Fixed-bed adsorption of furfural onto granular activated carbon prepared from sawdust

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Abstract. Furfural is a toxic aromatic aldehyde that can cause a severe environmental problem especially the wastewater drone from petroleum refinery units. In the present work, a useless by-product from local furniture manufacturing industry sawdust was used as raw material for preparation of activated carbon which is chemically activated with phosphoric acid. The effect of adsorption variable which include The effect of volumetric flow rate (13, 38, 68) ml/min, the bed depth (0.03, 0.05, 0.09) m, the particle size (0.297, 0.595, 1.19) mm and initial furfural concentration (50, 150, 250) mg/l on break through curve for fixed bed adsorption column were evaluated. A comparison was made when using commercial activated carbon and prepared activated carbon at the same operation conditions. The results obtained from experimental investigation show that in fixed bed column increasing the volumetric flow rate lead to fast removal of furfural and reducing breakthrough time. Also the breakthrough curve and breakthrough time increase with bed length and decrease volumetric flow rate. And decreasing with increasing furfural concentration and particle size. In the interval of (120) min the value of $C_t / C_0$ reach 0.911 and 0.931 for CAC and PAC ,respectively. At the best condition, which obtained at volumetric flow rate 38 ml/min, bed depth 0.5 m, particle size 0.595 mm and initial furfural concentration 250 mg/l.

1. Introduction
Petroleum refineries are confrontation pollution problems linked with the accidental losses of furfural. This forms an economical loss as well as environmental hazards. Furfural is a toxic aromatic aldehyde with the chemical formula C₄H₃OCHO. It is pale yellow or colorless oily liquid and turns into brown or red in the presence of air or light [1].

Human exposure to concentrations of 1.9-14 ppm of furfural causes headache, flushing of the eyes and tears. Furfural has been classified as a hazardous material that can damage the lungs, liver, kidneys and spleen [2]. The permissible exposure limit (PEL) for the furfural is 5 ppm [3].

Furfural has got main applications like in lube oil refining, in pharmaceuticals, and in the manufacture of phenolic resins. It is widely used in the solvent extraction processes of the petroleum refineries as a solvent extracting. It is also used as a chemical intermediate, weed killer, fungicide, and also as a flavoring agent. Sulfite pulping processes used in the pulp and paper industry are a major source of furfural contamination. Synthetic rubber plant wastewater has been found to have 1.7 g/l furfural. Leakage of furfural not only causes a pollution problem but also constitutes a sizable economic loss [4], [5].

Batch experiments are usually done to measure the effectiveness of adsorption for removing specific adsorbates as well as to determine the maximum adsorption capacity. The continuous adsorption in fixed-bed column is often desired from industrial point of view. It is simple to operate and can be
scaled-up from behavior and mass transfer aspects become peculiar beyond a particular length to diameter ratio of the column. In order to design and operate fixed-bed adsorption process successfully, the breakthrough curves under specified operating conditions must be predictable. The shape of this curve is influenced by the individual transport process in the column and in the adsorbent. Breakthrough determines bed height and the operating life span of the bed and regeneration times. Adsorption in fixed-bed columns using activated carbon has been widely used in industrial processes for the removal of contaminants from aqueous textile industry effluents, since it does not require the addition of chemical compounds in the separation process.[6]

Activated carbons are among the best adsorbents utilized for adsorption processes. Activated carbons possess high surface area per unit mass and exhibit high adsorption capacities for many adsorbates. Essentially, the structure of Activated carbons contains pores which are arranged by the International Union of Pure and Applied Chemistry (IUPAC, 1972) order into three groups: micropores (pore measure < 2nm), mesopores (pore estimate 2–50 nm) and macropores (pore estimate > 50 nm) as appeared in Fig 1 [7].

