# REMOVAL OF THE FURFURAL FROM WASTEWATER BY THE GRANULAR ACTIVATED CARBON

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## ABSTRACT
The aim of the present work is the adsorption of the furfural onto activated carbon where Langmuir and Freundlich equation were used to determine the adsorption isotherm in the batch experiment. Continuous adsorption experiments of fixed-bed were carried out to study the effects of flow rate, bed depth, initial furfural concentration, carbon particle size to determine breakpoint time and adsorption capacity.

## الخلاصة
الهدف من العمل التجريبي هو امتزاز الفورفورال على فحم منشط حيث تم استخدام معادلتين (لانكمير) و(فرندليش) لفحص منحنى الامتزاز. تجارب الامتزاز لنظام مستمر لحشوة ثابتة أجريت لغرض دراسة تأثير كل من معدل الجريان وعمق الحشوة وتركيز الفورفورال الداخل وحجم حبيبات الفحم وتم حساب وقت ظهور نقطة انكسار منحنى الامتزاز وكمية المادة الممتزة بالنسبة إلى كمية الفحم المستخدم (سعة الامتزاز)

## KEY WARDS
Furfural, adsorption, Activated carbon, Break point time, adsorption capacity, waste water treatment, Langmuir and Freundlich equations

## INTRODUCTION
Adsorption onto solid can be defined as the phenomena that takes up the molecules from the fluid phase onto the solid surface (Kirk and Othmer, 1947) and adsorption is probably one of the most common advanced waste water treatment processes, and it finding in creased use in the waste water treatment for removal of refractory toxic substances (Weber 1972).
Adsorption techniques are widely used in the field of removing small quantities of the pollutants present in large volumes of fluid. Removing pollutants by adsorption can be carried out in a batch wise or continuous manner of practice (Rao 1994).
In continuous adsorption systems, there are many types of adsorber generally used in the waste water applications, down flow fixed-bed, packed moving-bed and up flow expanded-bed adsorbers (Cavaseno 1980).

## EXPERIMENTAL WORK

### Material
Waste water used in this study was obtained from Al-Dora refinery treatment plant after the stage of primary treatment.

The adsorbate is the Furfural which is a red-brown liquid used as a solvent in oil manufacturing. Furfural properties are tabulated in **Table (1)**. (Foste and Lesile 1971)

Table (1) Physical properties of Furfural

| | |
|---|---|
| Color | Colorless to yellow and red-brown when exposure to light and air |
| Odor | Aromatic odor as benzaldehyde |
| Specific gravity 20°C | 1.1598 |
| Flash point, open cup °C | 68.3 |
| Heat of vaporization (kcal/mol) at 160 °C | 9.22 |
| Heat of combustion (kcal/mol) | 560.2 |
| Lower explosive limit in air at (125°C) vol.% | 2.1% |
| Ignition temperature °C | 39.3 |

The adsorbent is granular activated carbon (provided by Unicarbo co. Italia). It's physical properties are tabulated in **Table (2)** (Carbochem 2004).

**Table (2)** Properties of activated carbon

| Item of analysis | Specification | Results | Method |
|---|---|---|---|
| Dimensions (granular) | - | 12X40 mesh (0.4-1.6)mm | - |
| Bulk density(kg/m3) | 460-520 | 460-480 | ASTM D 2854-96 |
| Particle density ($kg/m^3$) | - | 1100-1200 | |
| Void fraction | - | 0.45 | |
| Surface area ($m^2/gm$) | 1000 (min) | 1100-1130 | ASTM D4607-94 |
| Hardness (%) | 97 (min) | 98 (min) | ASTM D3802-94 |
| Ash (%) | 5 (Max) | 5(Max) | ASTM D4607-94 |
| *Micropore* | - | high | |

Activated carbon was washed with distilled water before being used remove fines and dried at 100°C for 24 hour

**Equilibrium isotherm experiment (Batch experiment)**

Granular activated carbon weighting (1.0,0.75,0.5,0.3,0.1,0.03,0.003)gm were placed in individual flasks of (100ml) volume.

