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Adsorption of Furfural from Aqueous Solution onto Activated Carbon: Kinetic, Equilibrium and Thermodynamic Study

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Abstract: The present study aims to evaluate the influence of various experimental parameters viz. initial pH (pH_0), adsorbent dose, contact time, initial concentration and temperature on the adsorptive removal of furfural from aqueous solution by commercial grade activated carbon (ACC). Optimum conditions for furfural removal were found to be $pH_0 \approx 5.9$, adsorbent dose $\approx$ 10 g/l of solution and equilibrium time $\approx$ 6.0 h. The adsorption followed pseudo-second-order kinetics. The effective diffusion coefficient of furfural was of the order of 10^{-13} m^2/s. Furfural adsorption onto ACC was found to be best represented by the Redlich-Peterson isotherm. A decrease in the temperature of the operation favorably influenced the adsorption of furfural onto ACC. The positive values of the change in entropy (ΔS^0); and the negatived value of heat of adsorption (ΔH^0) and change in Gibbs free energy (ΔG^0) indicated feasible, exothermic, and spontaneous nature of furfural adsorption onto ACC.

Keywords: Furfurals, activated carbon, adsorption kinetics, isotherms, adsorption thermodynamics

INTRODUCTION

Furfural or furan-2-caraldehyde (Synonyms: 2-furaldehyde, furan, 2-formylfuran etc.; Chemical formula: $C_5H_4O_2$; Molecular weight: 96.09; Physical state: oily

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liquid; Appearance: colorless, when freshly distilled, darkens in contact with air; Odor: pungent aromatic; Melting Point: −36.5°C; Boiling point: 162°C; Relative vapor density (air = 1): 3.31; Relative density (water = 1): 1.16; Solubility in water, g/100 ml at 20°C: 8.3; Vapour pressure, kPa at 20°C: 0.144; Flash point: 60°C; Auto-ignition temperature: 315°C (1)) is a colorless, readily volatile oily liquid, with a pungent aromatic odor.

Furfural is produced from agro-industrial wastes and residues containing carbohydrates known as pentosans. It also gets produced as a by-product in the production and storage of fruit juices, wines, and medical solutions. Furfural has been identified in many foods, viz. fruits, vegetables, bread, and beverages such as cognac, rum, malt whiskey, port wine, and coffee (2). Furfural is an irritant to the skin, mucous membranes, and the respiratory track. Furfural may enter the body by respiratory and/or percutaneous route (3). Concentration of 1.9 to 14 ppm produces symptoms of irritation in exposed persons.

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 extractant. It is also used as a chemical intermediate, weed killer, fungicide, and also as a flavoring agent (4, 5). Sulfite pulping processes used in the pulp and paper industry are a major source of furfural contamination (6, 7). Synthetic rubber plant wastewater has been found to have 1.7 g/l furfural (8). Leakage of furfural not only causes a pollution problem but also constitutes a sizable economic loss.

Biological method, adsorption, solvent extraction, etc. are the commonly employed techniques for furfural removal from aqueous streams. Difficulty of solvent recovery and solvent solubility in the water streams are the major constraints for the solvent extraction process. Biological degradation of furfural, including both the aerobic and the anaerobic process, has been used by many researchers (9–11). However, these processes are costly and cannot be used by small industries to treat furfural-laden wastewater. Borghei and Hosseini (12) investigated the degradation of furfural in aqueous solution by photooxidation technology using UV, UV/H_2O_2, $UV/H_2O_2/O_2$, $UV/H_2O_2/Fe^{2+}$, $UV/O_2/Fe^{2+}$, O_3, UV/O_3 process, and also oxidation by sodium hypochlorite in a lab-scale batch photo-reactor. Adsorption as a wastewater treatment process has aroused considerable interest during recent years. Amberlite polymeric adsorbents, XAD-4 and XAD-7, have been used for the removal of furfural from pretreated and hydrolyzed plant biomass (13–15). Activated carbons are widely used as adsorbents for the treatment of polluted water or wastewater. Commonly, most commercially available activated carbons have good porosity and are of high surface area, and consequently they have high efficiency for the adsorption of various types of compounds. In our previous study (16), we used low-cost bagasse fly ash for adsorptive removal of furfural from aqueous solution. Review of literature shows that the adsorption data for removal of furfural from aqueous solution onto activated carbon are non-existent. The aim of the present work is, therefore, to explore the possibility of utilizing commercial grade activated carbon (ACC) for the adsorptive removal of furfural from aqueous solution.

MATERIALS AND METHODS

Adsorbent and its Characterization

Coconut-based ACC was supplied by ZeoTech Adsorbents Pvt. Ltd., New Delhi, India. It was used as procured, except for the removal of very fine size particles by sieving. Detailed physico-chemical characteristics of the ACC have already been presented elsewhere (17). The physico-chemical characterization of ACC was performed using standard procedures. Proximate analysis and chemical analysis of the ACC were carried out as per IS 1350: 1984 and IS 355: 1984, respectively (18, 19). Bulk density was determined using MAC bulk density meter whereas particle size analysis was done using standard sieves. Carbon, hydrogen, and nitrogen (CHN) analysis of ACC was done using Perkin Elmer CHN elemental analyser. The structure of ACC was studied using X-ray diffractograms (XRDs) obtained from an X-ray diffractometer (Bruker AXS, Diffractometer D8, Germany). Textural characteristics of the ACC were determined by nitrogen adsorption at 77.15 K using an automatic Micromeritics ASAP-2010 volumetric sorption analyzer. The Brunauer-Emmett-Teller (BET) surface area, micropore volume, and micropore surface area of the activated carbons were determined using BET method (20), using the software available with the instrument. The Barrett-Joyner-Halenda (BJH) method (21) was used to calculate the pore size distribution.