The raw materials that are classified for the preparation of activated carbon are coal and biomass previously used coal. Include anthracite, lignite, and bituminous coals. But these days have been replaced by biomass because of very high cost and a few resources, biomass which is the most used in the preparation of carbon because of the availability and low cost and also must take into account the quality of manufacturing the product [8]. The raw material sawdust was obtained as a useless by-product from a local furniture manufacturing industry, which uses for preparing activated carbon. These adsorbent materials were used for removing furfural from wastewater. The activation agents utilized in the chemical process are ordinary alkali and alkaline earth metal containing substances and some acid like KOH, NaOH, H₃PO₄, ZnCl₂, Na₃PO₄, Na₂Cl, and KMnO₄ [9]. The activation of lignocellulosic materials with H₃PO₄ has become an increasingly utilized method for the large-scale manufacture of activated carbon as a result of the utilized of this reagent has some environmental advantages, for example, simple recovery, low energy cost, and high carbon yield. H₃PO₄ plays two roles throughout the preparation of activated carbon i) H₃PO₄ acts as an acid catalyst to advance bond cleavage, hydrolysis, dehydration, and condensation, joined by cross-linking reactions between phosphoric acid and biopolymers; ii) H₃PO₄ may work as a template because the volume possessed by phosphoric acid in the inside of the activated precursor is correspondent with the micropore volume of the activated carbon obtained. Experimental conditions for the preparation of activated carbon such acid concentration, time of activation, impregnation ratio, carbonization temperature and
heating rate. All these conditions affect the physical and chemical properties of the activated carbon by activating phosphoric acid [10]. The methods of activation commonly employed can broadly be divided into two main types: thermal (or physical) activation and chemical activation. Thermal activation involves primary carbonization (below 700 °C) followed by controlled gasification under the action of oxidizing gases at high temperature (up to 1100 °C). In chemical activation the precursor is mixed with a chemical restricting the formation of tars (e.g. ZnCl₂, H₃PO₄, etc.), after kneading carbonized and washed to produce the final activated carbon. The chemical incorporated into the interior of the precursor particles reacts with the thermal decomposition products reducing the evolution of volatiles and inhibits the shrinkage of the particles. In this way, the conversion of the precursor to carbon is high, and once the chemical is eliminated after the heat treatment, a large internal porosity is formed [6].

Phosphoric acid activation only involves a single heat treatment step and is achieved at lower temperatures (400–600 °C), higher yields are obtained and most of the phosphoric acid can be recovered after the process is completed. The chemical activation of lignocellulosic materials with phosphoric acid has been extensively investigated from the development of porosity and mechanism of degradation from the precursor point of view [11][12].

The time for breakthrough appearance and the shape of the breakthrough curve are very important characteristics. Adsorption fixed-bed column and the bed depth and the flow rate are the significant design parameter and have a large effect on the saturation time. Generally, the obtained breakthrough curve has a flat profile compared with the favorable adsorption isotherm of system [13]. This means that the favorable profiles form a sharp mass transfer zone in column and the concentration gradient in the both systems is different which resulting that the profile of batch condition is favorable. As a result, the stirring phenomena in batch process has a significant effect on the boundary layer in the surface of adsorbent, the mass transfer resistance would reduce leading to higher capacity of adsorption [14] [13].

2. Experimental

2.1 Adsorbate

Furfural (C₅H₄O₂), molecular weight (96.06 gm/mol) was used as an adsorbate; it has synonyms of (2-furaldehyde, Furyl and 2 Furfyl methanol) as shown in Fig 2. It is production by mixed plant raw material (i.e corn seed hulls, cane bagasso, and residues of olive extraction) with dilute sulfuric acid the formed furfural is acidic hydrolyaztion, recovered by steam distillation and fractionation with (98-99)% purity of furfural [15].

![Figure 2. Molecular structure of furfural.](image)

2.2 Preparation of Activated Carbon

The sawdust was sieved in the size ranges (2.4-4.8) mm, washed with distilled water to remove impurities. After that, the sawdust was individually filtered and placed in an electrical oven at 100-110°C. Four hundred gm of dry sawdust was activated by mixing with 50% (v/v) phosphoric acid and left the mixture at room temperature overnight. The second steps were pyrolysis of the filtered sample. The reactor was closed from one side and had a hole in it to allow nitrogen gas to enter. The reactor (20 cm width x 29 cm length x 16.5 cm height) was putted in the electrical oven at 500°C under the influence of nitrogen flow (100 ml/min) for 2 hrs as shown in Figure 3. The activated carbon thus
produced was then cooled, washed with distilled water to remove the excess acid and organic until the PH of solution reach about 6.5 to 7. Then the sample was dried in the oven at 110°C for 4 hr. After that, the sample was weighted to calculate the yield of activated carbon by the following eqn.

\[ \text{yield(\%)} = \frac{w_f}{w_o} \times 100 \]

Where \( w_f \) and \( w_o \) are the weight of activated carbon and dried sawdust respectively.

