbed at flow rate of 20 cm3/min and the concentration of benzene of C8 aromatic was monitored at these time intervals . The desorbed of C8 aromatics from adsorbent is finished at time 20 min while for benzene the desorption is finished from adsorbent at time 25 min [6].

The present study is a trial to separate BTX from the reformate feed supplied from Al-Daura refinary by adsorption technique using molecular sieve zeolite 13X.

Experimental work

Materials

Reformate

Reformate is obtained from catalytic reforming of naphtha. Catalytic reforming leaves the number of carbon atoms in the feed stock unchanged but increases the aromatic content. The feedstock (reformate) in this study is received from Al-Duara refinary. The properties of reformate are given in table 1.

Table 1 Properties of reformate

API gravity	54.9
Specific gravity at 60°F/60°F	0.759
Boiling range (°C)	90-180
Flash point (°C)	25
BTX content, vol%	
Benzene	3.18
Toluene	14.49
P and m xylene	17.66
o-xylene	11.58
ASTM distillation Distillate, vol.%	Boiling point,(°C)
IBP	43
10	71
20	80
30	86
40	92
50	97
60	103
70	110
80	121
90	144
95	154
FBP	180

Adsorbent

The adsorbent column is packed with 13 X molecular sieve obtained from”Rhone Poulene”. Table 2 shows the properties of 13X molecular sieve

Table 2 properties of 13X molecular sieve

Typical properties	**Description**
Normal pore diameter (A°)	10
Bulk density (gm/cm^3)	0.64
Extrudate diameter (mm)	1.6
Loss on ignition (wt %)	1
Average crushing strength (Kg/m)	3
Static adsorption at 10% relative humidity (grams of H_2O /100 gm adsorbent)	21.5
Static adsorption at 60% relative humidity (grams of H_2O /100 gm adsorbent)	25.5
Total pore volume (cm^3/gm)	0.285
Apparent porosity (%)	35.85
Particle density (gm/cm^3)	1.2579
Void fraction of the bed	0.4912

Adsorption procedure

The experimental apparatus show in Figure 1 consists of 2.5 liter glass container, connected with dosing pump. The flow inducer dosing pump is supplied from Watson –Marlow-Limited. Adsorption column has 1.5 cm inside diameter and 100 cm long. It is packed with 13X molecular sieve adsorbent. The bottom of adsorption column is fitted with valve. 50 ml receiver is used for collection of effluent. The collected product is analyses by gas chromatograph for determination the concentration of aromatic hydrocarbons.

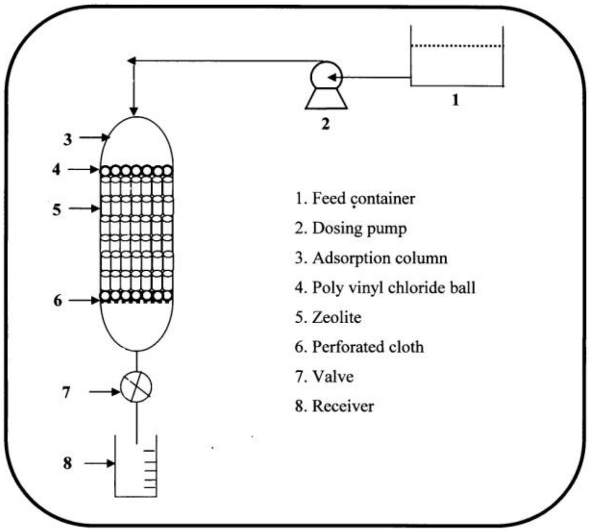

Fig.1: Schematic flow diagram of experimental apparatus

A known quantity of 13X molecular sieve was activated by heating in electronic furnace (Nabertherm) to remove the water of hydration and empty the pores at 275°C for 2 hours. The polymer balls are placed in the bottom of column then a known quantity of zeolite 13X is charged in the adsorption column. The zeolite is packed by gentle tapping through it's length to avoid or reduce the channeling and voidage, which effect the adsorption capacity by loss the actual surface area of 13X zeolite. In the top of adsorption bed polymeric balls PVC is added for good feed distribution. The feed is pumped to adsorption bed at desired flow rate. The feed is moved through the bed until the product begins to collect continuously. The product is received at intervals time for obtaining the concentration of adsorbate at each time to build the breakthrough curve. This means that the saturation of adsorbent is over. The parameters, which is affected on adsorption capacity are flow rate and bed weight. The effect of bed weight in the range 40-70 gm and the flow rate in the range of 0.16-1 cm^3 /min on adsorption capacity was studied.