The same volume of waste water (100ml) with furfural concentration ($0.2kg/m^3$) was added to each flask then shaked for about 10 hours. The solution was filtered by filter paper and 5ml of the filtrate was analyzed (after adding 65ml of 27.5 vol.% ethanol, 5ml of 10vol. Acetic acid and 0.5ml of distilled aniline) using calorimetric (type, Jenway, 6030,UK) at λ(430)nm.

**Continuous adsorption experiments**

The Laboratory apparatus **Fig.2** was used for investigating the adsorption of furfural from the aqueous solution onto activated carbon under the conditions which ere listed in **Table (3).**

Polyvinyl chloride (PVC) column was used as a vertical fixed-bed column with inner diameter (4cm) and (100cm) height. This column was packed with different heights of activated carbon. The waste water was introduced at the top of column and the samples were taken at interval time of (15min) from the bottom of the column.

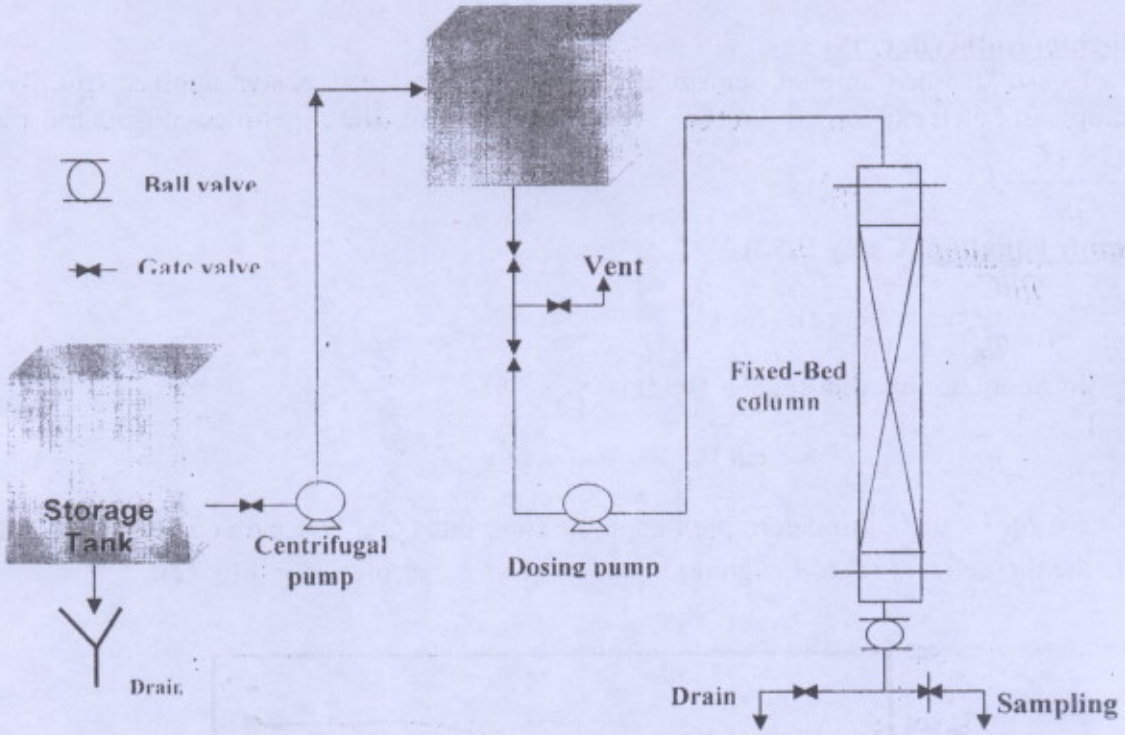


Fig. (1) A schematic representation of experimental equipment

Table (3). Column system experimental data

| Experiment No. | Co ($Kg/m^3$)* $10^{-3}$ | d.p (m) $10^{3}$ | Q ($m^3/min$) $10^{-5}$ | d (m) $10^{-2}$ | Carbon Mass (kg)$10^{-2}$ | Observation |
|---|---|---|---|---|---|---|
| 1 | 200 | 0.5-1.5 | 8.33 | 5 | 28.9 | Variable Flow rate |
| 2 | 200 | 0.5-1.5 | 16.66 | 5 | 28.9 | |
| 3 | 200 | 0.5-1.5 | 41.6 | 5 | 28.9 | |
| 4 | 200 | 0.5-1.5 | 58 | 5 | 28.9 | |
| 5 | 200 | 0.5-1.5 | 75 | 5 | 28.9 | |