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Adsorbate

Furfural was supplied by s.d. Fine Chemicals Ltd, India. The structure of furfural is illustrated in Fig. 1. The stock solution (1000 mg/l) was prepared by dissolving an accurate amount of compound in the distilled water. Experimental solutions of the desired concentrations were obtained by successive dilutions with distilled water.

Analytical Measurements

The furfural in the aqueous solution was analyzed by using UV-spectrophotometer (Perkin Elmer Lambda 35, Schimadzu, Japan). A standard solution of the furfural was scanned to determine the wavelength (λ_{max}) corresponding to maximum absorbance. The wavelength corresponding to maximum absorbance was 275 nm. By using this wavelength a standard graph of absorbance versus concentration of furfural was prepared (not shown here). This graph

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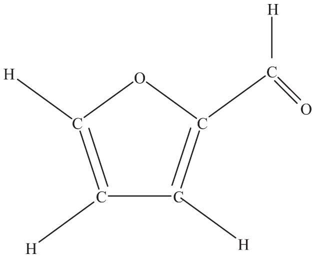

Figure 1. Molecular structure of furfural.

showed a linear variation up to 10 mg/l concentration. Therefore, the samples with higher concentration of furfural (> 10 mg/l) were diluted with distilled water, whenever necessary, to make the concentration less than 10 mg/l, for the accurate determination of the furfural concentration.

Batch Experimental Program

Batch adsorption tests were performed to study the effect of parameters like initial pH (pH_0), adsorbent dose (m), contact time (t), initial concentration (C_0), and temperature (T) on the adsorptive removal of furfural from aqueous solution by ACC. For each experimental run, 100 ml of furfural solution of known C_0, pH_0, and a known amount of the adsorbent were taken in a 500 ml stoppered conical flask. This mixture was agitated in a temperature-controlled orbital shaker at a constant speed of 150 rpm at 303 ± 1 K. Samples were withdrawn at appropriate time intervals, centrifuged (Research Centrifuge, Remi scientific works, Mumbai) at 8000 rpm for 10 min, and analyzed for the residual furfural concentration. The effect of pH_0 on furfural removal was studied over a pH_0 range of 2 to 12. pH_0 was adjusted by the addition of 0.1 N H_2SO_4 or 0.1 N NaOH. For the optimum dose of adsorbent per liter of aqueous solution, a 100 ml furfural solution was contacted with different amounts of ACC till equilibrium was attained. The kinetics of adsorption was determined by analyzing adsorptive uptake of the furfural from the furfural solutions of different initial concentrations at different time intervals. For adsorption isotherms, furfural solutions of different concentrations ($C_o = 50-1000$ mg/l) were agitated with the known amount of adsorbent till the equilibrium was achieved. The effect of temperature on the sorption characteristics was investigated by determining the adsorption isotherms at 293, 303, 313, and 323 K. Blank experimental runs, with only the adsorbent in 100 ml of distilled water, were conducted simultaneously at similar conditions to account for any adsorbate leached by the adsorbents and adsorbed by glass containers. Also, the blank aqueous solution of furfural without adding adsorbent dose was agitated to check the stability of furfural over a time period of 6.0 h. It is found that the furfural is stable in the solution, no change in concentration was observed during the time.

Adsorption Kinetic Theory

Pseudo-First-Order- and Pseudo-Second-Order-Model

The sorption of furfural molecules from liquid phase to a solid phase can be considered as a reversible process with equilibrium being established between the solution and the solid phase. Assuming a non-dissociating molecular adsorption of furfural molecules on ACC particles, the sorption phenomenon can be described as the diffusion controlled process.

$$A + S \underset{K_D}{\overset{k_A}{\rightleftharpoons}} A\,.\,S \tag{1}$$

where, A is the adsorbate and S is the active site on the adsorbent, and $A\,.\,S$ is the activated complex. k_A and k_D are the adsorption and desorption rate constants, respectively. Using first order kinetics it can be shown that with no adsorbate initially present on the adsorbent (i.e. $C_{AS0} = 0$ at $t = 0$), the uptake of the adsorbate by the adsorbent at any instant t is given as (22)

$$q_t = q_e[1 - \exp(-k_f t)] \tag{2}$$

where, $q_e =$ amount of the adsorbate adsorbed on the adsorbent under equilibrium condition,

$k_f = (k_A C_S + k_D)$ is the pseudo-first order rate constant
$C_S =$ adsorbent concentration in the solution

The pseudo-second-order model is represented as (23):

$$q_t = \frac{t k_S q_e^2}{1 + t k_S q_e} \tag{3}$$

The initial sorption rate, h (mg/g min), at $t \rightarrow 0$ is defined as

$$h = k_S q_e^2 \tag{4}$$

Intra-particle Diffusion Study

The possibility of intra-particle diffusion was explored by using the intra-particle diffusion model (24).

$$q_t = k_{id} t^{1/2} + I \tag{5}$$

where, k_{id} is the intra-particle diffusion rate constant, and values of I give an idea about the thickness of the boundary layer.