Chromatographic analysis

The gas chromatography of type Shimadzu-GC 14A was used. Nitrogen was used as a mobile phase, supplied from the gas cylinder, purity of 99.9%.

The chromatographic system used consists of three essential elements. These are injection system, temperature-controlled column, and detector.

Stainless steel packed column used has outside diameter 1/8 inch and 4 m long. The column was packed with chromosorb PAW. The particle size of the support is 60-80 mesh. This support coated with stationary phase of type 1, 2, 3- Tris (cyanoethoxy)-propane (TCEP). The loading of TCEP is 25%.

The isothermal temperature of column TCEP, injection temperature, and detector temperature are 100,200, and 210°C, respectively. The flow rate of the nitrogen carrier gas is $25cm^3$/min. The flow rate of hydrogen and air, which are used for flame ignition of FID, are 25 and 400 cm^3 /min, respectively. The retention times of benzene, toluene , p and m xylenes, and o-xylene , determined by injection of the standard samples , are 6.526, 10.097, 15.440 and 20.867 minutes, respectively.

RESULTS AND DISCUSSION

Effect of multicomponent system on adsorption

For a multicomponent system where coadsorption takes place, the design almost totally depends on experimental and field performance data. In general, the adsorbent bed behaves as a chromatographic column because of difference in affinities of various adsorbents [8]. The multicomponent of aromatic hydrocarbons in reformate are listed in table (1).

Detailed design of multicomponent adsorption may also have to take into consideration the "rollup" effects due to coadsorption[9].

The tendency of aromatic hydrocarbons adsorption from reformate is in the order :benzene >toluene >xylenes. These components in the beginning of the run may be adsorbed compared with o-xylene; therefore, o xylene displaced from the adsorbent to give higher concentration in the effluent streams than originally presented in the feed. When p and m xylenes begin to adsorb some of the o-xylene is readsorbed. This leads to rollup the concentration of o-xylene in the effluent stream to a level above that of the feed. As shown in tables (3)-(5) the C/C0 of o-xylene are 1.732, 2.532 and 1.759 at flow rates 0.16, 0.35, and 1 cm3/min, respectively. These higher concentrations of o-xylene indicate that the bed is saturated with respect to o-xylene. Similarly the more strongly adsorbed toluene displaces some of p and m xylenes from the surface of adsorbent until finally toluene begins to break the bed. These lead to rollup the concentration of p and m xylenes above feed concentration. This behavior of xylenes may be due to the different speed of adsorption for these components, so, xylenes propagate with the faster moving front at the first.

Benzene, which more strongly adsorbed, compared with the other components will rollup the toluene at some runs to higher concentration, which depends on the equilibrium between benzene and toluene at different operating condition. But, the rollup effect on toluene is less than of p and m xylenes and o-xylene. So, the increasing in the concentration of xylenes in the effluent streams is not represented the actual concentration or separation of these component, therefore, the calculation of cumulative adsorption on zeolite and the analysis of effect on adsorption is done for benzene and toluene separation.

Table 3 Breakthrough data for BTX at Q=0.16 cm^3/min, M=50gm, and z=34cm

Time (min)	Effluent concentration /Influent concentration C/Co			
	Benzene	Toluene	P and m Xylenes	O-Xylene
0	0.000	0.000	0.000	0.000
5	0.000	0.325	1.483	1.732
25	0.000	0.437	1.556	1.660
40	0.098	0.644	1.470	1.540
70	0.101	0.665	1.456	1.522
100	0.134	0.757	1.442	1.451
170	0.341	0.719	1.168	1.206
400	0.440	0.840	1.230	1.240
650	0.560	0.980	1.156	1.135