| 6 | 200 | 0.5-1.5 | 16.66 | 3 | 17.33 | Variable Bed depth |
| 7 | 200 | 0.5-1.5 | 16.66 | 5 | 28.9 | |
| 8 | 200 | 0.5-1.5 | 16.66 | 8 | 46.2 | |
| 9 | 200 | 0.5-1.5 | 16.66 | 11 | 63.6 | |
| 10 | 50 | 0.5-1.5 | 16.66 | 5 | 28.9 | Variable Influent concent-ration |
| 11 | 100 | 0.5-1.5 | 16.66 | 5 | 28.9 | |
| 12 | 200 | 0.5-1.5 | 16.66 | 5 | 28.9 | |
| 13 | 300 | 0.5-1.5 | 16.66 | 5 | 28.9 | |
| 14 | 200 | 0.5 | 16.66 | 5 | 30.77 | Variable Particle size |
| 15 | 200 | 1 | 16.66 | 5 | 28 | |
| 16 | 200 | 1.5 | 16.66 | 5 | 27 | |
| 17 | 200 | 0.5-1.5 | 16.66 | 5 | 28.9 | Different methods of regener-ation |
| 18 | 200 | 0.5-1.5 | 16.66 | 5 | 28.9 | |
| 19 | 200 | 0.5-1.5 | 16.66 | 5 | 28.9 | |

## RESULTS AND DISCUSSION

**Equilibrium isotherm curve**

A plot of qe (Adsorbed amount per amount of carbon) Vs. Ce (Concentration at equilibrium for each sample of batch experiment (Weber 1972)). **Fig. (2)** gives the experimental isotherm curves

$$qe = \frac{C_o - C_e}{m}.V \qquad \text{eq(1)}$$

**-Langmuir equation** (Casey 1992)

$$qe = \frac{x}{m} = \frac{QbC_e}{1 + bC_e} \qquad \text{eq(2)}$$

And the linear equation (Abu Regeba 1992) is

$$\frac{Ce}{qe} = \frac{1}{\overline{Q}b} + \frac{1Ce}{\overline{Q}} \qquad \text{eq(3)}$$

A plot of ($C_e$/qe) Vs. ($C_e$) to determine Langmuir constants ($\overline{Q}$ ,b) as shown in table (4) in order to estimate the theoretical (qc) of Langmuir equation qe vs. $C_e$ as plotted in **Fig. (2).**

