Adsorbtion of Nitrogen Compounds from Hydrocarbon Liquids by Using Fixed Packed Bed Activated Carbon

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Abstract:

The Extraction behavior of nitrogen compounds (quionoline, indole, and pyridine) from a liquid hydrocarbon (nonane, C9) was studied by using batch and fixed bed activated carbon experiments. The adsorption isotherm curves and the extraction percentage were determined in batch experiments in the conditions of initial concentration 20,40,60,80,and 100 ppm of either of quionoline, indole, and pyridine, fuel/(AC) ratio of 20 wt/wt, room temperature $30 \pm 1°C$, and stirring time of 2h.

In the fixed bed experiments the breakthrough curves were determined as a function of the following variables:

✓ Bed height of activated carbon 3, 5, and10 cm.

✓ Initial concentration of nitrogen compounds 50, 75, and100 ppm.

✓ Flow rate of the feed (15, 25, and35) ml/min.

✓ Particle Diameter of activated carbon 1.5, 1.2, and1 mm.

The adsorption capacity increases with increasing equilibrium concentration of the nitrogen compounds in the liquid phase, which is a very favorable isotherm irreversible adsorption. Also the activated carbon has very high affinity for the nitrogen compounds in the order indole > quinoline > pyridine and the conversion values were (50, 46,

and42) % respectively. In fixed bed experiments the time to breakthrough point decreases with:

- ✓ Decreasing in bed height.
- ✓ The increase in flow rate.
- ✓ The increase in initial concentration of nitrogen compounds.
- ✓ There is no effect of varying the particle diameter of the activated carbon because the experimental values of the activated carbon lies in the region of the large particle size and macrospore volume and there is no gradient in the particle size.

الخلاصة

تمت دراسة سلوكية أستخلاص المركبات النتروجينية (الكيونيلين،الاندول و البريدين) في السائل الهيدرو كربوني (النونان) بأستخدام تجارب الدفعات وتجارب عمود الحشو الثابت بأستخدتم الكربون المنشط. تم أيجاد منحنيات الامتزاز ثابت الحرارة ونسبة الامتزاز لتجارب الدفعات في ضروف التركيز الابتدائي (100,20,40,60,80) جزء من المليون لكل من (الكيونيلين،الاندول و البريدين) ونسبة المركب النفطي الى الكربون المنشط (20) وزن / وزن ، تحت درجة حرارة ثابتة تقريبا (30)م وبزمن خلط (2) ساعة.

تم أيجاد منحنيات الاختراق لتجارب عمود الحشو الثابت بدلالة المتغيرات التالي:-

- ✓ أرتفاع عمود الكربون المنشط (10,3.5) سم
- ✓ التركيز الابتدائي للمركبات النتروجينية (100 ,50,75) جزء من المليون .
- ✓ معدل جريان السائل (35,25,15) ملم / دقيقة .
- ✓ قطر حبيبات الكربون المنشط (1,1.5,1.2) ملم.

وجد أن كفاءة الامتزاز تزداد بأزدياد تركيز المركبات النتروجينية في السائل الهيدروكربوني عند التوازن. وأن منحنيات الامتزاز تعتبر منحنيات مثالية لأمتزاز غير أنعكاسي ثابت للحرارة ، كذلك وجد أن للكربون المنشط الفة للمركبات النتروجينية وبمستوى (الاندول> الكيونيلين > البريدين) وبنسب أستخلاص تصل الى (50,46,42) % على التوالي.

✔ وجد أن زمن نقاط الاختراق في تجارب عمود الحشو الثابت يقل:-

✔ بنقصان أرتفاع عمود الحشو الثابت.

✔ بزيادة معدل الجريان .

✔ بزيادة التركيز الابتدائي للمركب النتروجيني.

✔ لا يوجد تاثير ملموس جراء تغيير قطر حبيبات الكربون المنشط ، لان القيم المستخدمة تقع ضمن مستوى الدقائق الكبيرة الحجم ولا يوجد تدرج دقائقي للحبيبات.

Introduction

Adsorption is a process of accumulation substances that are found in the solution, called solute, on a suitable interface [1].

Adsorption is the most commonly used process because it is fairly simple and convenient unit operation and that the cost for its application is relatively low compared to other treatment processes. Adsorption can be equally effective in removing trace component from the liquid phase and may be used either to recover the component or simply to rid an industrial effluent of a noxious substance [2].

In recent years, the removal of nitrogen compounds (NCs) has received great attention [3]. Due to the relative difficulties and costs of the catalytic removal of NCs through hydrodenitrogenation (HDN),

researchers worldwide are seeking alternative approaches to achieve deep denitrogenation of liquid hydrocarbon streams [3].

A great attention has been paid to use of adsorbents for selective removal of NCs in recent years, which can be beneficial not only for nitrogen reduction, but also for achieving the desired sulfur level in the subsequent HDS Process [4].

Batch and fixed bed absorber are the most efficient arrangement in the adsorption process [5]. It is necessary to know the adsorption capacity to design adsorption equipment. Adsorption capacity is usually expressed by an isotherm based on measured data. Also the breakthrough curves under specific operating condition must be predictable to design and operate a fixed bed adsorption process successfully [5-7]. In fixed bed granular adsorbents the most effectively used in columns where the liquid to be purified is passed through a stationary bed of the adsorbent, and to achieve a very large surface area for adsorption per unit volume. [8]. Activated carbons (AC) remain the most used adsorbents, mainly due to their superior physical and chemical properties, such as highly developed porous structure, large specific surface area, good mechanical properties, biocompatibility and chemical stability, as well as their low cost and great accessibility. They are produced from a wide variety of carbonaceous precursors   such as lignite, coal, wood.etc) [9].

Typically breakthrough is said to have occurred when the effluent concentration reaches 5 percent of the influent value.

Exhaustion of the adsorption bed is assumed to have occurred when the effluent concentration is equal to 95% of influent concentration [1].

Several studies were developed to have a good selectivity for the removal of nitrogen compounds; some of the scientist used promoted and unpromoted M_OO **3** /alumina with coker kerosene and find the difference between them [10]. The others studied the adsorption of benzene and toluene vapours using fixed bed activated carbon [9].

Denitrogenation of the liquid hydrocarbons using metal ions and metal salts had reported good results [11].

Several types of activated carbon from different sources were tested to have the best denitrogenation of the liquid hydrocarbons using batch technique [3].