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Determination of Diffusivity

Kinetic data could be treated by models given by Boyd et al. (25) which is valid under the experimental conditions used. Applying Vermeulen's approximation (26) to the solution of the simultaneous set of differential and algebric equations (27) leads to calculation of effective particle diffusivity by the following eq.:

$$\ln\left[\frac{1}{(1 - F^2(t))}\right] = \frac{\pi^2 D_e t}{R_a^2} \tag{6}$$

where $F(t) = q_t/q_e$ is the fractional attainment of equilibrium at time t, D_e is the effective diffusion coefficient of adsorbates in the adsorbent phase (m^2/s), R_a is radius of the adsorbent particle assumed to be spherical (m), and t is the time (min). Thus, the slope of the plot of $\ln\lfloor 1/(1 - F^2(t))\rfloor$ versus t gives D_e.

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RESULTS AND DISCUSSION

Characterization of Adsorbent

The particle sizes of ACC were: <90 μm (0.28%), 90–180 μm (0.05%), 180–250 μm (0.03%), 250–500 μm (0.47%), 500–1000 μm (3.86%), 1000–1700 μm (19.55%), 1700–3350 μm (71.29%), 3350–4000 μm (3.94%) and > 4000 μm (0.53%). The average particle size was 1.671 mm. Proximate analysis showed the presence of 2.24% moisture, 2.70% volatile matter, 54.25% ash and 40.81% fixed carbon in ACC. Chemical analysis of the ash of ACC showed the presence of mineral oxides such as SiO_2 (0.41%), Al_2O_3 and Fe_2O_3 (5.45%), CaO (1.75%), and MgO (4.5%). Bulk density and the heating value of ACC were determined as 599.32 kg/m^3 and 18.81 MJ/kg, respectively. CHN analysis showed 41.35% carbon, 15.75% hydrogen, 1.54% nitrogen and rest others. Due to its high carbon content, ACC can be good adsorbent. The d-spacing values provided by the XRD spectra of ACC (Fig. 2) reflected the presence of Moganite (SiO_2), Akdalaite ($(Al_2O_3)_4 \cdot H_2O$), Tamarugite ($NaAl(SO_4)_2 \cdot 6H_2O$), Fersilicate (FeSi) and Majorite ($Mg_3(Fe,Al,Si)_2(SiO_4)_3$) as major components. The broad peak in the XRD spectra indicates the presence of amorphous form of silica. Diffraction peaks corresponding to crystalline carbon were not found. The SEM micrographs of the ACC at various magnifications were shown in Fig. 3. It can be inferred from these figures that the surface texture of the blank ACC has porous structures with pores of varying sizes.

ACC showed wide pore size distribution giving wide distribution of surface area. The BET surface area was ACC is 171.05 m^2/g, whereas BJH adsorption/desorption surface area of pores was 131.98/92.22 m^2/g. The

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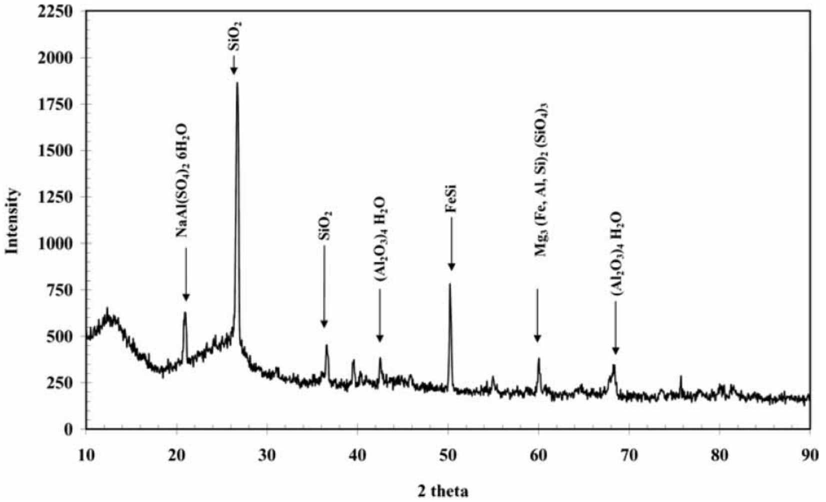
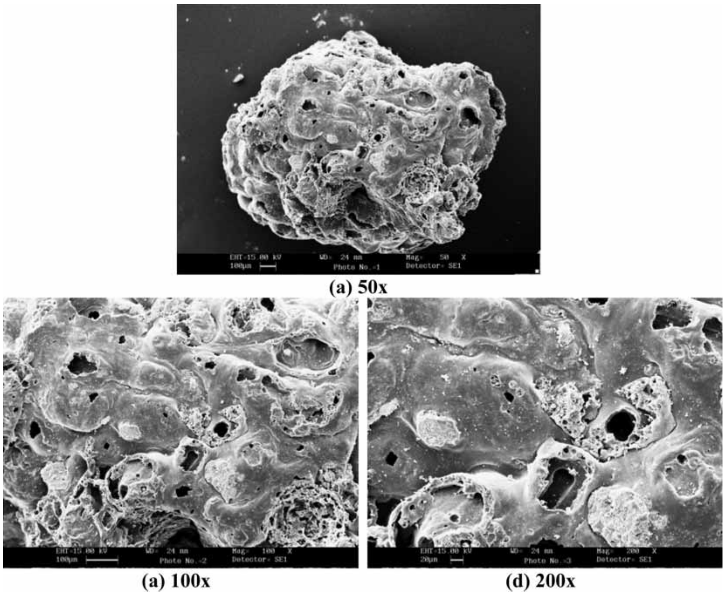


Figure 2. XRD pattern of ACC.

single point total pore volume of pores is found to be 0.1327 cm^3/g, whereas cumulative adsorption/desorption pore volume of the pores (17 $A^0 < d <$ 3000 A^0) is 0.1231/0.1081 cm^3/g, respectively. The BET average pore diameter of ACC is found to be 31.03 Å. The analysis of the BJH adsorption


(a) 50x

(a) 100x

(d) 200x

Figure 3. SEM of ACC at various magnifications.

