

# REDUCTION OF AROMATIC CONTENT FROM HEXANE BY SILICA GEL

Adil A. Al-Hemiri and Rabih Allon

Chemical Engineering Department – College of Engineering – University of Baghdad – Iraq

## ABSTRACT

*This study was conducted to lower the aromatic content (2.23 wt.% benzene) of hexane used as a solvent in the oil-seed extraction at The State Company For Vegetable Manufacture, so as to meet international requirements for food grade materials (less than 300 ppm i.e. 0.03 wt.% of aromatics) by adsorption through a fixed bed of Iraqi silica gel.*

*The results showed that the adsorptive capacity of the local silica gel increases with decreasing hexane flow and decreasing particle size.*

*Compared with the imported silica gel the locally produced was found to be less efficient for the adsorption of benzene by a factor of 2.4. The respective surface areas being 516 and 201 m<sup>2</sup>/g.*

*The best adsorptive capacity of the local silica gel (50 grams of gel yielded 25 mls of benzene-free effluent) was achieved using a gel size of 250-600 μm at a hexane flow rate of 2 mls/min.*

## INTRODUCTION

The most important adsorbents used in adsorption systems are: activated carbon, aluminum oxide, molecular sieves and silica gel<sup>[1]</sup>.

It is well known that the adsorption affinity of silica gel and like adsorbents is more important for aromatics than for olefins, naphthenes and paraffin<sup>[2]</sup>. In this investigation, silica gel is selected to adsorb aromatics from hexane used as solvent for oil seed extraction.

Beveridge and White<sup>[3]</sup> presented a simple laboratory method for the complete removal of aromatics from naphthenes or paraffins by adsorption on silica gel with recovery of 98 % or better. Using two grades of silica gel obtained from the Davison Chemical Corp., Baltimore, Md., grade "150-F-850" (40 to 200 mesh) and "Intermediate" (200 mesh and finer), they fractionated a number of binary mixtures of pure hydrocarbons boiling from 80°C to 175°C. The effectiveness of the coarse gel in removing aromatics was somewhat less than that for the fine gel. Its capacity as an adsorbent for aromatics was found to depend on the concentration of solution and also to some extent on the components of the solution from which the aromatic hydrocarbon is being adsorbed.

Beveridge and Forziati<sup>[4]</sup> described a method for separating by the process of adsorption, the aromatic hydrocarbons from their mixture with paraffin and naphthene hydrocarbons. Two lots of silica gel obtained from Davison Chemical Corp., Baltimore Md.(28-200) and (28-42) mesh size were tested. These were stabilized at normal temperature. It was found that these two lots of different particle size have substantially the same adsorptive capacity for aromatics.

Beveridge<sup>[5]</sup> presented a method for separating and determining aromatic and mono-olefin hydrocarbons in mixture with paraffins and naphthenes by adsorption through silica gel. Three lots of silica gel obtained from the Davison Chemical Corporation were used. .

Experiments with lot I (28-200 mesh) showed that this material, with the natural rate of flow obtained with no external pressure, was too coarse to give satisfactory results. Lots II (150-325 mesh) and III (150 mesh) differed considerably in the distribution of their particle size, as indicated. The second lot of adsorbent was satisfactory at all rates of flow tested. The third lot of silica gel was not satisfactory at any rate of flow tested.

It was found that the sharpness of separation does not depend significantly on the rate of flow within the range investigated (5-240 cm/hr).

A contact tower containing 1 ton of 28-200 mesh silica gel was used by Lipkin (2) in a cyclic operation wherein an east Texas straight-run gasoline fraction containing 7.5 % aromatics and pentane are alternatively percolated there through to effect alternate adsorption and desorption of aromatics. The heated gasoline-pentane mixture resulting still contains approximately 2% aromatics and may be used directly as motor fuel stock or may be subjected to distillation for recovery of pentane.

Hepp<sup>[6]</sup> separated aromatic hydrocarbons from paraffins by a silica gel adsorption process in which heat of adsorption is conserved. A system of three or more adsorption chambers is used in a continuous process, one being "on stream" or adsorbing while the other two are in the desorption stage. 3330 gal/hr of hexane containing 3% by volume of benzene were percolated through 87500 pounds of silica gel contained in one of the chambers. A total of 3200 gal of butane at 150 oF was used as desorbing agent. 333 gal/hr of benzene was yielded as main product.