Aim of the Present Work

The objective of the present study is to:

❖ Understand the adsorption mechanism of different types of nitrogen compounds on activated carbon through the evaluation of the adsorption capacity, and the adsorption isotherm curves.

❖ Study the effects of various important parameters such as the height of the bed, inlet nitrogen ions concentration, flow rate, and size of the adsorbent particles on (breakthrough curves,) of the adsorption denitrogenation process using fixed bed activated carbon techniques.

Materials and Experiments

Materials
Adsorbate:

A model diesel fuel (MDF), containing various molar concentrations of either Indole or Quinoline or pyridine, was prepared using nonane (C_9) as a solvent.

Adsorbent:

Granulated activated carbon (GAC) was used as an adsorbent in the present work. It was supplied from the Iraqi commercial markets. The physical properties were measured by the oil research and development center and were coincided with that supplied by the manufacturer. These physical properties are listed in Table (1).

Table (1) Physical properties of activated carbon

Bulk Density (kg/m^3)	0.35×10^3
Particle Density (kg/m^3)	1.8×10^3
Surface Area(m^2/kg)	680×10^3
Void Fraction supplied from	0.4
Internal Porosity	0.2

The adsorbents were first washed with distilled water and then dried in oven at 110^oC for one hour, to remove undesired moisture within particles. The GAC was sieved into three mesh sizes with geometric mean diameter of 1, 1.2, and 1.5 mm.

Experiments:

Two types of experiments were carried out:

- Batch experiments
- Fixed bed column experiments

Batch experiments:

In order to compare the adsorption selectivity, a model diesel fuel was prepared by adding 20, 40, 60, 80,100 ppm of either In dole or Quinoline or pyridine into liquid alkane (nonane (C_9)).All compounds added in MDF were purchased from Aldrich chemical co. and used without further purification. The adsorption experiments were conducted in a batch system with a magnetic stirrer at room temperature $30 \pm 1°C$, stirring time 2h , and fuel/adsorbent (AC) ratio: 20wt/wt.After adsorption ,the treated MDF was separated from the spent adsorbent by filtration and the nitrogen compounds concentration in the treated MDF were quantitatively analyzed by using 6800 UV/vis spectrophotometer ,Jenway.A series of adsorption experiments were performed to estimate and compare adsorption capacity of each of the nitrogen compounds using the following equation:

$$q_e = V/W \ (C_i - C_e) \qquad \text{.......................................} (1)$$

Where:

V: volume of solution.

W: wheight of adsorbent (AC).

The percentage adsorption is calculated as follows:

$$\% \, Adsorption = \frac{(C_i - C_e)}{C_i} * 100 \qquad \dots\dots\dots\dots\dots\dots \, (2)$$

Fixed bed column experiments:

Equipment:

The fixed bed adsorber studies were carried out in Q.V.F. glass column of 2cm I.D. and 30 cm in height. The activated carbon bed was confined in the column by fine screen with mesh size equal to 50 micron at the bottom and a glass ball packing at the top of the bed to ensure a uniform distribution of influent through the carbon bed. (250 ml) Boehner funnel was placed at the top of the absorber as a container of MDF. The temperature of the liquid in the feed tank was kept at room temperature ($\approx 30°C \pm 1$) which varied very little through the day.(Alldos,Primus .Serie) dozing pump was used to measure the influence flow rate to the adsorber.Cylindrical calibration tube (burette) of volume 50 ml and stop watch were used to check the influence flow rate to the adsorber.Sampling valves were connected at the feed tank and at the end of the adsorber.The general arrangement of fixed bed adsorber is shown in Fig. (1).
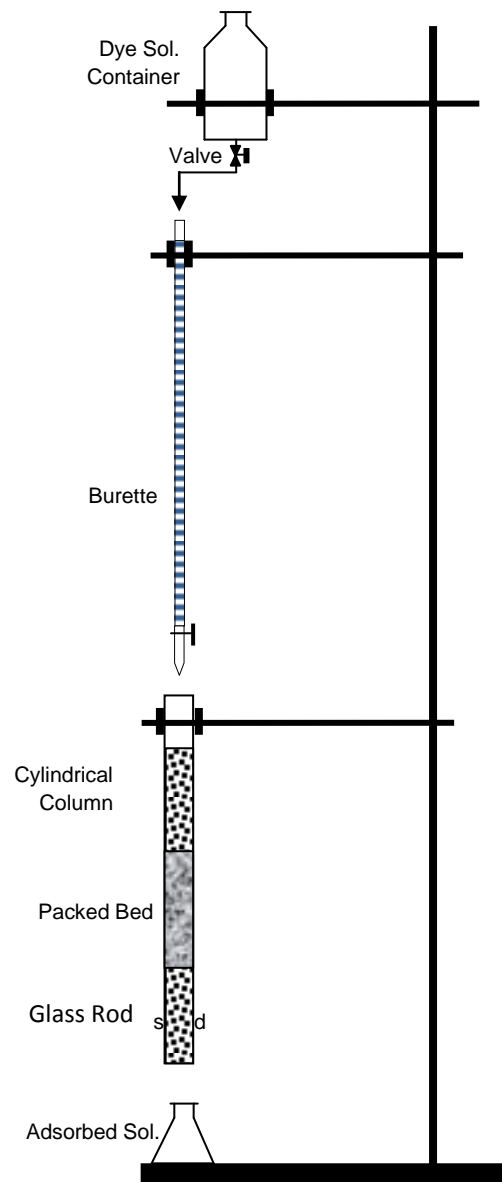
Experiments:

❖ A model diesel fuel MDF was prepared by adding (100) ppm of either of Indole or Quinoline or pyridine into liquid alkane (nonane (C_9)). The adsorber column is filled with the activated carbon with sieve opening size (1.5) mm for the desired bed height 3, 5, and10

cm under 2 cm of glass ball packing. The solution is passed to the adsorber column at room temperature (30°C ± 1)   through the (Alldos, Primus .Serie) calibrated dozing pump at the flow rate (15ml/min). fig(1).

❖ Studying the effect of the concentration by varying the concentration of either of Indole or Quinoline or pyridine with 100, 75, and50 ppm and fix the sieve opening size to 1.5 mm, the bed height to 5 cm, and the flow rate to 15ml/min the procedure above was repeated.