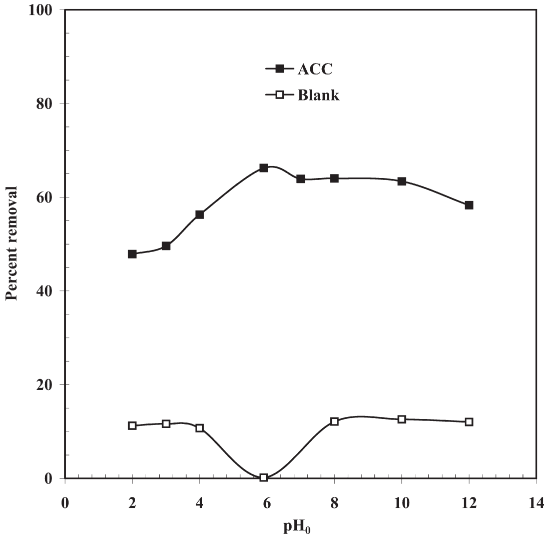


Figure 4. Effect of pH_0 on the adsorption of furfural by ACC. T = 303 K, $t = 6.0$ h, $C_0 = 100$ mg/l, ACC dose = 6 g/l.

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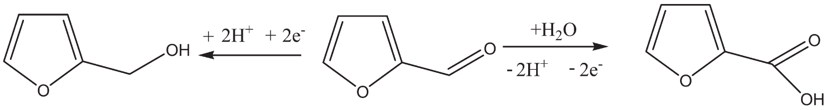
pore distribution of ACC shows that the micro-pores ($d < 20$ Å) have a total pore area of about 24% and the meso-pores account for about 76%. The ACC, thus, is found to consist of mesopores predominantly. This is what is desirable for the liquid phase adsorptive removal of furfural.

Effect of Initial pH (pH_0)

pH affects the structural stability of furfural and, therefore, its concentration. Fig. 4 shows the furfural removal trend from aqueous solution ($C_0 = 100$ mg/l having natural $pH_0 = 5.9$) with and without ACC over a pH_0 range of 2 to 12. It may be inferred from the figure that pH_0 5.9 is optimum for the furfural adsorption onto ACC. Increase in pH_0 from 5.9 to 12 marginally decreases the furfural removal. Therefore, the adsorption of furfural by ACC was relatively constant for the range of pH values used in the study. The effect of pH_0 on the stability of furfural solution was also studied. Furfural solution having pH_0 in the range of 2 to 12 was kept for 1.0 h without ACC, after which the absorbance of the solution was found out. There was insignificant change in absorbance of furfural solution after 1.0 h with respect to that after 15 min. It is inferred that the furfural solution is stable at the natural $pH_0 = 5.9$, and solution becomes unstable if the solution pH is either increased or decreased. Furfural is at an intermediate oxidation state between the corresponding alcohol and acid. Therefore, it can be reduced into furfurylic alcohol or oxidized into furoic acid (28):



The change in natural pH of furfural solution, therefore, changes the structure of furfural and, hence, destabilizes the solution. It may be seen that the furfural removal is maximum at pH_0 5.9 and also the solution is most stable at this pH_0. Therefore, further adsorption experiments were carried out at pH_0 5.9.

Effect of Adsorbent Dosage (*m*)

An increase in *m* value, generally, increases the degree of adsorption owing to greater surface area and the availability of more adsorption sites. Figure 5 shows the effect of *m* on the removal of furfural by ACC at $C_0 = 100$ mg/l. It can be seen that the furfural removal increases up to $m < 10$ g/l, and then it remains almost constant for $m \geq 10$ g/l. The adsorbent surface becomes saturated with furfural for $m < 10$ g/l, and the residual concentration in the solution is large. With increase in *m*, the furfural removal increases due to increased furfural uptake by the increases amount of adsorbent. However, for $m \geq 10$ g/l the surface furfural concentration and the solution furfural concentration come to saturation limit with each other, and the incremental

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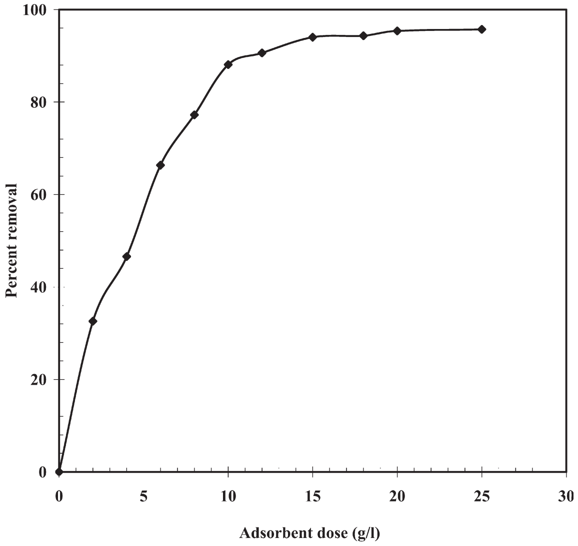

Figure 5. Effect of adsorbent dose on the adsorption of furfural by ACC. $T = 303$ K, $t = 6.0$ h, $C_0 = 100$ mg/l.

furfural removal becomes very low. At about $m = 10$ g/l, the removal efficiency becomes almost constant.