Recently, Kaul, et al.<sup>[7]</sup> proposed the use of NaX zeolite, and Sweet, et al.<sup>[8]</sup> the use of a polyester succinate to remove aromatics from gasoline and refinery hydrotreated distillate.

This study is intended to lower the aromatic (benzene) content of hexane used as solvent in oil-seed extraction so as to meet international requirements (Less than 300 ppm (0.03 wt. %) of benzene)-relative to food grade materials-by adsorption using local silica gel, in a fixed bed column.

Local silica gel particle size and hexane flow rate were studied to obtain the best operating conditions. The adsorptive capacity of the local silica gel was compared to that of an imported silica gel.

## EXPERIMENTAL WORK

### Chemicals

Two grades of hexane were available; the first (produced by The State Company for Gas Manufacture (Al-Taji) and used at The State Company for Vegetable Oils Manufacture as solvent for oil seed extraction is percolated through silica gel in order to eliminate its aromatic content (benzene with a concentration of 2.23 wt.%). The second is a laboratory grade (supplied by fluka chemical Co.). It was used in preparing solutions (hexane-benzene) of different concentrations in order to determine the adsorption isotherm for the system studied.

Laboratory grade benzene (supplied by BDH chemical Co.) was used in preparing solutions (hexane-benzene) of different concentrations in order to determine the adsorption isotherm for the system studied.

Silica gel (supplied by The State Company for Phosphate Manufacture (Akashat) of random particle size was selected as adsorbent in the present research. After sieving, 3 grades of (250-600  $\mu\text{m}^{-1}$ ), (600  $\mu\text{m}^{-1}$  mm) and (1-2 mm) size were obtained, dried at 70°C for 24 hours, kept in desiccators, then tested. Its performance is estimated comparatively to an imported silica gel.

The properties of the two grades of silica gel are given in Table (1).<sup>[12]</sup>

Table (1) Properties of Local and Imported Silica Gel

Property	Local silica gel			Imported silica gel		
	250-600 $\mu\text{m}$	600 $\mu\text{m}$ -1mm	1-2mm	250-600 $\mu\text{m}$	600 $\mu\text{m}$ -1mm	1-2mm
Bulk density (kg/m <sup>3</sup> )	680	710	826	726	746	796
Particle density (kg/m <sup>3</sup> )	1854	1775	1600	1816	1723	1542
Void fraction of bed	0.63	0.59	0.48	0.6	0.57	0.48
Surface area		201			516	

## Equipment

It consists of a reservoir containing hexane (1); a dosing pump (Watson Marlow, MHRE 200 type) (2); a glass column (0.0174 m inside diameter and 0.5 m length) (3); holding the bulk of the adsorbent (silica gel) (4); retained by a sieve of fine porosity (5); a stopcock (6); and graduated receivers (7). A schematic representation of the adsorption system is shown in Figure (1).

A chromatographic system was used to analyze the inlet and outlet liquid from the adsorption column. It consisted of G.C. chromatograph (Pye Unicam 4500) its detector was of flame ionization type (F. I. D.), the flame is created by burning hydrogen with air. The detector was linked to an integrator (Varian 4290 type). The liquid to be analyzed was injected through the septum using a micro liter syringe (Hamilton type), introduced to the column (contained in the gas chromatograph) by the carrier gas (Nitrogen), then analyzed by the (F. I. D) detector. As a result, a signal is generated and recorded by the integrator as peaks; each peak represents one of the components of the liquid analyzed. The area under the peak representing the concentration of that component.

## Experimental Procedure

A known quantity of silica gel is placed in the adsorption column and packed by gentle tapping through its length. The feed (hexane) in whatever amount is required, is introduced at the top of the column by means of the dosing-pump at the desired flow rate. When the volume of effluent desired for a fraction has collected in the receiver, the volume contained is measured and withdrawn. The concentration of each fraction is measured by the gas chromatograph. Breakthrough curves are determined by plotting effluent concentration against effluent volume.