Table 4 Breakthrough data for BTX at Q=0.35 cm^3/min m=50 gm and z=34cm

Time (min)	Effluent concentration /Influent concentration C/C_o			
	Benzene	Toluene	P and m Xylenes	O-Xylene
0	0.000	0.000	0.000	0.000
10	0.000	0.621	1.413	2.538
20	0.225	0.749	1.390	1.806
35	0.273	0.785	1.270	1.428
65	0.355	0.830	1.257	1.245
95	0.382	0.960	1.373	1.349
209	0.467	0.987	1.366	1.290
269	0.435	1.029	1.460	1.557
329	0.524	0.979	1.336	1.406
359	0.590	1.010	1.290	1.335

Table 5 Breakthrough data for BTX at Q=1 cm^3/min M=50 gm and z=34cm

Time (min)	Effluent concentration /Influent concentration C/C_o			
	Benzene	Toluene	P and m Xylenes	O-Xylene
0	0.000	0.000	0.000	0.000
10	0.237	0.922	1.576	1.759
35	0.319	0.876	1.498	1.559
65	0.528	0.979	1.253	1.320
185	0.566	1.125	1.402	1.443
305	0.612	1.151	1.397	1.437

Effect of feed flow rate:

Tables (3)-(5) show the values of C/C_o in the different period of time for benzene, toluene, p and m xylenes, and o-xylene at different feed flow rates These data are plotted in figures (2)-(4) as breakthrough curves of these components. These figures indicate that the higher flow rate generally responsible for earlier break points. This is because a high flow rates exhaust the bed more rapidly, the increasing in the flow rate leads to decreasing the contact time between the adsorbate and the adsorbent along the adsorption bed.

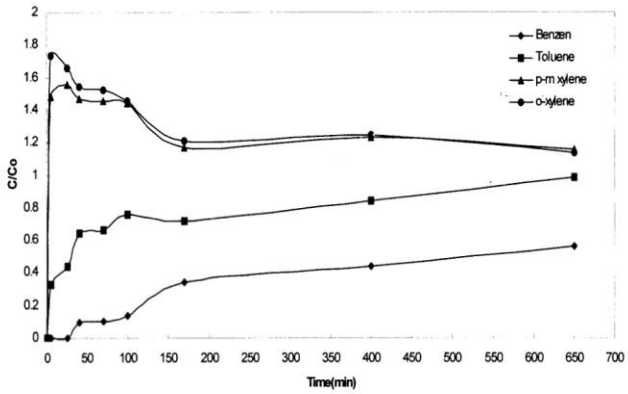

Fig.2: Breakthrough curves for adsorption BTX at Q=0.16 cm3/min and M=50gm

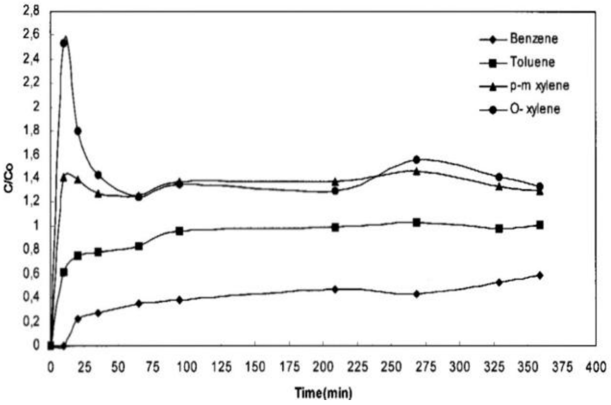

Fig.3: Breakthrough curves for adsorption BTX at Q=0.35 cm3/min and M=50 gm

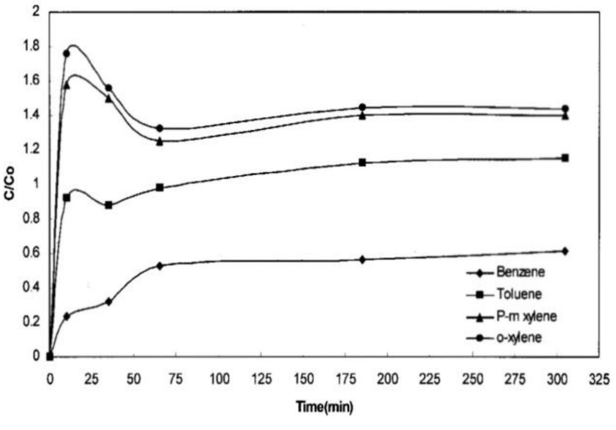

Fig.4: Breakthrough curves for adsorption BTX at Q=1 cm3/min and M=50 gm

The effect of the flow rate on adsorption is noted clearly for benzene and toluene. The flow rate increasing decreases the breakthrough and saturation times. For example, in figures (2)-(4) for flow rate 0.16,0.35, and 1 cm^3/min benzene reaches the breakthrough concentration $C/C_0=0.1$ at time 40,15, and 5min, respectively. Using the same figure and conditions for toluene, at time 10 min the value of C/C_0 are 0.53, 0.62 and 0.92, respectively. The short breakthrough time of toluene is because toluene has the higher concentration in the influent stream therefore high driving force between adsorbate and adsorbent was obtained.

