Chemical, Petroleum and Environmental Engineering

Adsorptive Removal of Furfural from Wastewater on Prepared Activated Carbon from Sawdust

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ABSTRACT

Furfural is a toxic aromatic aldehyde that can cause a severe environmental problem especially the wastewater drawn from petroleum refinery units. In the present work, a useless by-product from local furniture manufacturing industry; sawdust was used as raw material for the preparation of activated carbon which is chemically activated with phosphoric acid. The effect of adsorption variables which include initial pH of solution (2-9), agitation speed (50-250) rpm, agitation time (15-120) min, initial concentration of furfural (50-250) ppm, and amount of adsorbent material (0.5-2.5) g for the three adsorbents used (prepared activated carbon, commercial activated carbon and raw sawdust) were investigated in a batch process in order to obtain the maximum furfural removal from wastewater. The results obtained from the experimental investigation show that the percentage removal of furfural increases with increasing pH and agitation speed until a maximum value after that it decreased with increasing pH and agitation speed. Also increases with increasing amount of adsorbent material and agitation time until a maximum value then reaches a constant value approximately, and decreasing with increasing furfural concentration. The maximum removal percent of furfural was 97.8, 94.4 and 55.9% for prepared activated carbon, commercial activated carbon, and raw sawdust respectively, which is obtained at a pH of 7.0, agitation speed of 150 revolutions per minute, agitation time of 105 minutes, furfural concentration of 100mg/L, and adsorbent amount of 1.5gm. Langmuir model is best fitted the data than Freundlich model.

Keywords: Furfural, adsorption, activated carbon, sawdust, wastewater.

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1. INTRODUCTION

Petroleum refineries are confrontation pollution problems linked with the accidental losses of furfural. This forms an economic loss as well as environmental hazards. Furfural is a toxic aromatic aldehyde with the chemical formula C₄H₄OCHO. It is pale yellow or colorless oily liquid and turns into brown or red in the presence of air or light, Hassan, et al., 2012. Human exposure to concentrations of 1.9-14 ppm of furfural causes a headache, flushing of the eyes and tears. Furfural has been classified as a hazardous material that can damage the lungs, liver, kidneys, and spleen, Samarghandi, et al., 2015. The permissible exposure limit (PEL) for the furfural is 5 ppm, OSHA, 2000.

Wastewater discharged from refinery units involved high concentrations of non-biodegradability toxicity compounds such as furfural. Furfural concentration must be reduced before entering the biological treatment processes because this component can damage the microorganisms' cells in the waste streams of the industry, Basheer, et al., 2011. In many cases, the use of tertiary biological treatment processes for the purification of industrial wastewater is more cost-effective than chemical treatment processes, but the biological process undergoes different operating conditions.

In industry, large volumes of wastewater are generated. Hence the appropriate method is required to handle such a load. Furfural can be removed from aqueous solutions by different techniques, Sulaymon and Hayfa, 2014 such as oxidation, Alsaaqar, et al., 2015, precipitation, ion exchange, solvent extraction, Kun, et al., 2016 and adsorption. Adsorption has been recognized as an effective process in most of the industrial water and wastewater treatment, Ghazi, 2012.

Some studies used hydrophobic polymeric resins (XAD-4 and XAD-7), nanoporous material MCM-48 and activated carbon, for removing furfural by adsorption techniques, Mebrek and Derriche, 2010.

Activated carbon has large surface area and high adsorption capacity that makes it one of the most sorbents generally used in the removing of hazardous pollutants from wastewater. Batch wise or continuous manner of operation can be carried out in adsorption processes, Abbas and Darweesh, 2016. Two processes are used for the preparation of activated carbon: physical activation and chemical activation. Physical activation includes carbonization of carbonsaceous content and then activation of resulting char by activation agents such as steam or CO₂. Chemical activation involves the impregnation of raw material by an activation agent such as KOH, Foo, and Hameed, 2011, ZnCl₂, Wang, et al., 2009, H₃PO₄, Liu, et al., 2010, etc. and then heated in an inert atmosphere.