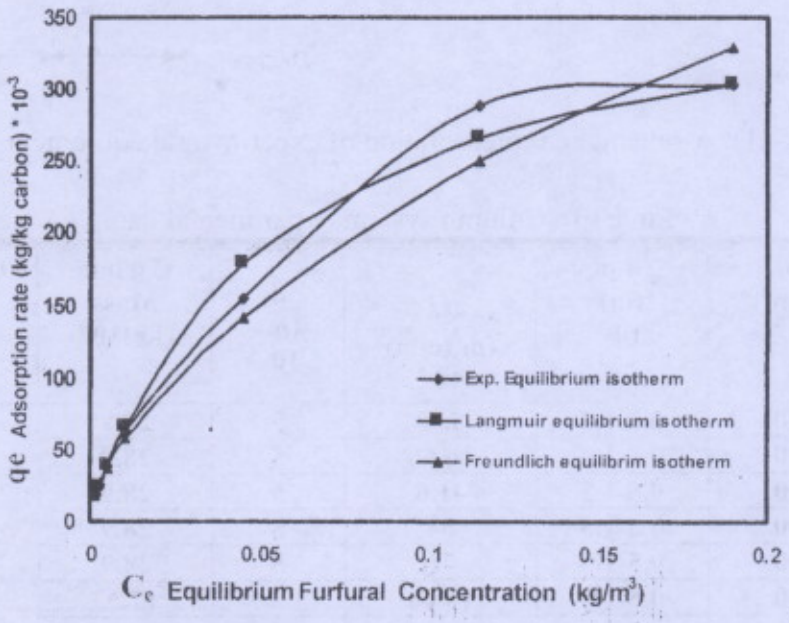


Fig. (2) Experimental and theoretical curves (obtained from the Langmuir and Frurndlich's equations)

**Freundlich equation (Casey 1992)**

$qe = K\,C_e^{1/n}$ eq(4)

and the linear equation is

$\text{Log eq} = \text{Log k} + 1/n\ \log C_e$ eq (5)

A plot of (log qe) Vs. (Log Ce) on log-log paper to determine friendlich constant (k,n) (Weber 1972). **Table (4)** shows these constants.

**Table (4)** Langmuir and freundlich constants.

| Equations | $\overline{Q}$ (kg/kg) | b($m^3$/kg) | K(kg/kg) | 1/n($m^3$/kg) |
|---|---|---|---|---|
| Langmuir | 0.375 | 23 | | |
| Freundlich | | | 14.17 | 0.605 |

**Effect of the flow rate**

The break through curves at different flow rates **Fig. (3)** are shown in, when flow rate increases the break point time of the curve decreases (Poots et al 1976) and adsorption capacity decreases too **Fig.(4).**

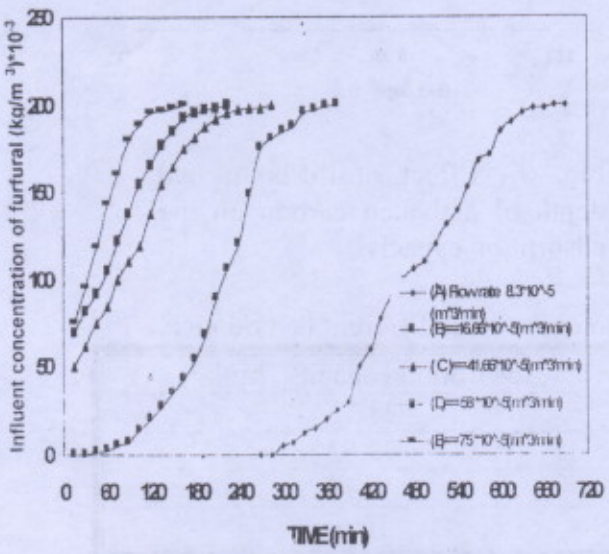


Fig. (3) break through curves of isotherm adsorption for different wastewater flow rate

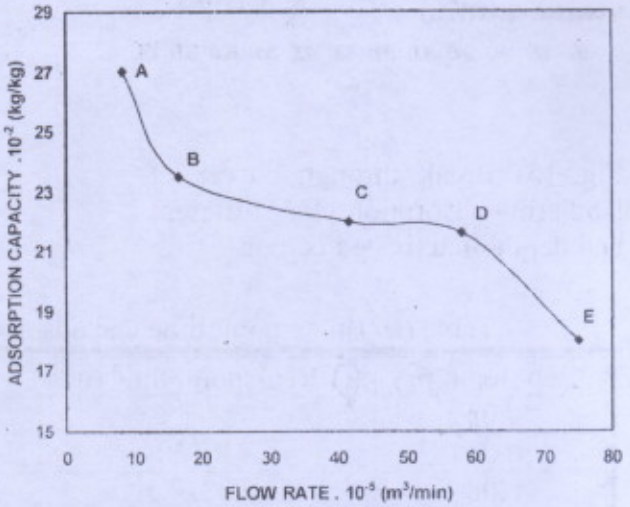


Fig. (4)Effect of the wastewater 's flow rate on the adsorption capacity of activated carbon