Nine runs were conducted using 50 g of local silica gel (250-600  $\mu\text{m}$ ; 600  $\mu\text{m}$ -1mm and 1-2 mm) in size at a hexane flow rate of (2, 4, and 8 ml/min). Three runs, using 120 g of local silica gel (250-600  $\mu\text{m}$ ; 600  $\mu\text{m}$ -1mm and 1-2 mm) in size at a hexane flow rate of 2 ml/min and three runs were carried out using 50 g of imported silica gel (250-600  $\mu\text{m}$ ; 600  $\mu\text{m}$ -1mm and 1-2 mm) in size at a hexane flow rate of 2 ml/min.

## RESULTS AND DISCUSSION

### Effect of Hexane Flow Rate

The effect of hexane flow rate on the adsorptive capacity of silica gel of size (250-600  $\mu\text{m}$ ), (600  $\mu\text{m}$   $\text{m}^{-1}\text{mm}$ ) and (1-2 mm) for benzene is shown respectively in Figures (2), (3) and (4). 50 g of silica gel of size (250-600  $\mu\text{m}$ ) yielded 25 ml of benzene-free effluent at a hexane flow rate of ( $F = 2$  ml/min) as well as at ( $F = 4$  ml/min) whereas, only 20 ml of benzene-free effluent are obtained at ( $F = 8$  ml/min) as illustrated by Figure (2).

With 50 g of silica gel of size (600  $\mu\text{m}$   $\text{m}^{-1}\text{mm}$ ), no benzene-free effluent was yielded. At hexane flow rates of 2, 4 and 8 ml/min, the first cuts of effluent amounting to 5 ml contained benzene at a concentration of 0.094 wt %, 0.143 wt % and 0.168 wt % respectively, as shown in Figure (3).

With 50 g of silica gel of size (1-2 mm), no benzene-free effluent was yielded. At hexane flow rates of 2, 4 and 8 ml/min, the first 5 ml of effluent recovered, contained benzene at a concentration of 0.489 wt %, 0.565 wt % and 0.711 wt % respectively, as shown in Figure (4).

Generally, the benzene concentration in effluent increases with increasing hexane flow rate. That is the adsorptive capacity of silica gel for benzene is inversely proportional to the hexane flow rate. This can be attributed to the increasing residence time at lower hexane flow rates.

Different results were obtained by Beveridge<sup>[5]</sup> who found that the sharpness of aromatics separation from paraffin's, naphthenes and monoolefins does not depend significantly on the feed flow rate within the range investigated (5-240 cm/hr).

### Effect of Silica Gel Particle Size

Figures (2), (3) and (4) show the effect of silica gel particle size on the adsorptive capacity of local silica gel for benzene at hexane flow rates of 2, 4 and 8 ml/min respectively.

At a hexane flow rate of 2 ml/min, 50 g of silica gel of size (250-600  $\mu\text{m}$ ) yielded 25 ml of benzene-free effluent, however, with silica gel (600  $\mu\text{m}$   $\text{m}^{-1}\text{mm}$ ) and (1-2 mm) of size, no benzene-free effluent was yielded, the first cuts of effluent recovered amounting to 5 ml contained benzene at a concentration of 0.094 wt % and 0.489 wt % respectively.

At a hexane flow rate of 4 ml/min, 50 g of silica gel of size (250-600  $\mu$  m) yielded 25 ml of benzene-free effluent, but with silica gel (600  $\mu$  m-1 mm) and (1-2 mm) of size, no benzene-free effluent was obtained, the first cuts of effluent recovered amounting to 5 ml contained benzene at a concentration of 0.143 wt % and 0.565 wt % respectively.

At a hexane flow rate of 8 ml/min, the 50 g of silica gel of size (250-600  $\mu$  m) yielded 20 ml of benzene-free effluent, however, with silica gel of size (600  $\mu$  m-1 mm) and (1-2 mm), no benzene-free effluent was yielded, the first cuts of effluent recovered amounting to 5 ml contained benzene at a concentration of 0.168 wt % and 0.711 wt % respectively.

Because the amount of 50 g of silica gel of sizes (600  $\mu$  m-1 mm) and (1-2 mm) was not sufficient to yield benzene-free effluent, we have used 120 g of silica gel to adsorb benzene from hexane solution at the flow rate which allowed to achieve the best adsorptive capacity for silica gel in the range investigated; 2 ml/min.