❖ The procedure above was repeated but, by varying the flow rate of the feed MDF to the equipment with 15, 25, and35 ml/min and fixing the sieve opening size to 1.5 mm, the bed height to 5 cm, and the concentration of either of Indole or Quinoline or pyridine with 75 ppm as moderate value.

❖ Finally the effect of the particle size of the adsorbent AC was also studied by varying the sieve opening size to 1.5, 1.2, and1 mm, and fixed the concentration of either of Indole or Quinoline or pyridine with 75 ppm as moderate value, the flow rate of the feed MDF to the equipment with 15 ml/min, and the bed height to 5 cm.

❖ The samples are taken in certain periods of time (5 min), and the concentration of nitrogen compounds in each sample is measured using   6800 UV/vis spectrophotometer Jenway. Also the experimental breakthrough curve was determined by plotting relating effluent concentration (C_e/C_o) to time (t).

Dye Sol.
Container

Valve

Burette

Cylindrical
Column

Packed Bed

Glass Rod   sand

Adsorbed Sol.

**Fig. (1) Schematic Representation of Experimental Apparatus**

Results and Discussion

Batch experiments:

It is clear from fig. (2) that the adsorption capacity increases with increasing equilibrium concentration of the nitrogen compounds in the liquid phase, which is limiting case of a very favorable isotherm irreversible adsorption, where the amount adsorbed is independent of concentration down to very low values [12], also the activated carbon has very high affinity for the nitrogen compounds and the conversion (%) shown in fig. (3) is increased in the order indole> quinoline> pyridine because indole can polymerize electrochemically or chemically to form a polymerized materials which is in good agreement with other works [13] and the conversion values of quinoline, indole, pyridine were 50,46,and42 % in the conditions of initial concentration (100)ppm,Fuel/ (AC)ratio=20wt/wt,stirring time(2h).
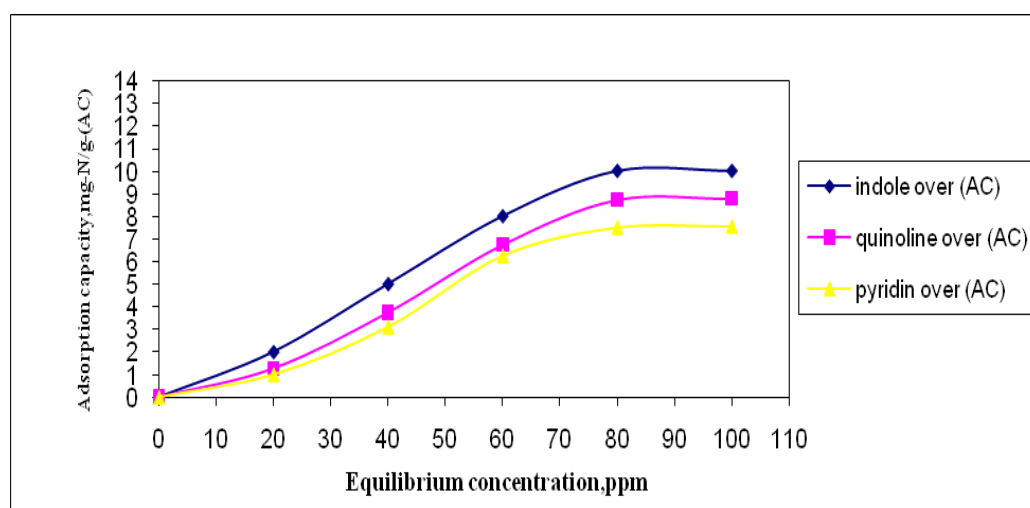
Fig. (2) Adsorption isotherm for nitrogen compounds at room temperature, stirring time (2h), fuel/AC ratio = 20wt/wt.
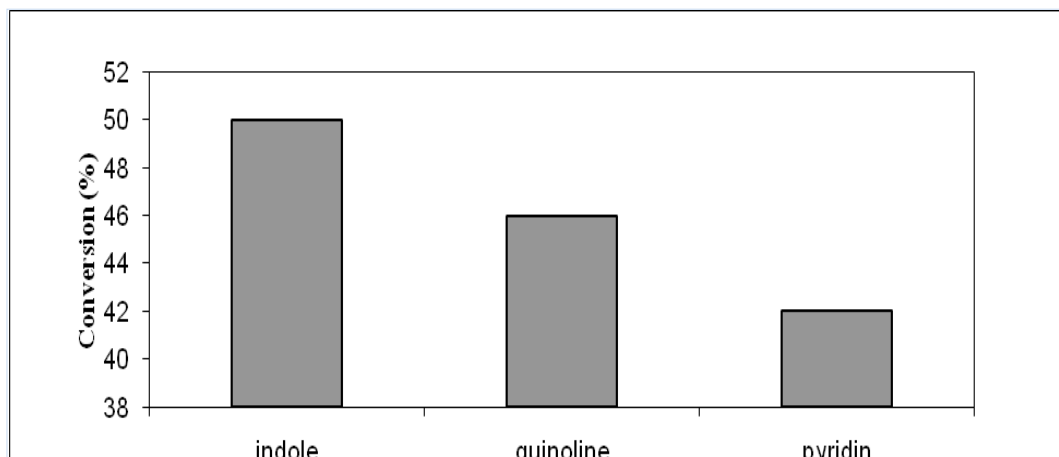
Fig. (3) Denitrogenation activities of nitrogen compounds at room temperature, stirring time (2h), fuel/AC ratio = 20wt/wt, initial concentration (Ci) = 100 ppm

## Fixed bed column experiments

Effect of Bed Height:

The bed depth is one of the major parameters in the design of fixed bed adsorption column. The effect of bed height on the breakthrough curve was studied for indole, quinoline, and pyridine respectively for adsorption onto activated carbon at constant flow rate, constant concentration, and constant particle size are presented in Figs. (4-6). These figures show that as the bed height increases the time of breakthrough point and the residence time will increase. It is clear from these figures that at smaller bed height the effluent metal ion concentration ratio increases more rapidly than at a higher bed height. Furthermore at smaller bed height the bed is saturated in less time compared with the higher bed height. Smaller bed height means lesser amount of activated carbon than for the higher one.
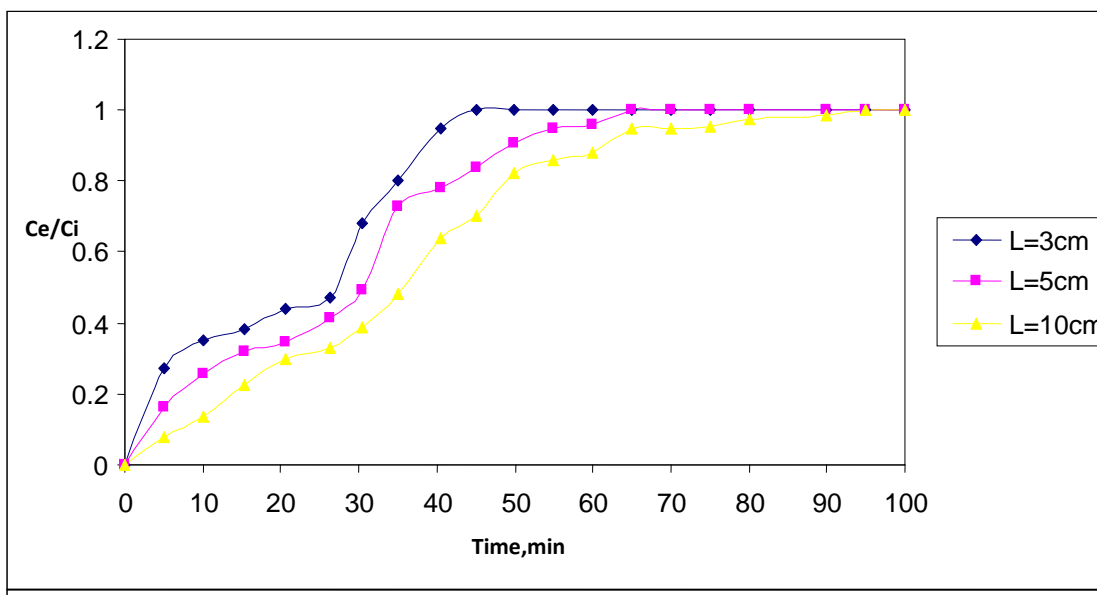
Fig.(4)The experimental breakthrough curves for adsorption of Quinoline onto activated carbon at different bed heights(L), flow rate (Q) = 15 ml/min , initial concentration(Ci)=100ppm,(AC) size=1.5mm.
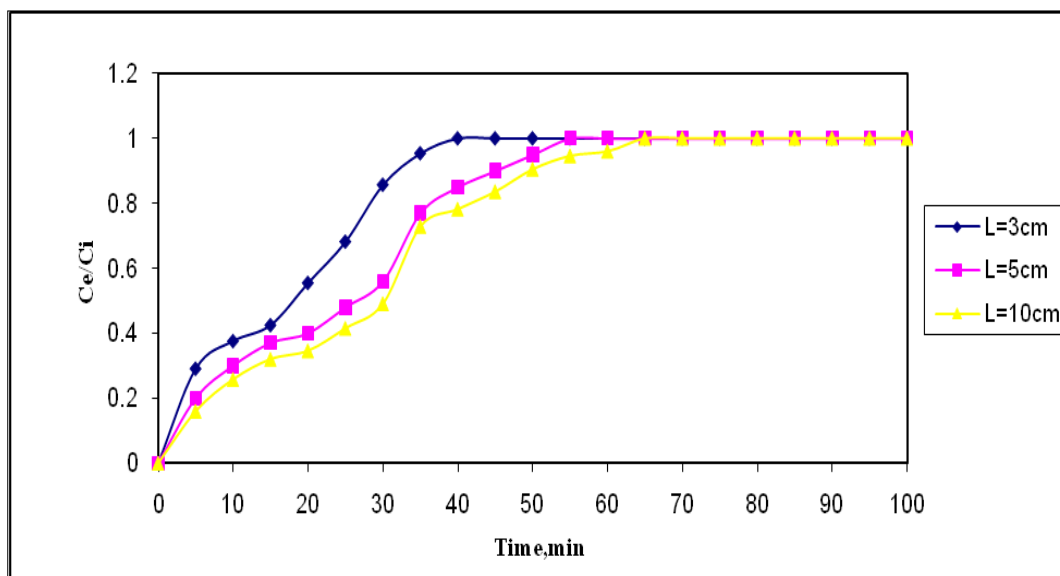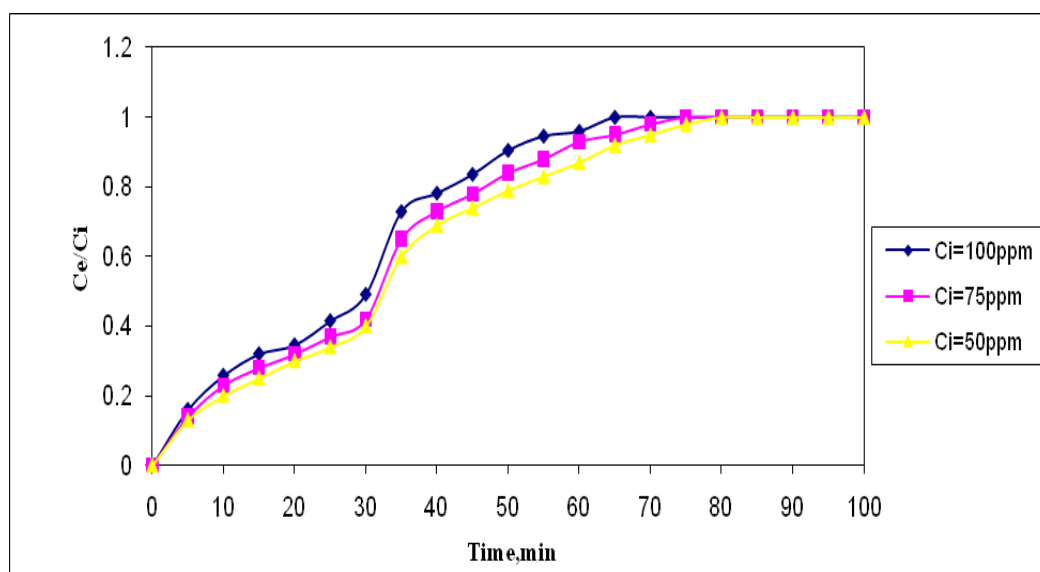