Effect of Initial Furfural Concentration (C_0)

C_0 provides the necessary driving force to overcome the resistances to the mass transfer of adsorbate between the aqueous and the solid phases. The increase in C_0 also enhances the interaction between adsorbate and the adsorbent. Therefore, an increase in C_0 enhances the adsorption uptake of adsorbate. Similar trend may be seen in Fig. 6 for the effect of C_0 on the removal of furfural by ACC. It is evident that the amount of furfural adsorbed per unit mass of ACC (q_e) increased with the increase in C_0, although percent furfural removal decreased with the increase in C_0. It may also be seen that the rate of adsorption also increases with an increase in C_0 due to the increase in driving force.

Effect of Contact Time

Figure 6 shows the effect of contact time for the removal of furfural by the ACC at $C_0 = 100$, 200, 300, and 500 mg/l for m = 10 g/l. It may be seen that in the first 1 h, brisk adsorption of furfural occurs and, thereafter, the adsorption rate decreased gradually and the adsorption reached equilibrium

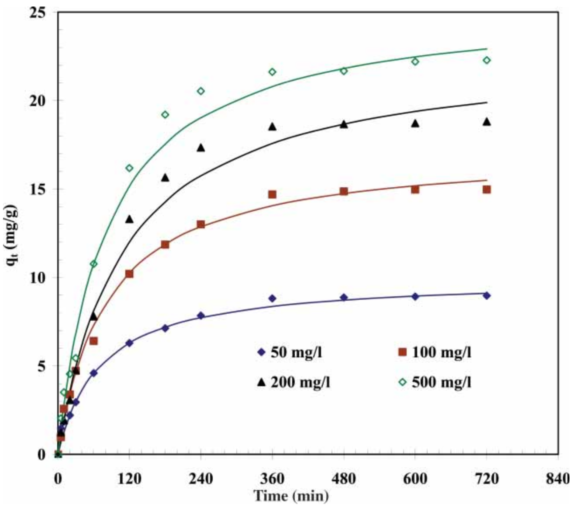

Figure 6. Effect of contact time on the adsorption of furfural by ACC. Experimental data points given by the symbols and the lines predicted by the pseudo-second-order model. $T = 303$ K, $m = 10$ g/l.

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in about 6.0 h. The adsorption of furfural by ACC for 24.0 h contact time was only marginally higher (1%) over those obtained for 6.0 h contact time. For higher contact time, bigger size, and aggregation of furfural molecules make it almost impossible to diffuse deeper into the adsorbent structure at highest energy sites. Also, at higher contact time, the mesopores are almost filled up and start offering resistance to diffusion of aggregated furfural molecules into the ACC. Since the difference in the adsorption values at 6.0 h and at 24.0 h is very small, thus, after 6.0 h contact, a steady-state approximation was assumed and a quasi-equilibrium situation was accepted. Further experiments were conducted for 6 h contact time only.

Adsorption Kinetic Study

Pseudo-First-Order- and Pseudo-Second-Order- Model

The best-fit values of k_f, h, q_e and k_S along with correlation coefficients for the pseudo-first-order and pseudo-second-order models are shown in Table 1. The $q_{e,\text{exp}}$ and the $q_{e,\text{cal}}$ values for the pseudo-first-order model and pseudo-second-order models are also shown in Table 1. The $q_{e,\text{exp}}$ and the $q_{e,\text{cal}}$ values from the pseudo-second-order kinetic model are very close to each other. The calculated correlation coefficients are also closer to unity for pseudo-second-order model than that for the pseudo first-order kinetic model. Therefore, the sorption can be approximated more appropriately by the pseudo-second-order kinetic model than the first-order kinetic model for the adsorption of furfural by ACC. Srivastava et al. (22) and Mall et al. (29) have reported k_S values of 0.0292 and 1.9767 g/mg min for phenol and malachite green adsorption onto ACC, respectively. But due to different nature of the adsorbate-adsorbent systems, a direct comparison of k_S between values obtained in this study with those reported in literature is not possible.

Intra-particle Diffusion Study

In Fig. 7, the Weber-Morris plot of q_t versus $t^{0.5}$ is presented for adsorption of furfural onto ACC for $C_0 = 50$, 100, 300, and 500 mg/l. In the figure, the plots are not linear over the whole time range, implying that the more than one process is controlling the sorption process. If the two steps are independent of one another, the plot of q_t versus $t^{0.5}$ plot appears as a combination of two or more intersecting lines (30), the first of the lines represents surface adsorption and the second intra-particle diffusion. The presence of such distinctive features in the plots of the present work could be interpreted as due to distinction between the two steps. Surface adsorption and intra-particle diffusion were likely to take place separately. The first portion (line not drawn for the clarity of picture) in Fig. 7 gives boundary layer diffusion, and further two linear portions depict intra-particle diffusion. The first straight portion

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Table 1. Kinetic parameters for the removal of furfural by ACC ($t = 6.0$ h, $C_0 = 100–500$ mg/l, $m = 10$ g/l).