As shown in Figure (5), we can establish that the silica gel of sizes (250-600  $\mu$  m), (600  $\mu$  m-1 mm) and (1-2 mm) yielded benzene-free effluent amounting to 90 ml, 55 ml and 1ml respectively.

So, generally the benzene concentration in effluent increases with increasing silica gel particle size, that is the adsorptive capacity of the local silica gel is inversely proportional to its particle size. In other words, as the silica gel is fine as its adsorptive capacity for benzene is important. This may be attributed to channeling and misdistribution caused by the increasing void size of the packed bed as the silica gel is coarser, additionally to the increase of mass transfer rate as the silica gel is finer, as noticed by Keller, Anderson and Yon (11).

There are two major considerations to be made when selecting the particle size of the adsorbent. They are the effect of size on mass transfer characteristics and on pressure drop. The calculation of pressure drop through packed beds of adsorbent is necessary to assure that it is neither too low nor too high. When the pressure drop is too low, the flow distribution in bed will be poor. High pressure drop is an economic detractor since it increases the power necessary for compression.

Generally, the pressure drop per unit length of packed bed is inversely proportional to the

particle size to a power not less than unity. Thus, pressure drop can be reduced by selecting the larger particle size. The mass transfer rate for adsorption is also inversely proportional to the particle size to a power not less than unity. High mass transfer rates are desirable, since less adsorbent is required for the same separation. Therefore, the size of the packed bed can be reduced by selecting the smaller particle size. Since, these two criteria are not compatible, trade-offs must be made in the design (10).

Similar results were obtained by Mair and White<sup>[3]</sup> since they found that the effectiveness of the coarse silica gel (40-200 mesh) in removing aromatics is less than that for the fine silica gel (200 mesh and finer). However, Beveridge and Forziati<sup>[4]</sup> concluded that 2 lots of silica gel of different particle size; (28-42 mesh) and (28-200 mesh) have substantially the same adsorptive capacity for aromatics.

### Comparison between Local and Imported Silica Gel

Figures (6), (7) and (8) establish a comparison between the local and imported silica gel both of sizes (250-600  $\mu$  m), (600  $\mu$  m-1 mm) and (1-2 mm) respectively at 2 ml/min, the best hexane flow rate in the range investigated.

The 50 g of local and imported silica gel, both of size (250-600  $\mu$  m) yielded 25 ml and 60 ml of benzene-free effluent respectively, as shown in Figure (6).

Whereas the imported silica gel of size (600  $\mu$  m-1 mm) yielded 40 ml of benzene-free effluent, the local silica gel of the same size yielded no benzene-free effluent, the first 5 ml of effluent recovered contained benzene at a concentration of 0.094 wt % as shown in Figure (7).

Both local and imported silica gel of size (1-2 mm) yielded no benzene-free effluent, the first 5 ml of effluent recovered in each case contained benzene at a concentration of 0.489 wt % and 0.088 wt % respectively as shown in Figure (8).

Generally, we conclude that the adsorptive capacity of the local silica gel for benzene is less important than that of the imported silica gel. That is the imported silica gel is more effective to separate benzene from hexane solution than the local one. This may be attributed to its higher surface area.