For determination the capacity of zeolite 13X and the accumulative adsorption (q) gm/gm adsorbent after a given time of adsorption equation 1 was used.

$$q_i = (C_0-C)/M*Q*t \quad \text{……………..}(1)$$

Where,

q_i=the quantity of solute adsorbed per unit mass of adsorbent at any given time, gm/gm adsorbent .

C_0=Initial concentration of adsorbate (benzene and toluene), gm/cm^3.

C=Effluent concentration of adsorbate at each time, gm/cm^3.

M=Mass of adsorbent, gm.

Q=Volumetric flow rate,cm^3/min

t =Time of sample min.

The accumulative adsorbed versis time at different flow rate is plotted in figures (5)-(7). These figures indicate that the amount of toluene adsorbed is higher than that of benzene at any time. This is because of the higher driving force for toluene and higher amount in the feed. These figures also show that when toluene reaches the saturation time, q of toluene is reduced and q of benzene becomes higher that toluene. The later phenomenon is due to, zeolite saturation by toluene which leads to the absent of driving force to transfer.

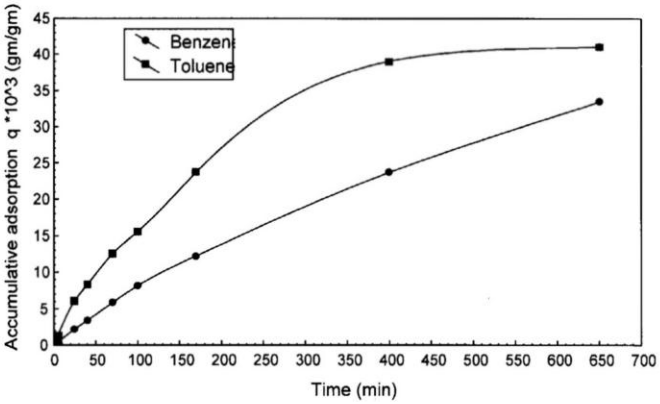

Fig.5: Cumulative adsorption of benzene and toluene Q=0.16 cm^3/min and M=50 gm

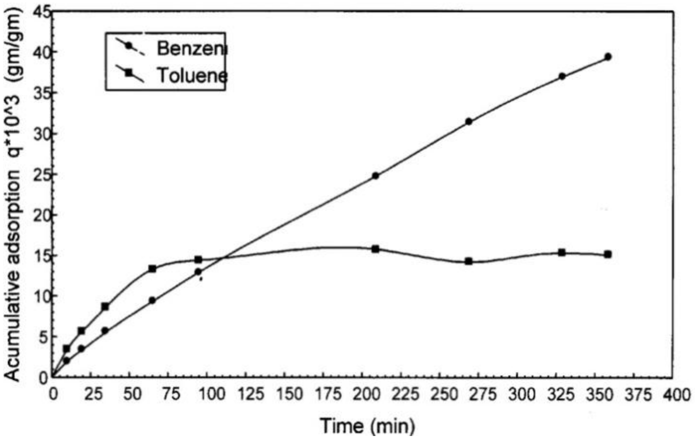

Fig.6: Cumulative adsorption of benzene and toluene Q=0.35 cm^3/min and M=50 gm

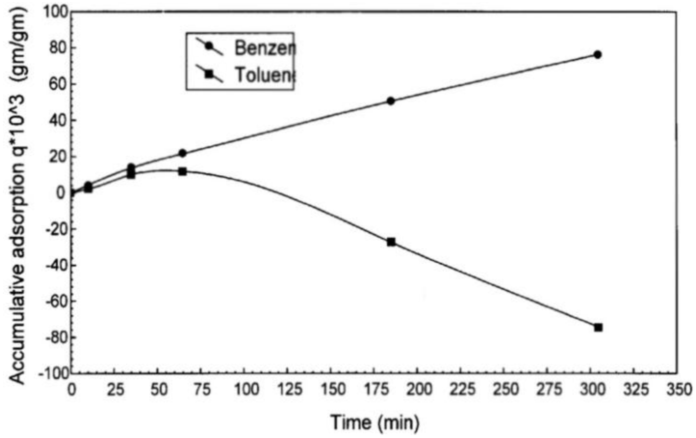

Fig.7: Cumulative adsorption of benzene and toluene Q=1 cm^3/min and M=50 gm

The effect of flow rate on adsorption capacity is shown in figure (8). This figure indicates that the adsorption capacity of zeolite for toluene decreases with the flow rate increasing. This is because the higher rate of toluene adsorption and high flow rate which leads to insufficient times of contact between toluene and zeolite for transfer. So, benzene will have active surface area of adsorbent for transfer and this increase its capacity.

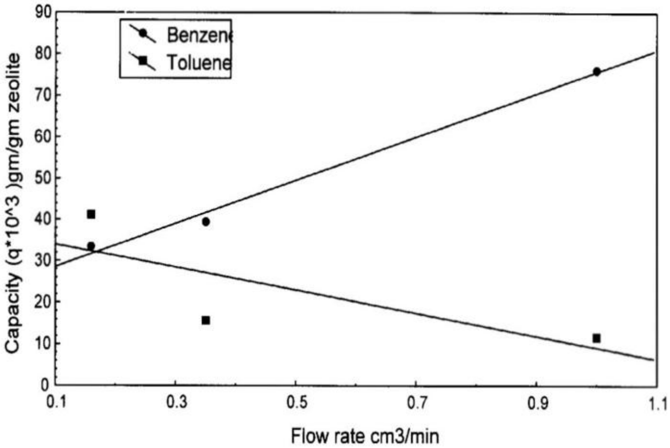

Fig.8: Effect of flow rate on the capacity of zeolite for benzene and toluene

Effect of bed length

The diameter of adsorption column is constant; therefore the used weight of adsorbent corresponds to different bed lengths. Data are plotted as breakthrough curves in figure (9)-(11).