Fig. (5) The experimental breakthrough curves of indole onto activated carbon in different bed heights (L), flow rate (Q)= 15ml/min, initial concentration (Ci)= 100ppm, (AC) size= 1.5 m.m.
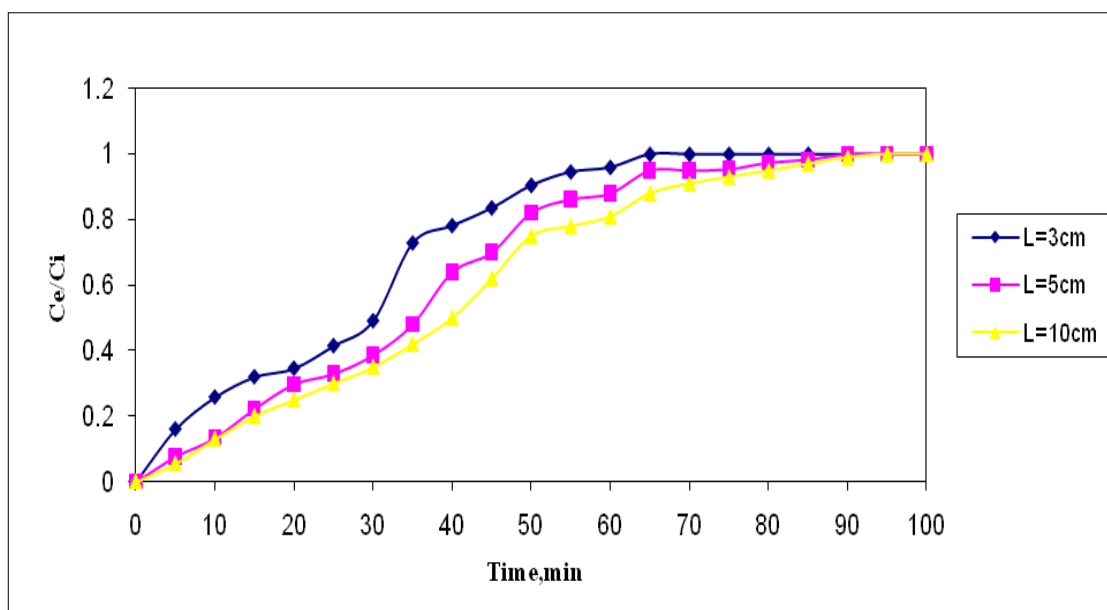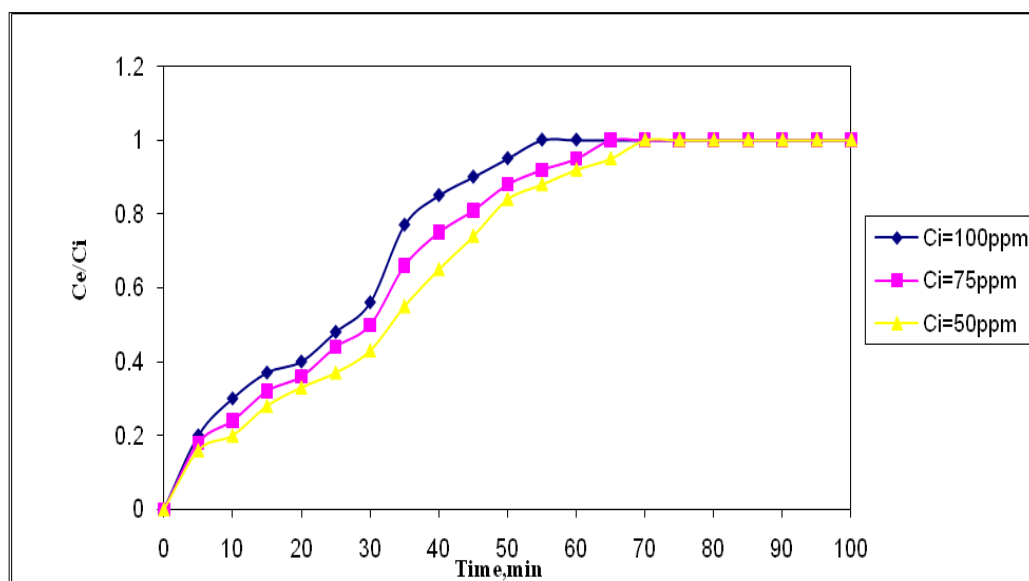
Fig. (6) The experimental breakthrough curves for adsorption of pyridine onto activated carbon at different bed heights(L), flow rate(Q)= 15ml/min, initial concentration(Ci)=100 ppm,(AC) size=1.5mm
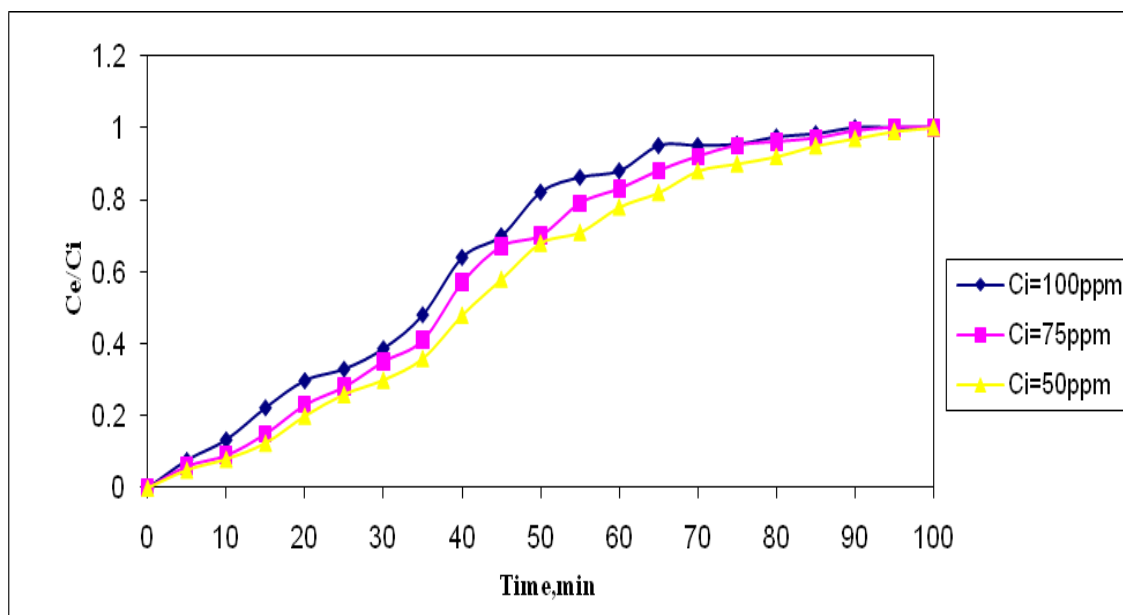
Effect of Initial Concentration:

The effect of initial nitrogen concentration on the breakthrough curves for nitrogen compounds was investigated for all the systems. The change in initial nitrogen concentration will have a significant effect on the breakthrough curves. Figs. (7-9) show the experimental breakthrough curves at different initial nitrogen concentrations at constant flow rate, constant bed height, and constant particle size of activated carbon.