Break point values decrease from 360 min– 0 min and absorption capacities decrease from 27.036 -10.03 kg/kg when flow rate increase from (8. 33- 75)X$10^{-5}$ $m^3$/min as shown in **Table (5).**

**Table (5)**Break point time and adsorption capacity at different flow rate.

| Flow rate. $m^3$/min . X$10^{-5}$ | Break point time (min) | Adsorption capacity (kg/kg) |
|---|---|---|
| 8.33 | 360 | 27.036 |
| 16.66 | 120 | 23.49 |
| 41.6 | 0 | 2 |
| 58 | 0 | 21 |
| 75 | 0 | 18.03 |

This is due to increase the linear velocity and also decreases the contact time (Poots et al 1976).

**Effect of bed depth**

Increasing the depth of bed causes an increase in the break-point times and adsorption capacity **Figs. ( 5, 6) and Table (6).**

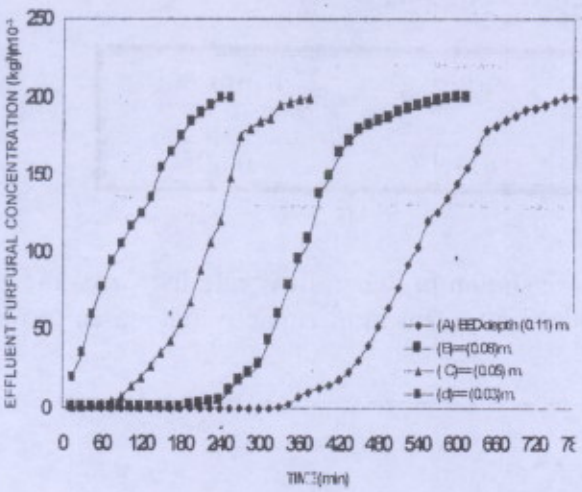


Fig. (5) Break through curves of isotherm adsorption for different bed depth of activated carbon

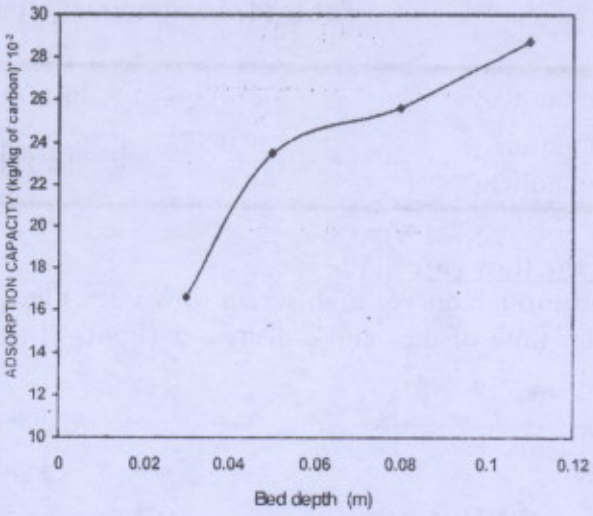


Fig. (6) Effect of different bed depth of activated carbon on the adsorption capaciy

Table (6) Break point time and adsorption capacity at different bed depths

| Bed-depth m | Break point time (min) | Adsorption capacity (kg/kg) |
|---|---|---|
| 0.03 | 15 | 28.73 |
| 0.05 | 120 | 25.62 |
| 0.08 | 227.5 | 23.49 |
| 0.11 | 435 | 16.6 |

Increasing the depth will increase the service life of bed which will provide extra surface area for adsorption (Martin and Al-Bahrani 1978).