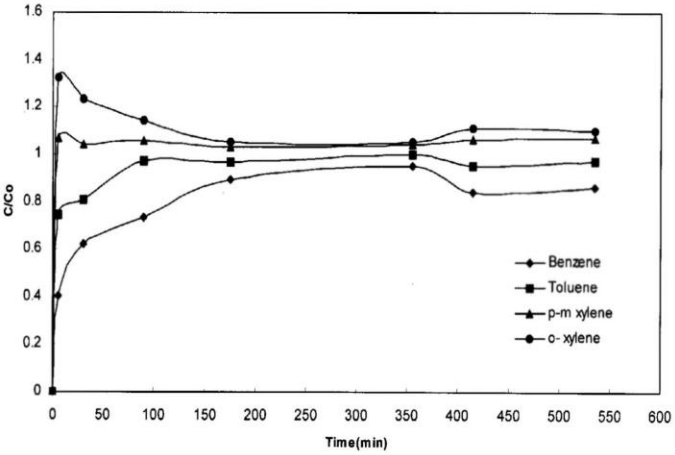

Fig.9: Breakthrough curves for adsorption BTX at Q=0.8 cm^3/min and M=40 gm

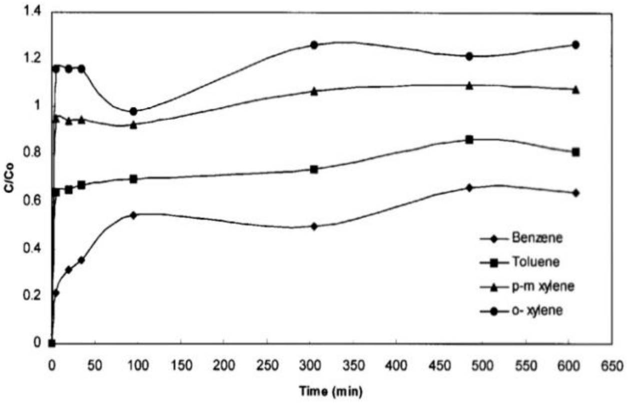

Fig.10: Breakthrough curves for adsorption BTX at $Q=0.8\ cm^3/min$ and M=60 gm

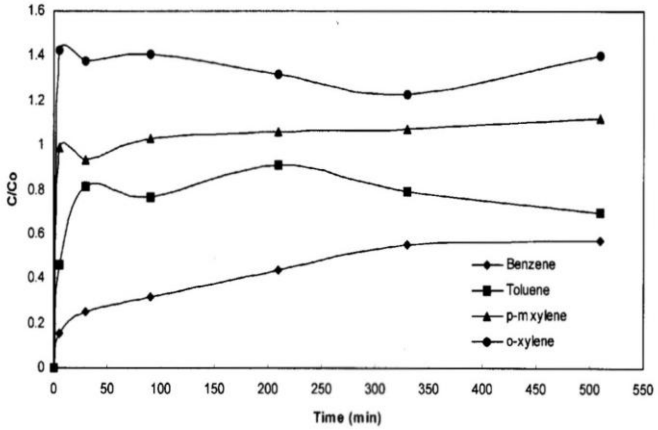

Fig.11: Breakthrough curves for adsorption BTX at $Q=0.8\ cm^3/min$ and M=70 gm

Thee figures show that the shorter bed lengths are generally responsible for earlier break point. The use of short bed length as in figure (9) leads to shorten the contact time between the adsorbate and adsorbent and reduced the available area to transfer.

For example, figures (9)-(11) show that for bed length 29,34 and 45 cm, the benzene reaches the breakthrough concentration C/C_0 =0.1at times 1.3 and 4 min., respectively, and