Fig. (7) The experimental breakthrough curves of quinoline onto activated carbon at different initial concentration(Ci), flow rate(Q) = 15ml/min, bed heights(L)=5cm,(AC) size=1.5mm

Fig. (8) The experimental breakthrough curves of indole onto activated carbon at different initial concentration(Ci), flow rate(Q) = 15ml/min, bed heights(L)=5cm,(AC) size=1.5mm

Fig. (9) The experimental breakthrough curves of pyridin onto activated carbon at different initial concentration (Ci), flow rate(Q) = 15ml/min, bed heights(L)=5cm,(AC) size=1.5mm

Figs. (7-9) show that as the initial nitrogen compounds concentration increases the time of breakthrough point will decrease.

The high initial concentration the faster breakthrough, however the activated carbon loadings are larger at higher initial nitrogen concentration. For high initial nitrogen compounds concentration, steeper breakthrough curves are found because the equilibrium is attained faster for higher initial metal ion concentration, which would be anticipated with the basic increase in the driving force for mass transfer with increase in initial concentration. The time of breakthrough point is inversely related to the initial concentration, i.e. the time required to reach saturation decreases with increasing the inlet solute concentration. This may be explained by the fact that since

the rate of adsorption is controlled by the concentration gradient, it takes a longer time to reach equilibrium for the case of low value of initial solute concentration.

Effect of Flow Rate:

The contact time is an important variable in the design of a fixed bed adsorption column; therefore the flow rate is one of the major design parameter [14]. The effect of varying flow rate on breakthrough curve was studied for all the systems. Figs. (10-12) show the experimental breakthrough curves for quinoline, indole, and pyridine respectively obtained for different flow rates and at constant bed height, constant concentration, and constant particle size of activated carbon, in term of C_e/C_i versus time:
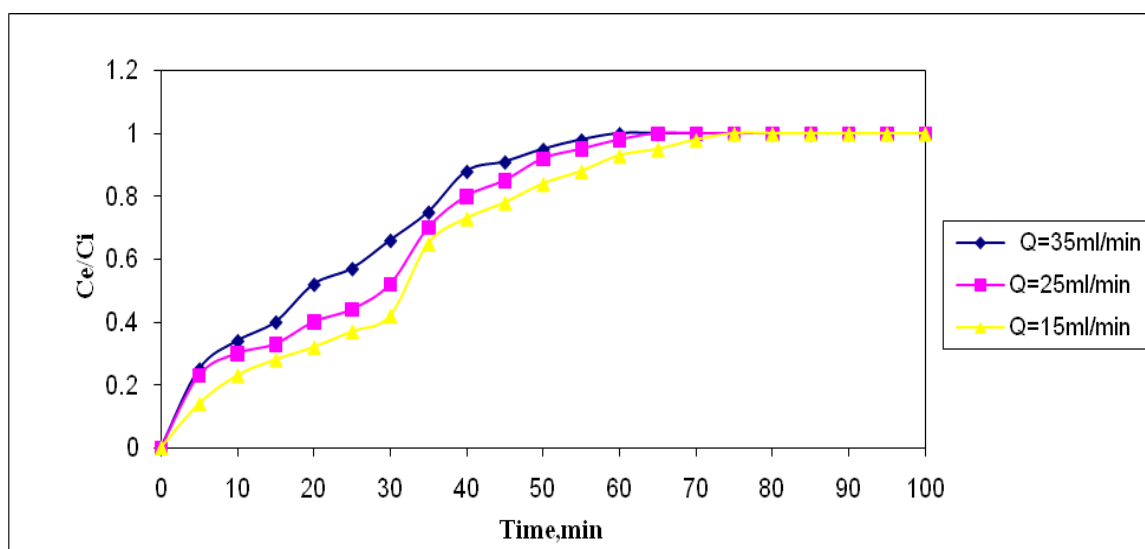
Fig. (10) The experimental breakthrough curves of quinoline onto activated carbon at different flow rate(Q), initial concentration(Ci), = 75ppm, bed heights(L)=5cm,(AC) size=1.5mm
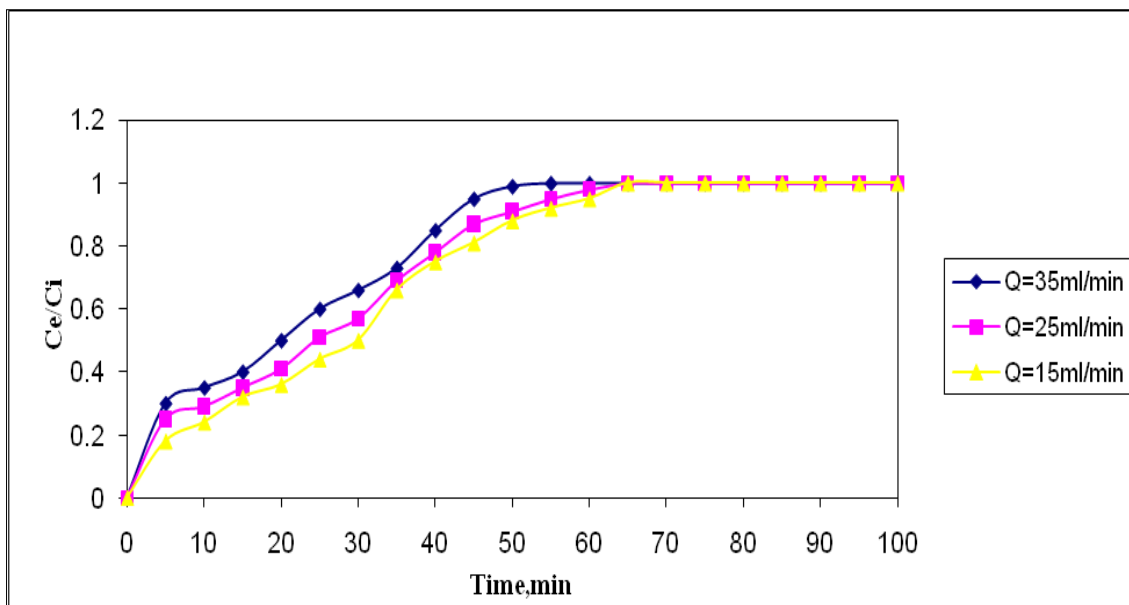
Fig. (11) The experimental breakthrough curves of indole onto activated carbon at different flow rate(Q), initial concentration(Ci) = 75ppm, bed heights(L)=5cm,(AC) size=1.5mm
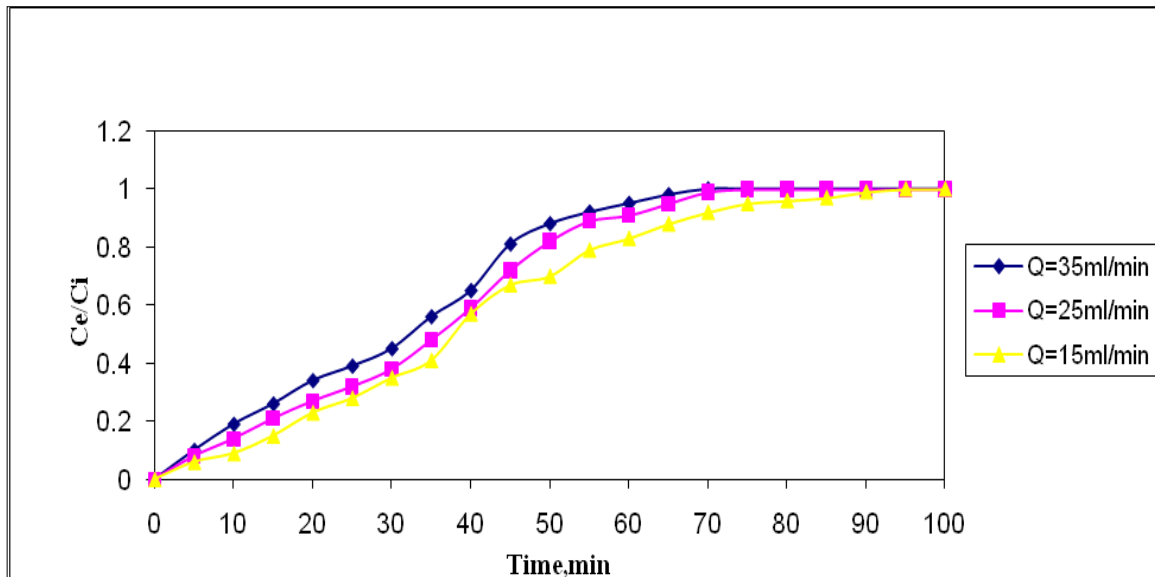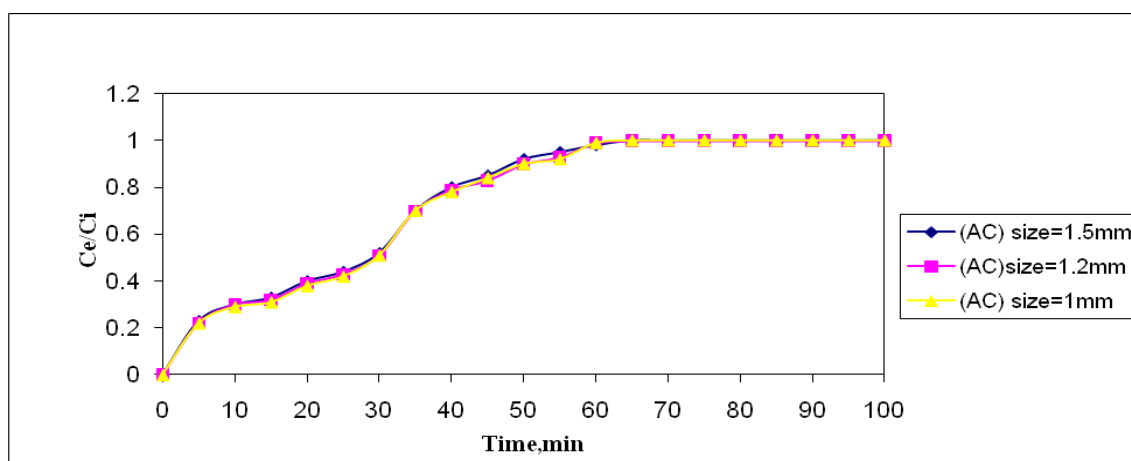

Fig. (12) The experimental breakthrough curves of pyridin onto activated carbon at different flow rate(Q), initial concentration(Ci) = 75ppm, bed heights(L)=5cm,(AC) size=1.5mm

It is clear from the above figures that as the flow rate increase the time of breakthrough point decreases. This is because the residence time of solute in the bed decreases as the flow rate increases and therefore there is not enough time for adsorption equilibrium to be reached which results in lower bed utilization and the adsorbate solution leaves the column before equilibrium. It is expected that the change in flow rate will affect the film diffusion but not the intraparticle diffusion. The higher the flow rate the smaller the film resistance to mass transfer [15,16].

Effect of Particle Diameter:

Figs. (13-15) show the experimental breakthrough curves for quinoline, indole, and pyridine respectively obtained for different particle size of activated carbon 1.5, 1.2, and1 mm and at flow rates, constant bed height, constant concentration, in term of C_e/C_i versus time:

Fig. (13) The experimental breakthrough curves of quinoline onto activated carbon at different size (AC), flow rate(Q)=25ml/min, initial concentration(Ci) = 75ppm, bed heights(L)=5cm.

Fig. (14) The experimental breakthrough curves of indole onto activated carbon at different size (AC), flow rate(Q)=25ml/min, initial concentration(Ci) = 75ppm, bed heights(L)=5cm.