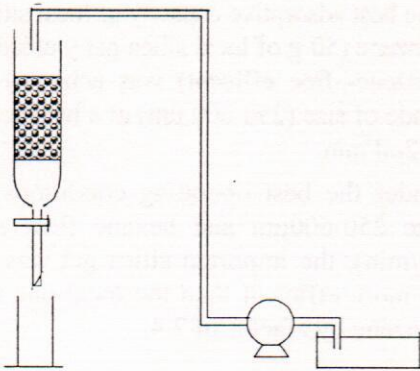


Fig. (1) Schematic Representation of the Adsorption System

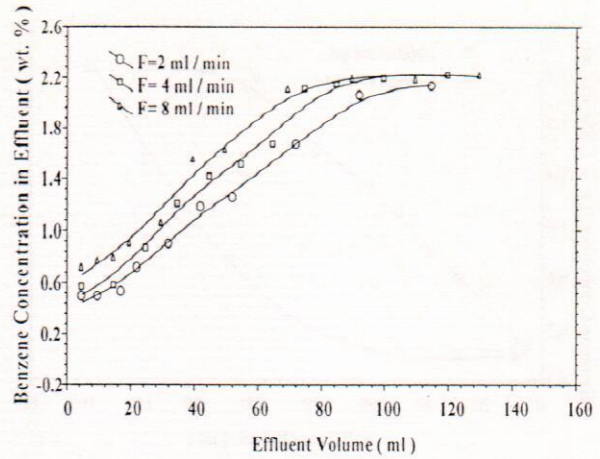


Fig. (4) Breakthrough Curves for Adsorption on 50 g of Local Silica Gel of Various Sizes at a Hexane Flow Rate ( $F = 2 \text{ ml / min}$ ).

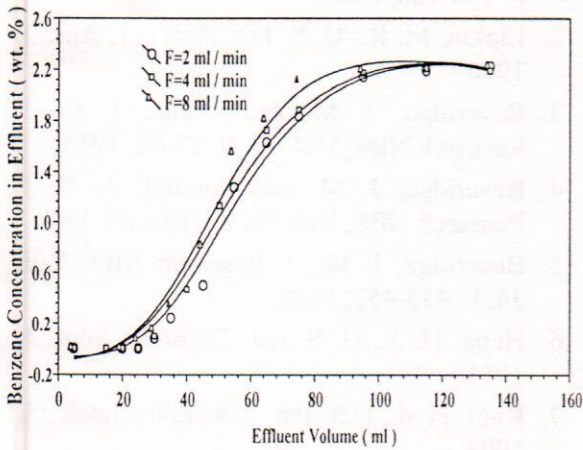


Fig. (2) Breakthrough Curves for Adsorption on 50 g of Local Silica Gel of Size ( $S = 250-600 \mu\text{m}$ ) at Various Hexane flow Rates

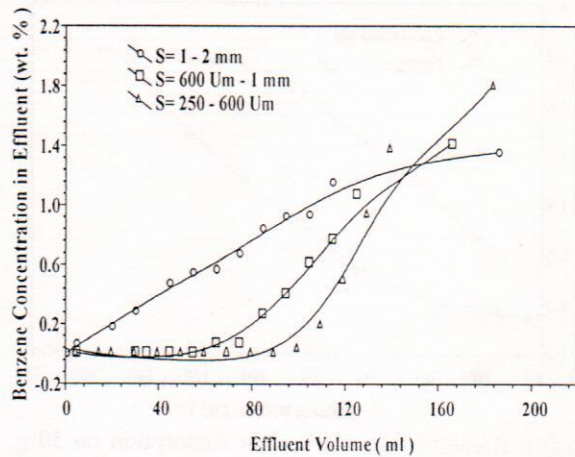


Fig. (5): Breakthrough Curves for Adsorption on 120 g of Local Silica Gel of Various Sizes at a Hexane Flow Rate ( $F = 2 \text{ ml / min}$ ).

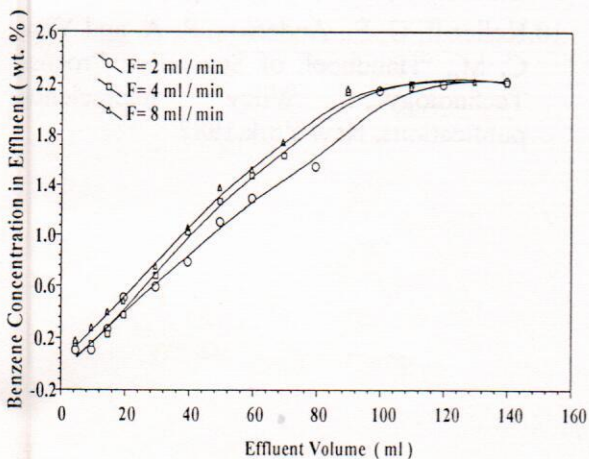


Fig. (3) Breakthrough Curves for Adsorption on 50 g of Local Silica Gel of Size ( $S = 600 \mu\text{m}-1 \text{ mm}$ ) at Various Hexane Flow Rates