for toluene for the same bed lengths, at time 5min the values of C/C_0 are 0.746, 0.638, and 0.45, respectively. These results indicate that the increasing in the bed length leads to breakthrough time increase for benzene and toluene.

Figure (12)-(14) show the plot of these data between cumulative adsorbed (q) against time. These results show that the amount of toluene adsorbed is higher than benzene at any time for different bed length and solute adsorbed increases with bed length increasing for benzene and toluene.

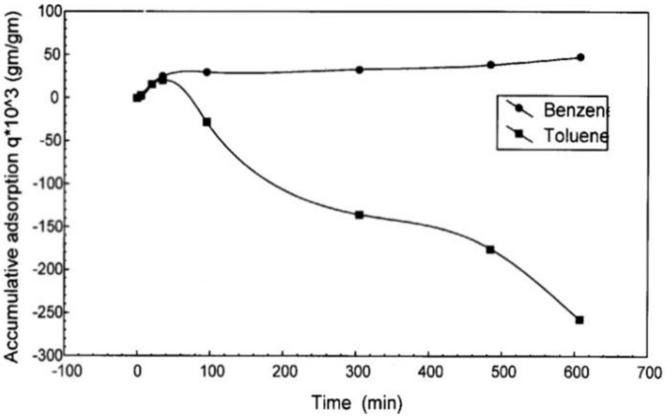

Fig.12: cumulative adsorption of benzene and toluene $Q=0.8\ cm^3/min$ and M=40 gm

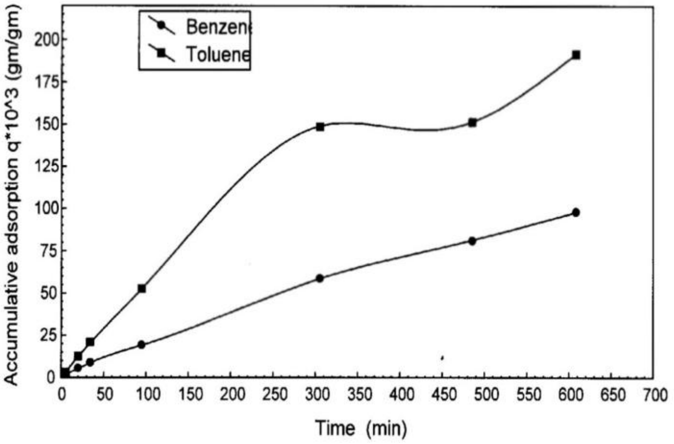

Fig.13: cumulative adsorption of benzene and toluene $Q=0.8\ cm^3/min$ and M=60 gm