2.3 Experimental set-up
Fixed bed adsorption experiment two Perspex column with inner diameter (0.0125 m) and length (0.5 m) of each one were used in parallel manner which filled with commercial activated carbon and prepared activated carbon bed individual respectively which can be operated at same time by distribution the feeding of solution by gravity from upper glass tank (5 liters) with adjustable valve through flow meter type (Rotameter GER). The level of solution in the feeding tank was kept constant by continuous feeding solution from lower tank (10 liters) using centrifugal pump and an overflow valve for the excess solution from upper tank to lower one as shown in Figure 4.

Each column containing one type of adsorbent and was fixed by means of glass ball and fine plastic mesh at bottom to prevent the escape of adsorbent and at the top to provide uniform distribution of solution. Distilled water was fed initially to column in order to wet the adsorbent[16] [17]. Mass of adsorbent was weighted by means of electronic balance type (Mettler, AI 163, SWISS) after determined the required bed hight. Samplings were collected from the bottom of the column and analyzed by using UV Visible Spectrophotometer.
3. Results and discussion

3.1 Characterizations of Activated Carbon

The important properties of activated carbon are surface area and pore volume. The table 1 shows the characterization of both types of activated carbon. From this table the surface area was 793 m$^2$/g and 800 m$^2$/g For prepared activated carbon and commercial respectively.

The table 1 shows the precise analysis of the ash content and moisture content and the apparent density of both activated carbon in the best conditions.

| Characteristics        | P A C  | C A C  |
|------------------------|--------|--------|
| Surface area, m$^2$/g  | 793    | 800    |
| Pore volume, cm$^3$/g  | 0.565  | 0.676  |
| Ash content, %         | 3.968  | 1.51   |
| Moisture content, %    | 4.9    | 1.5    |
| Bulk density, g/ml     | 0.311  | 0.687  |

3.1.1 The Surface Area of Activated Carbon

The surface area of the adsorbent is the most important factor in determining the adsorption capacity. Commercial activated carbon which has surface area of 800 m$^2$/g. The prepared activated carbon has surface area of 793 m$^2$/g, when activated with phosphoric acid. This increase in surface area may be attributed to the C-H$_2$O reaction to remove some of carbon atoms and formation of micro pores on the prepared activated carbon surface.

3.1.2 Surface Morphology

The surface morphology of prepared activated carbon and commercial activated carbon using physical-chemical process were identified using SEM. The results can be seen in the following figure 5 and 6.

![Figure 5. SEM of prepared Activated Carbon](image)

![Figure 6. SEM of commercial Activated Carbon](image)

Based on the figure above it can see the difference of surface morphology of prepared activated carbon and commercial activated carbon. It can be found that surface of commercial activated carbon, smooth, plane and there are slight pores on it. While prepared activated carbon contain some cavities.
which are resulted from the activation using H$_3$PO$_4$ can make more cavities and dissolve impurities so the pores more established and adsorption process become maximum. These cavities provide channels for the adsorption molecules to access the micropores and mesopores inside a carbon particle [18][19][20].

3.1.3 FTIR spectroscopy

FTIR test exhibit better information on the quality of functional groups available into the surface of PAC and CAC. Abundant of functional groups have been definite an effective adsorbed site for binding a furfural. IR spectra of PAC and CAC were shown in Figures 7 and 8. From Figure 7 prepared activated carbon IR spectrum exhibit several intense bands. The intense band between 3940 – 3800 cm$^{-1}$ attributed to free (-OH) group. The band about 3510 - 3410 was imputed to the surface hydroxyl groups (-OH) elongation vibration bonding of polymeric compounds such as carboxylic acids, alcohols and phenols due to inter molecular bonding. The bands at 2927 and 2897 can be assigned to the surface C-H stretches of symmetric and asymmetric methylene groups and to chelated H-bridges. The bands at 1690 -1580 were attributed to C=O stretching vibration of carboxyl in carboxylic acid , carbonyl in ketone ,carbonyl group in quinone ,aromatic ring and amino stretching respectively. The bands at 1520 -1420 can be assigned to aromatic compound C=C, and C-O-C respectively. The intensity of band 1380 -1210 was attributed to C-O groups in carboxylic acid and ester. The band 865 – 490 in FTIR spectra refers to C-H bending. From the above can be observed that functional groups of phenolic contain oxygenated surface causes acidic surface properties while functional groups of carbonyl, quinone causes basicity surface properties which are removal the furfural from wastewater due to the different in the charges between them. This agrees with [21][22].