C_0 (mg/l)	$q_{e,\text{exp}}$ (mg/g)	$q_{e,\text{calc}}$ (mg/g)	k_f (min^{-1})	R^2	MPSD
Pseudo-first-order model					
100	8.97	8.88	0.0134	0.991	56.40
200	14.97	14.84	0.0128	0.992	37.45
300	18.81	32.34	0.0024	0.930	172.65
500	22.28	78.17	0.0009	0.872	231.42
	$q_{e,\text{calc}}$(mg/g)	k_s (g/mg min)	h(mg/g min)	R^2	MPSD
Pseudo-second-order model					
100	9.99	0.0014	0.1416	0.997	37.81
200	17.25	0.0007	0.2106	0.997	21.38
300	22.91	0.0004	0.2098	0.994	32.24
500	25.55	0.0005	0.3103	0.995	43.60
	$k_{id,1}$ (mg/g min$^{1/2}$)		I_1 (mg/g)		R^2
W-M Intra-particle diffusion model					
100	0.511		0.269		0.987
200	0.915		−0.564		0.991
300	1.305		−2.132		0.991
500	1.505		−1.566		0.985
	$k_{id,2}$ (mg/g min$^{1/2}$)		I_2 (mg/g)		R^2
100	0.020		8.43		0.997
200	0.037		14.03		0.901
300	0.034		17.89		0.983
500	0.095		19.75		0.873

depicts meso-pore diffusion and the second represents micro-pore diffusion. These show only the pore diffusion data. Extrapolation of the linear portions of the plots back to the y-axis gives the intercepts i.e. the value of I, which provides the measure of the boundary layer thickness. If the intercept is large, the boundary layer effect will also be large. The deviation of straight lines from the origin may be due to difference in rate of mass transfer in the initial and final stages of adsorption. Further, such deviation of the straight line from the origin indicates that the pore diffusion is not the sole rate-controlling step (31). Therefore, the adsorption proceeds via a complex mechanism. It seems that the intra-particle diffusion of furfural into micro-pores is the rate controlling step in the adsorption process. Also, the slopes of the second and the third portions ($k_{id,1}$ and $k_{id,2}$) are higher for higher C_0, which corresponds to an enhanced diffusion of furfural through meso- and micro-pores at higher C_0. This is due to the higher driving force at higher C_0.

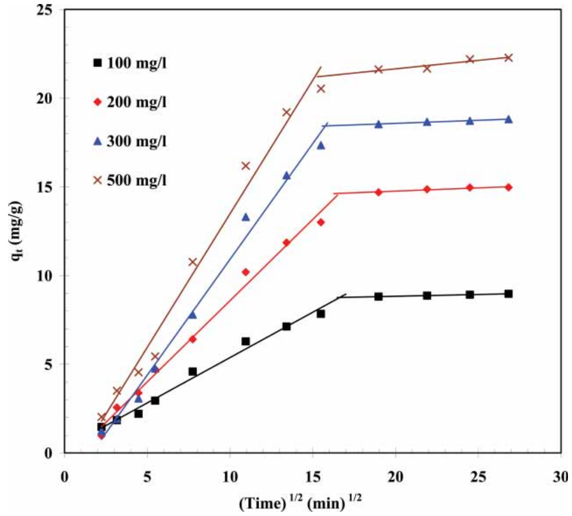

Figure 7. Weber and Morris intra-particle diffusion plot for the removal of furfural by ACC. $T = 303$ K, $m = 10$ g/l.

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Determination of Diffusivity

D_e was determined from the slope of the plot of $\ln\lfloor 1/(1 - F^2(t))\rfloor$ versus t (not given here). The average value of effective diffusion coefficient (D_e) as calculated from Eq. (10) was found to be 3.34×10^{-13} m^2/s for the adsorption of furfural onto ACC.

Effect of Temperature

Sorption is, generally, an exothermic process. Therefore, it is expected that an increase in temperature of the furfural-ACC system would result in decreased sorption capacity of ACC. The plots of adsorption isotherms, q_e versus C_e, for furfural adsorption onto ACC at temperatures 293, 303, 313, and 323 K are shown in Fig. 8. It may be seen that the adsorptive removal of furfural by ACC decreases with an increase in temperature as expected. At lower adsorbate concentrations, q_e rises sharply and thereafter, the increase is gradual with solute concentration in the solution.

Adsorption Equilibrium Study

The Freundlich and Langmuir equations are the most widely applied for isotherm modeling. Henry's Law is valid for extremely low concentrations and highly heterogeneous surfaces. Freundlich isotherm (32) is suitable for

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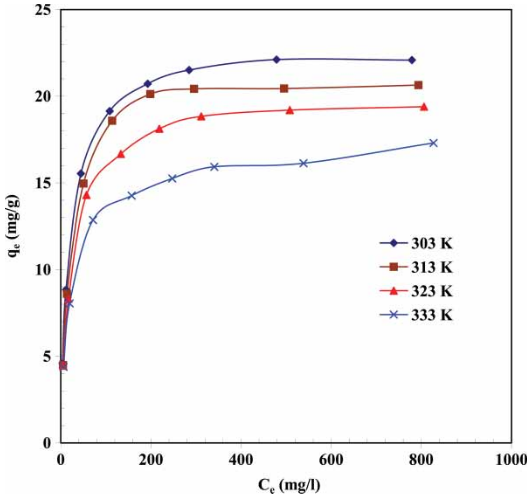

Figure 8. Equilibrium adsorption isotherms at different temperature for furfural-ACC system. $t = 6.0$ h, $C_0 = 50-1000$ mg/l, $m = 10$ g/l.

highly heterogeneous surfaces, however, it does not approach Henry's Law at vanishing concentrations. The Langmuir equation (33), although follows Henry's Law at vanishing concentrations, is valid for homogeneous surfaces. The Redlich and Peterson (R-P) equation (34) is a three parameter-equation, that reduces to Freundlich equation at high concentrations and to Henry's equation at very low concentrations. Temkin isotherm assumes that

(i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate-adsorbate interactions, and
(ii) adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy (35).