**Effect of initial furfural concentration**

**Figure (7)** showed low difference in breakpoint time at increasing of furfural concentration (less than 0.3 kg/m$^3$), but there is an increase in the adsorption capacity as show **Fig (8)**, this phenomena is due high influent furfural concentration act as a driving force that will increase the concentration difference between the bulk solution and solid phase (Abu, Regebaa 1992). **Table (7)** shows that increasing the con. 0.05-0.3 kg/m$^3$ the break point time decreses from 135 min -30 min and the adsorption capacities increase from 6.12 -25.15 kg/kg.

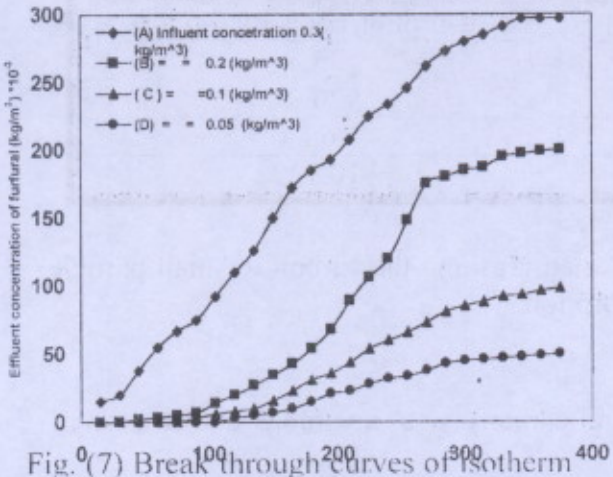


Fig. (7) Break through curves of isotherm adsorption for different influent concentration of furfural

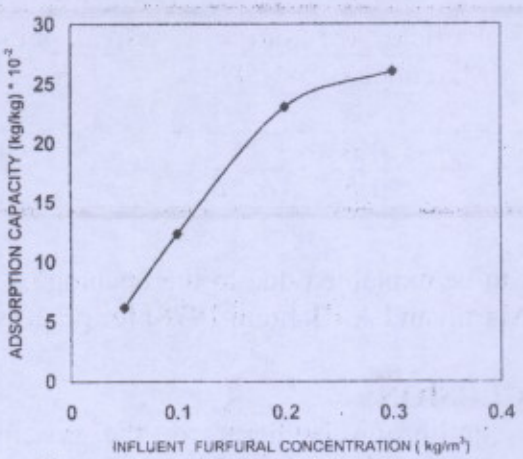


Fig (8) Effect of different influent concentration on the adsorption capacity of activated carbon

Table (7) Breakpoint time adsorption capacity at different influent furfural conc.

| Influent conc ($kg/m^3$) | Breakpoint time (min) | Adsorption capacity (kg/kg) |
|---|---|---|
| 0.05 | 135 | 6.12 |
| 0.1 | 135 | 12.36 |
| 0.2 | 120 | 23.49 |
| 0.3 | 30 | 25.15 |

**Effect of carbon particle size**

The required time to reach the breakpoint increased when particle size decreased **Fig. (9)** (Poots etal 1979) and adsorption capacity increased to **Fig. (10), Table (8)** shows that.