![Figure 7. FTIR of Prepared Activated Carbon](image-url)
3.2 Column Experiments

3.2.1 Effect of volumetric flow rate
In order to study the influence of volumetric flow rate on the breakthrough curves of furfural. Three experiment were carried out at different wastewater flow rate (13, 38, 68) (ml/min) and at given initial furfural concentration (C˳ = 250) mg/l, bed depth (d = 0.05 m), temperature 20 °C, PH=7 and particle size (0.595) mm. The break through curve were shown in Fig (9&10). As shown in Fig (9&10) in the interval of (120 min) the value of C⁄ t C˳ for CAC reach 0.63, 0.91 and 1.11 when the flow rate was 13, 38 and 68 ml/min respectively, also the value of C⁄ t C˳ for PAC reach 0.77, 0.93 and 1.14 when the flow rate was 13, 38 and 68 ml/min respectively.

Through the figure we observe that when the volumetric flow is high we will need less contact time to reach the equilibrium as increasing the volumetric flow leads to compression or saturation reduction of the surface film diffusion. Therefor the decreasing resistance to mass transfer and increasing the mass transfer. As the volumetric flow drops, will increase time for saturation [23] [24].

3.2.2 Effect of bed depth:
With the purpose of studying the influence of depth of bed on the breakthrough curve of furfural. Three experiments were carried out at different bed depth (0.03, 0.05, 0.09) m respectively, while other parameters are constant, initial furfural concentration (250) mg/l, temperature 20 °C, PH=7, wastewater flow rate (38) ml/min and particle size (0.595) mm. The break through curve were shown in Fig (11&12). As shown in Fig (11&12) in the interval of (60 min) the value of C⁄ t C˳ for CAC reach 0.92, 0.75 and 0.49 when the bed depth was 0.03,0.05 and 0.09 m respectively, also the value of C⁄ t C˳ for PAC reach 0.87,0.75 and 0.69 when the bed depth was 0.03, 0.05 and 0.09 m respectively.
Figure 9. Break through curves for furfural adsorption onto CAC at different wastewater flow rate (Initial furfural concentration \(C_{\text{r}}=250\) mg/l, bed depth \(d = 0.05\) m, temperature 20\(^\circ\) C, pH=7 and particle size \((0.595)\) mm).

Figure 10. Break through curves for furfural adsorption onto PAC at different wastewater flow rate (Initial furfural concentration \(C_{\text{r}}=250\) mg/l, bed depth \(d = 0.05\) m, temperature 20\(^\circ\) C, pH=7 and particle size \((0.595)\) mm).

Figure 11. Break through curves for furfural adsorption onto CAC at different bed depth of activated carbon (Initial furfural concentration \(250\) mg/l, temperature 20\(^\circ\) C, pH=7, wastewater flow rate \((38)\) ml/min and particle size \((0.595)\) mm).

Figure 12. Break through curves for furfural adsorption onto PAC at different bed depth of activated carbon (Initial furfural concentration \(250\) mg/l, temperature 20\(^\circ\) C, pH=7, wastewater flow rate \((38)\) ml/min and particle size \((0.595)\) mm).

Fig (11) and Fig(12), showed that the effluent concentration of furfural rose first gradually and then sharply before approaching the exhaustion point denoting the saturation of the bed and showed the increasing the depth lead to the increasing break through time.
When the total of the binding sites is greater, which resulting in increasing the adsorption area of adsorbent. In this case, an adsorbate has enough time to diffuse over pores of an adsorbent [25]. These results are in agreed with many previous researchers [13] [26] were used different length bed to study the breakthrough curves of adsorption on granular activated carbon.