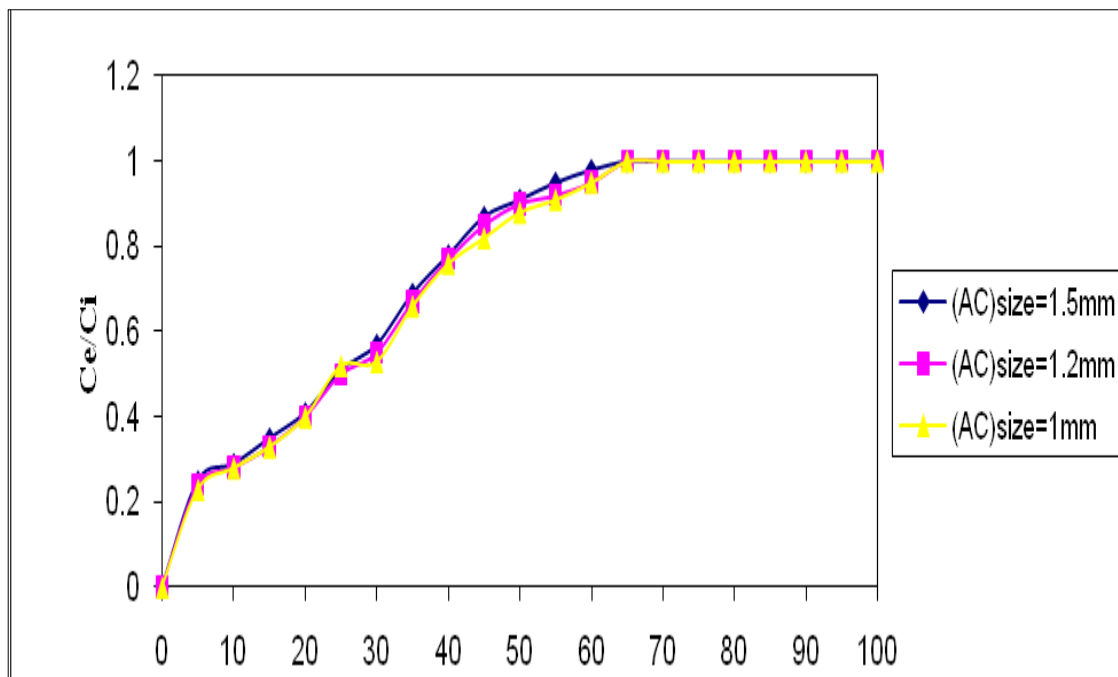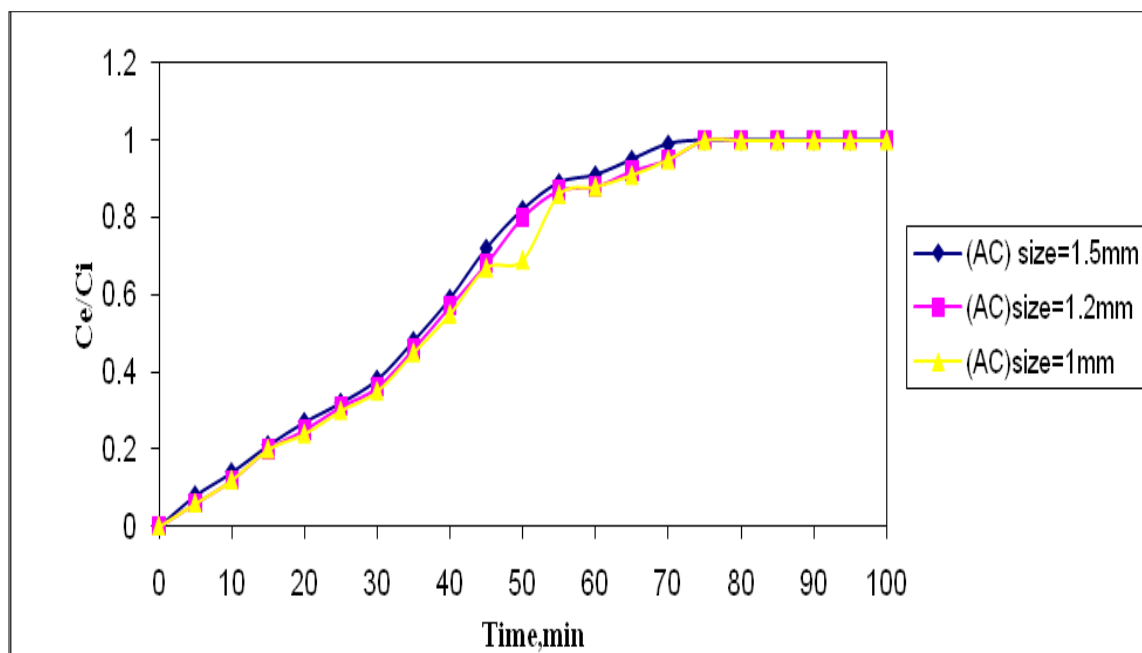**Fig. (15) The experimental breakthrough curves of pyridin onto activated carbon at different size (AC), flow rate(Q)=25ml/min, initial concentration(Ci) = 75ppm, bed heights(L)=5cm.**

It is clear from the above figures that there is no effect of varying the particle size of the activated carbon because the experimental values of the activated carbon lies in the reign of the and macrospore volume and there is no gradient in the particle size.

Also the   macrospore surface area is not a key factor for removal of the nitrogen compounds in the tested activated carbons. It is expected that the oxygen functionality of the activated carbons may play a more important role in determining the adsorption capacity for the nitrogen compounds since the adsorption capacity for nitrogen compounds increases with increase in the oxygen concentration of the activated carbons, and the type of the oxygen-functional groups may be crucial in determining their selectivity for various nitrogen compounds (Selective adsorption).

Conclusions:

In the present work the adsorption of nitrogen compounds named quinoline, indole, and pyridine onto activated carbon for single component system lead to the following conclusions:

1. The adsorption capacity increases with increasing equilibrium concentration of the nitrogen compounds in the liquid phase, which is limiting case of a very favorable isotherm irreversible adsorption.

2. The activated carbon has very high affinity for the nitrogen compounds in the order indole> quinoline> pyridine. And the conversion values of quinoline, indole, pyridine were

(50,46,and42)% in the conditions of initial concentration (100)ppm,Fuel/ (AC)ratio=20wt/wt,stirring time(2hr).

3. The time to breakthrough point decreases with:

   A. The decrease in bed height.

   B. The increase in flow rate.

   C. The increase in initial concentration of nitrogen compounds.

4. There is no effect of varying the particle size of the activated carbon because the experimental values of the activated carbon lies in the reign of the and macrospore volume and there is no gradient in the particle size.

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