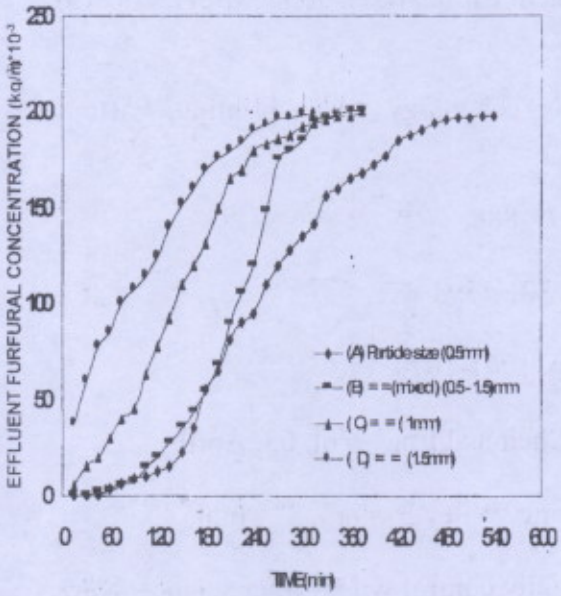


Fig. (9) Break through curves of isotherm adsorption for different particle size activated carbon

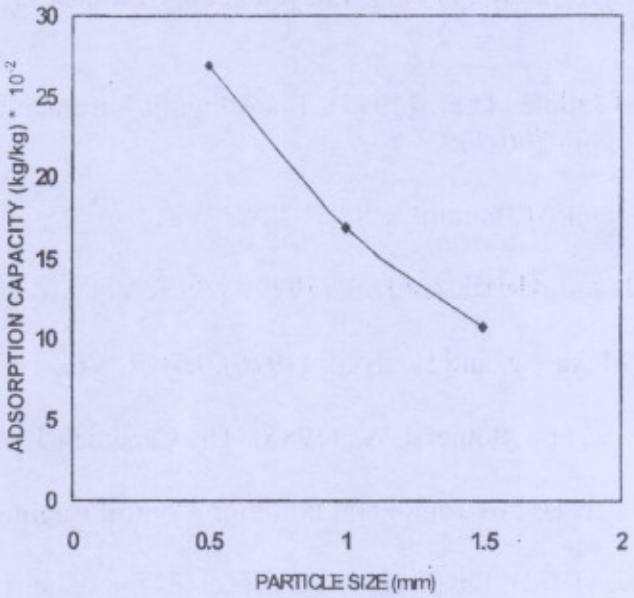


Fig. (10) Effect of the particle size on the adsorption capacity of the activated carbon

Table (8) Breakpoint time and adsorption capacity at different particle size of activated carbon

| Particle size (mm) | Break point time (min) | Adsorption capacity (kg/kg) |
|---|---|---|
| Mixedbed (0.5-1.5) | 120 | 23.4 |
| 0.5 | 140 | 26.9 |
| 1.0 | 45 | 16.88 |
| 1.5 | 0 | 10.727 |

This can be explained due to the opening of new pores when crushing the carbon to small particle size (Martin and Al-Bahrani 1978) for process of the adsorption.

## CONCLUSIONS

- The equilibrium isotherm for the system of (furfural-carbon) was favorable and was well represented by Langmuir or freundlich equation.
- The required time to reach the break point increased with the decreasing of the flow rate, influent cons. and particle size and increasing of the bed depth.
- The adsorption capacity increase with the decreasing of flow rate and particle size and increasing influent furfural concentration and bed depth.

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## NOMENCLATURE

b Langmuir equation parameter ($m^3/kg$)
C Concentration of adsorbate at given time ($kg/m^3$)
Ce Concentration of adsorbate at equilibrium in batch process ($kg/m^3$)
$C_o$ Initial concentration of adsorbate ($kg/m^3$)
d Diameter of the bed column (m)
$d_p$ Diameter of the carbon particle (mm)
k Freundlich equation parameter (kg/kg)
m Mass of carbon (kg)
1/n Freundlich equation parameter ($kg/m^3$)
$\overline{Q}$ Langmuir equation parameter (kg/kg)
Q Flow rate ($m^3/min$)
qe Adsorption quantity ($kg_{adsorbate}/kg_{carbon}$)
V Volume of the sample in the batch process (ml)
x Amount of adsorbed material (kg)
$\lambda$ Wave length (nm)