It contains a factor that explicitly takes into account the interactions between adsorbing species and the adsorbate. We tried to use the four isotherm equations given by, Freundlich, Langmuir, Temkin, and R-P to fit the experimental data for furfural on ACC at various temperatures. For each system and the isotherm equation all the experimental data were used. The Marquardt's percent standard deviation (MPSD) error function (36) was employed in this study to find out the most suitable isotherm model to represent the experimental data. This error function is given as

$$MPSD = 100\sqrt{\frac{1}{n-p}\sum_{i=1}^{n}\left(\frac{(q_{e,meas} - q_{e,calc})}{q_{e,meas}}\right)_i^2} \qquad (7)$$

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The isotherm constants for all the isotherms studied, and the correlation coefficient, R^2 with the experimental data are listed in Table 2. The R^2 values for R-P isotherm are closer to unity in comparison to the values obtained for other isotherms. And also the MPSD error values are minimum for the fit of R-P isotherm. Therefore, R-P is the best-fit isotherm equation for the adsorption of furfural on ACC at all temperatures. Figure 9 presents how well the four isotherms fit the data for furfural-ACC system. The data in Table 2 also indicate that the values of q_m and K_F decreased with an

Table 2. Isotherm parameters for the removal of furfural by ACC ($t = 6.0$ h, $C_0 = 50–1000$ mg/l, $m = 10$ g/l)

Freundlich		$q_e = K_F C_e^{1/n}$		
T (K)	K_F ((mg/g)/(l/mg)$^{1/n}$)	$1/n$	R^2	MPSD
293	4.08	0.29	0.911	51.91
303	4.01	0.28	0.896	54.34
313	3.88	0.27	0.923	45.67
323	3.94	0.24	0.948	36.01

Langmuir		$q_e = \dfrac{q_m K_L C_e}{1 + K_L C_e}$		
T (K)	K_L (l/mg)	q_m (mg/g)	R^2	MPSD
293	22.63	0.055	0.999	6.77
303	21.22	0.053	0.998	6.59
313	19.99	0.044	0.999	8.08
323	16.77	0.047	0.995	10.60

Temkin		$q_e = B_T \ln K_T + B_T \ln C_e$		
T (K)	K_T (l/mg)	B_T (kJ/mol)	R^2	MPSD
293	0.83	3.75	0.977	21.69
303	0.62	3.92	0.964	22.73
313	0.64	3.56	0.977	17.39
323	0.75	2.88	0.986	14.01

Redlich-Peterson		$q_e = \dfrac{K_R C_e}{1 + a_R C_e^{\beta}}$			
T (K)	K_R (l/g)	a_R (l/mg)$^{1/\beta}$	β	R^2	MPSD
293	1.36	0.071	0.97	0.999	5.08
303	1.12	0.053	0.99	0.998	6.59
313	1.03	0.059	0.98	0.998	7.16
323	1.01	0.068	0.98	0.995	8.23

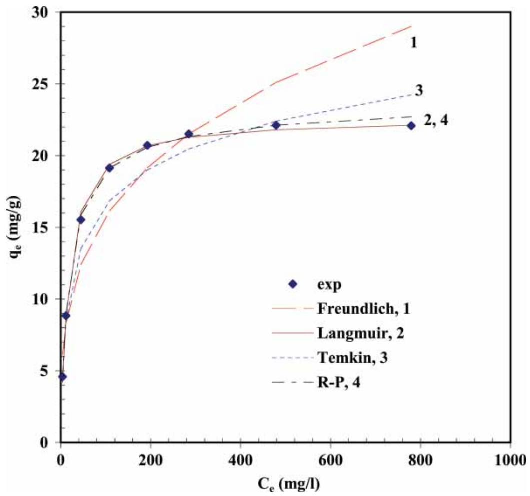

Figure 9. Comparison of various isotherm equations for the adsorption of furfural by ACC at 313 K. $t = 6.0$ h, $C_0 = 50-1000$ mg/l, $m = 10$ g/l.

increase in temperature confirming exothermic nature of overall sorption process for furfural-ACC system. Since $1/n < 1$, furfural is favorably adsorbed by ACC at all temperatures. The K_F value can be taken as a relative indicator of the adsorption capacity of ACC for a narrow subregion having equally distributed energy sites for the sorption of furfural. The magnitude of K_F also showed the lower uptake of furfural at higher temperature indicating exothermic nature of adsorption process. The value of Temkin constant (B_T) that related to the heat of furfural adsorption onto ACC is estimated to be in the range of 2.88 to 3.74 kJ/mol. The value of B_T in Temkin isotherm indicate physical nature of adsorption at each temperature.