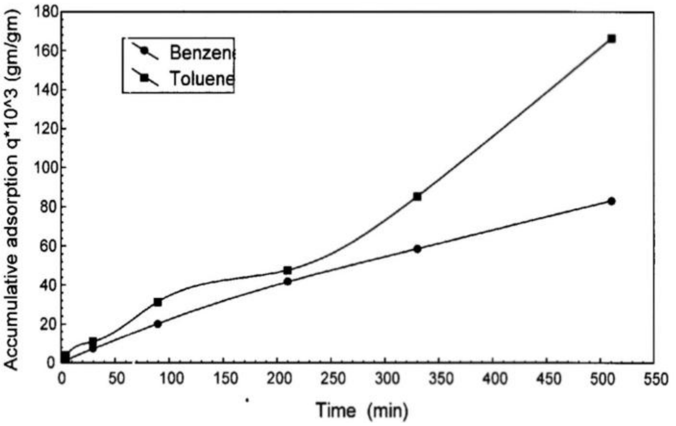

Fig.14: cumulative adsorption of benzene and toluene $Q=0.8\ cm^3/min$ and M=70 gm

The effect of bed length on the adsorption capacity of benzene and toluene shows in figure (15). The adsorption capacity increases by bed length increasing for benzene and toluene, because the increasing in bed length leads to increasing in the surface area available for adsorption.

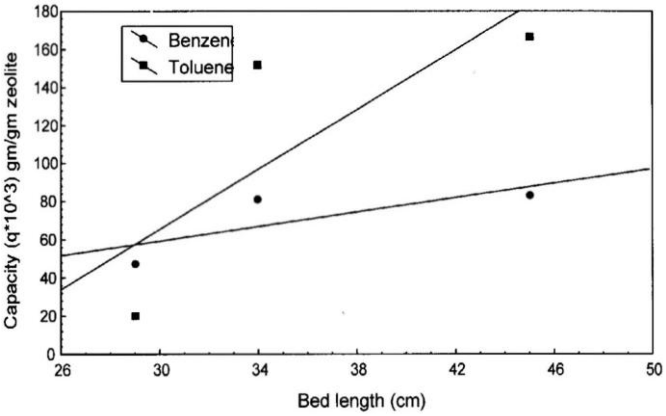

Fig.15: Effect of bed length on the capacity of zeolite for benzene and toluene

CONCLUSIONS

1. The strongly adsorbed component (benzene) leads to displace part of weakly component (toluene and xylene). So, higher outlet concentration of weak component (xylene) above that of inlet streams was observed.
2. The time of break points increases with flow rate decreasing and bed length increasing for benzene and toluene.
3. The time required to reach the saturation point for toluene is increasing by decreasing flow rate.
4. The capacity of zeolite 13X for adsorption of benzene increases with flow rate increasing.
5. The capacity of zeolitr 13X for benzene and toluene increases with increasing the bed length.

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أمتصاص المركبات الاروماتية(BTX) من البنزين المحسن باستخدام المناخل الجزيئية BX

الخلاصة

يتعامل هذا البحث مع فصل المركبات الاروماتية و بشكل خاص البنزول، التلوول، والزايلينات BTX من الريفورمينت. تم اختبار الفصل باستخدام الامتزاز عبر المناخل الجزيئية باستخدام الزيولايت 13X في العمود المحشو.

تم قياس تراكيز المركبات الاروماتية في التيارات الداخلة و الخارجة في العمود المحشو باستخدام كروموتوغرافي الغاز.

درس تاثير كل من معدل جريان المادة الاوية و ارتفاع العمود على نوع الامتزاز و سعة الامتزاز للمناخل الجزيئية.

ان ميل المركبات الاروماتية للامدصاص من الريفورميت هي بتدرج البنزول ثم التلوول وثم الزايلينات. وهذه المركبات تمدص في ان واحد عند بداية العملية. P و m زايلين، التلوول ، والبنزوول وتكون قوية الامدصاص مقارنة مع o- زايلين لذلك يحدث الى o- زايلين عملية ترحيف من الزيولايت و تعطى تراكيز عالية في المجاري الخارجة مقارنة بتركيزها الموجود بالداخل. التركيز الخارج p و m زايلين اعلى من تركيزها الداخل بسبب عملية التزحيف بواسطة المركب الاقوى قابلبة امدصاصية.