3.2.3 Effect of particle size:
With the purpose of studying the influence of particle size on the breakthrough curve of furfural adsorption, three Experiments were carried out at different particle size (0.297, 0.595, 1.19) mm. While other parameters are kept constant, initial furfural concentration (250 mg/L), wastewater flow rate (38 ml/min), temperature 20$^\circ$C, PH=7 and bed depth (0.05 m).

The breakthrough curves in Figures (13&14) were shown the interval of (90 min) the value of C$_t$/C$_o$ for CAC reach 0.89, 0.93 and 0.22 when the particle size was 1.19, 0.575 and 0.297mm respectively, also the value of C$_t$/C$_o$ for PAC reach 0.91, 0.93 and 0.78 when the particle size was 1.19, 0.575 and 0.297mm respectively.

These figures (13&14) showed that when the size of the particles decreases, the weight of the activated carbon increases with fixed bed depth so the surface area available for adsorption of the furfural particles is very high (i.e providing more space for the furfural molecules to occupy the new surface area, therefore, it will increase the time of saturation [27].

![Figure 13. Break through curves for furfural adsorption onto PAC at different particle size of activated carbon (Initial furfural concentration (250 mg/L), wastewater flow rate (38 ml/min), temperature 20$^\circ$C, pH=7 and bed depth (0.05 m)).](image)

![Figure 14. Break through curves for furfural adsorption onto CAC at different particle size of activated carbon (Initial furfural concentration (250 mg/L), wastewater flow rate (38 ml/min), temperature 20$^\circ$C, pH=7 and bed depth (0.05 m)).](image)

3.2.4 Effect of initial furfural concentration.
The effect of initial furfural concentration on the adsorption was investigated by varying the concentration in the range of 50, 150, and 250 mg/L. While other parameters are kept constant wastewater flow rate (38 ml/min), temperature 20$^\circ$C, pH=7, Particle size =0.575 mm and bed depth (0.05 m). The break through curves in Figures (15&16) were shown in the interval of (90 min) the value of C$_t$/C$_o$ for CAC reach 0.89, 0.79 and 0.69 when the initial concentration was 250, 150 and 50.
mg / L respectively, also the value of $C_t/C_0$ for PAC reach 0.93, 0.8 and 0.73 when the initial concentration was 250, 150 and 50 mg / L respectively.

These figures (15&16) showed that when increasing concentration the breakthrough curves time decreases and the breakthrough curves become more acute while wider curves are obtained at a lower concentration value. When the concentration increases from 50 mg / L to 250 mg / L, activated carbon surface sites obtained by the adsorption will become filled and the filling will be saturated faster than if the concentration is low [28].

![Figure 15. Break through curves for furfural adsorption onto PAC at different initial concentration of activated carbon (Wastewater flow rate (38 ml/min), temperature 20° C, pH=7, Particle size =0.575 mm and bed depth (0.05 m))](image1)

![Figure 16. Break through curves for furfural adsorption onto CAC at different initial concentration of activated carbon (Wastewater flow rate (38 ml/min), temperature 20° C, pH=7, Particle size =0.575 mm and bed depth (0.05 m))](image2)

4. **Conclusion**

The obtained result appears that the prepared activated carbon from sawdust which chemically activated by $\text{H}_3\text{PO}_4$ is an appropriate and an effective adsorbed material for removal furfural from refinery wastewater using fixed-bed adsorption column. Prepared activated carbon with BET surface area of 793 m$^2$/g and total pore volume of 0.567 m$^3$/g. Yield of PAC 44% was obtained at optimum condition at temperature 500 °C under the influence of nitrogen flow (100 ml / min) for 2 h and 0.5 impregnation ratio. The fixed-bed adsorption system was found to perform better with lower furfural inlet concentration, lower feed flow rate and higher activated carbon bed height. In fixed bed column increasing the volumetric flow rate lead to fast removal of furfural and reducing breakthrough time. Also the breakthrough curve and breakthrough time increase with bed length and decrease volumetric flow rate. And decreasing with increasing furfural concentration and particle size. In the interval of (120) min the value of $C_t/C_0$ reach 0.911 and 0.931 for CAC and PAC, respectively. At the best condition, which obtained at volumetric flow rate 38 ml / min, bed depth 0.5 m, particle size 0.595 mm and initial furfural concentration 250 mg / l.
5. **Reference**

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