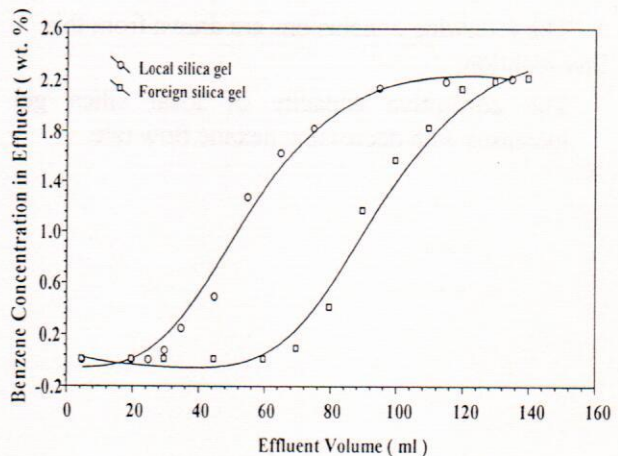


Fig. (6): Breakthrough Curves for Adsorption on 50 g of 2 Types of Silica Gel of Size ( $S = 250-600 \mu\text{m}$ ) at ( $F = 8 \text{ ml / min}$ ).

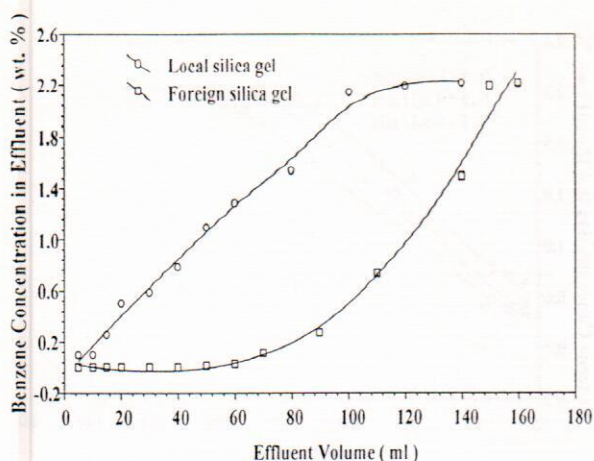


Fig. (7): Breakthrough Curves for Adsorption on 50 g of 2 Types of Silica Gel of Size ( $S = 600\mu\text{m} - 1\text{ mm}$ ) at ( $F = 2\text{ ml / min}$ ).

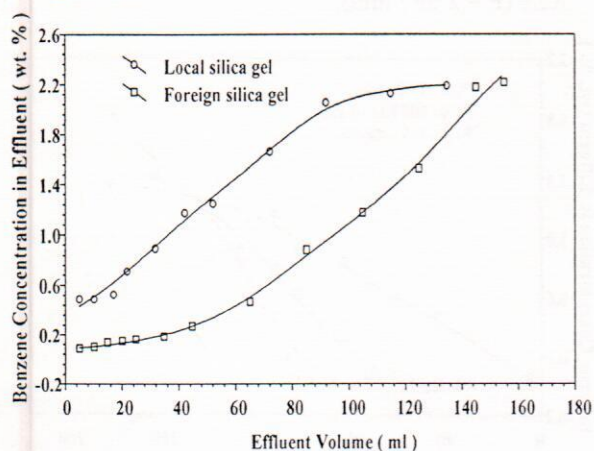


Fig. (8): Breakthrough Curves for Adsorption on 50 g of 2 Types of Silica Gel of Size ( $S = 1 - 2\text{ mm}$ ) at ( $F = 2\text{ ml / min}$ ).

## CONCLUSIONS

The following conclusions are drawn from this investigation:

1. The adsorptive capacity of local silica gel increases with decreasing hexane flow rate.

2. The adsorptive capacity of local silica gel increases with decreasing particle size.
3. The best adsorptive capacity of local silica gel for benzene (50 g of local silica gel yielded 25 ml of benzene-free effluent) was achieved with the grade of size (250-600  $\mu\text{m}$ ) at a hexane flow rate of 2 ml/min.
4. Under the best operating conditions (particle size 250-600  $\mu\text{m}$  and hexane flow rate of 2 ml/min), the imported silica gel was found to be more efficient than the local one to adsorb benzene by a factor of 2.4.

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