Estimation of Thermodynamic Parameters

The Gibbs free energy change of the adsorption process is related to the equilibrium constant by the classical Van't Hoff equation

$$\Delta G^0 = -RT \ln K_D \tag{8}$$

The Gibbs free energy change is also related to the entropy change and heat of adsorption at constant temperature according to the following equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{9}$$

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Table 3. Thermodynamics parameters for the adsorption of furfural by ACC ($t = 6.0$ h, $C_0 = 50-1000$ mg/l, $m = 10$ g/l)

Temp. (K)	$K \times 10^{-3}$ (l/kg)	ΔG_0 (kJ/mol)	ΔH_0 (kJ/mol)	ΔS_0 (kJ/mol K)
293	1.08	−17.03	−12.45	15.47
303	0.87	−17.06		
313	0.77	−17.31		
323	0.67	−17.47		

Combining the above two equations, one gets,

$$\ln K_D = \frac{-\Delta G^0}{RT} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R}\frac{1}{T} \tag{10}$$

where, ΔG^0 is the free energy change (kJ/mol), ΔH^0 is the change in enthalpy (kJ/mol), ΔS^0 is the entropy change (J/mol K), T is the absolute temperature (K), and R is the universal gas constant (8.314×10^{-3} kJ/mol K) ; and $K_D = (q_e/C_e)$ is a single point or linear sorption distribution coefficient. Thus, ΔH^0 is the enthalpy change (kJ/mol) which can be determined from the slope of the linear Van't Hoff plot i.e. ln K_D versus $(1/T)$, using the equation:

$$\Delta H^0 = \left[R\frac{d\ln K_D}{d(1/T)}\right] \tag{11}$$

This ΔH^0 corresponds to the isosteric heat of adsorption with zero surface coverage (i.e. $q_e = 0$) (37). ΔH^0 value provides a direct measure of strength of bonding between the adsorbate and adsorbent surface. K_D at $q_e = 0$ was obtained from the intercept of the ln (q_e/C_e) versus q_e plot. ΔH^0 and ΔS^0 values have been obtained from the Van't Hoff's plot (not shown here). The positive value of ΔS^0 suggests increased randomness at the solid/solution interface, and an increase in the degree of freedom of the adsorbed species. The negative ΔH^0 value confirms the exothermic nature of the overall-sorption process (Table 3). The heat of adsorption values between 0–20 kJ/mol are frequently assumed as to indicate physical nature of adsorption. ΔH^0 value was found as −12.45 kJ/mol for furfural adsorption onto ACC. It is obvious from the ΔH^0 value that physio-sorption is mainly taking part in the adsorption process. ΔG^0 values were negative (Table 3) indicating feasibility and spontaneity of the adsorption process that the sorption process.

CONCLUSION

The present study shows that furfural can be effectively removed from aqueous solution by adsorption onto commercial activated carbon (ACC). Higher percentage of furfural removal by ACC, was possible provided that

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the C_0 in the solution was low. The equilibrium between the adsorbate in the solution and on the adsorbent surface was practically achieved in 6.0 h. Adsorption kinetics was found to be best represented by pseudo-second-order rate expression. The effective diffusion coefficient of furfural was of the order of 10^{-13} m^2/s. Adsorption of furfural onto ACC was favorably influenced by decrease in the temperature of the operation. The enhanced sorption at lower temperature indicated exothermic adsorption process. Equilibrium isotherms were analyzed by different isotherm models using non-linear regression technique. Redlich-Peterson isotherm was found to best represent the equilibrium data for furfural adsorption onto ACC. ΔH^0 values indicated physical nature of the overall sorption process. The negative values of ΔG^0 indicated feasible and spontaneous adsorption of furfural onto ACC.

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NOMENCLATURE

$1/n$	heterogeneity factor, dimensionless
a_R	constant of Redlich-Peterson isotherm, l/mg
B_T	Temkin isotherm constant related to the heat of adsorption, kJ/mol
ACC	commercial grade activated carbon
C_0	initial concentration of adsorbate in solution, mg/l
C_e	equilibrium liquid phase concentration, mg/l
C_S	adsorbent concentration in the solution
h	initial sorption rate, mg/g min
I	constant that gives idea about the thickness of boundary layer, mg/g
k_f	rate constant of pseudo-first-order adsorption model, min^{-1}
k_{id}	intra-particle diffusion rate constant, mg/g $min^{1/2}$
k_S	rate constant of pseudo-second-order adsorption model, g/mg min
K_F	constant of Freundlich isotherm, $(mg/g)/(l/mg)^{1/n}$
K_L	constant of Langmuir isotherm, l/mg
K_R	constant of Redlich-Peterson isotherm, l/g
K_T	constant of Temkin isotherm, l/mg
m	mass of adsorbent per liter of solution, g/l
n	number of data points
p	number of parameters
MPSD	Marquardt's percent standard deviation
q_e	equilibrium solid phase concentration, mg/g
$q_{e,\mathrm{cal}}$	calculated value of solid phase concentration of adsorbate at equilibrium, mg/g
$q_{e,\mathrm{exp}}$	experimental value of solid phase concentration of adsorbate at equilibrium, mg/g

q_m	maximum adsorption capacity of adsorbent as per Langmuir isotherm, mg/g
q_t	amount of adsorbate adsorbed by adsorbent at time t, mg/g
R	universal gas constant, 8.314 J/K mol
t	time, min
T	absolute temperature, K
V	volume of the solution, l
w	mass of the adsorbent, g
ΔG^0	Gibbs free energy of adsorption, kJ/mol
ΔH^0	enthalpy of adsorption, kJ/mol
ΔS^0	entropy of adsorption, J/K mol

Greek Symbols

β	constant of Redlich-Peterson isotherm ($0 < \beta < 1$)

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