Many kinds of literature described the preparation of low cost activated carbon such as olive stone Blázquez, et al., 2005, Waste tea Yagmu, et al., 2008, rice husk Tyagi, et al., 2011.
Cottonseed hulls Klasson, et al., 2011, Sugarcane Bagasse Hamid, et al., 2016, Tree sawdust Amina, et al., 2015 and date stone Abbas and Darweesh, 2016. In batch system the rates mechanism for adsorption of solute from aqueous solutions by porous solid are greatly influenced by the mass transfer resistance outside the particles, diffusion resistance inside the particles, geometry of the pores, type of adsorption isotherm, operating conditions such as initial concentration, pH, temperature, phase ratio, agitation speed and vessels geometry, Amina, et al., 2015.

The aim of present work is to prepare an activated carbon from sawdust which chemically activated by H$_3$PO$_4$, then comparing the performance between sawdust (RSD) prepared activated carbon (PAC) from sawdust, and commercial activated carbon (CAC) for the removal of furfural from petroleum refinery wastewater. The effect of initial pH of the aqueous solution, shaking speed, shaking time, amount of adsorbed material, and the initial concentration of furfural on the removal percent of furfural have been investigated as a basis of comparison.

2. EXPERIMENTAL WORK

2.1 Raw material collection and preparation.

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 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 electric oven at 100-110°C. 100 gm of dry sawdust was activated by mixing with 50% (v/v) phosphoric acid and left the mixture at room temperature overnight. The second step was pyrolysis of the filtered sample at 500°C under the influence of nitrogen flow (100 ml/min) for 2 hrs, this furnace located at research and development laboratories – Ministry of Industry. The activated carbon thus produced was then cooled, washed with distilled water to remove the excess acid and dried. Fig.1 shows a diagram illustrating the steps of preparation of activated carbon.

2.2 Fourier transforms infrared spectroscopy (FT-IR)

The PAC and CAC were tested to observe frequencies have been assigned. The FT-IR applied to observe the presence or absence of effective group on the external surface of PAC and CAC which registered in the region 400-4000 cm$^{-1}$. This was achieved using Shimadzu FTIR 8400S type.

2.3 Surface area measurement

The adsorbent surface area was determined using BET method by Thermo Finnegan type, apparatus located at Oil Development and Research Center, Ministry of Oil.

2.4 The concentration of furfural determination.

The variation of furfural concentration in the aqueous solution due to adsorb by sawdust, perpetrate activated carbon and commercial activated carbon was determined calorimetrically at the wavelength (430 nm) by Shimadzu UV- Visible Spectrophotometer. The percent removal of furfural ($Y_R$) due to the adsorption process was calculated according to the equation:

$$Y_R = \frac{C_o-C_e}{C_o} \times 100$$

Where $C_o$ and $C_e$ the initial and equipoise concentration of furfural in the aqueous solution.
2.5 Investigation of the process variable.

A set of batch experiments mode were carried out to study the influence of five variables which include, pH of the aqueous solution was adjusted between 2.0 and 9.0 by the addition of 0.1 M of hydrochloric acid or 0.1 M sodium hydroxide solutions. The variation of furfural concentration in the range (50 - 250) mg /L was obtained by suitable dilution of original concentration 1000 mg/L with deionized water. Varying agitation times of 15, 30, 45, 60, 75, 90, 105 and 120 min, the agitation was changed from 50 to 250 revolutions per minute, and the amount of adsorbent was varied 0.5, 1.0, 1.5, 2.0 and 2.5 g. For each experiment 50 ml of furfural solution in conical flasks with suitable initial concentration and pH then added the appropriate amount of adsorbed material. After that, the conical flasks were agitated by electrical shaker with certain agitation speed for a certain time. At the end of the adsorption process, the content of conical flasks was filtrated and the filtrate was analyzed by using UV- Visible Spectrophotometer with wavelength 430 nm to determine the furfural concentration in the treated solution.

3. RESULTS AND DISCUSSION

3.1 The Surface Area of Activated Carbon

The surface area of the adsorbent is the most important factor in determining the adsorption capacity. The surface area of raw material (sawdust) is very low 290 m²/g compared with commercial activated carbon which has a surface area of 800 m²/g. The prepared activated carbon has a surface area of 825 m²/g when activated with phosphoric acid. This increase in surface area may be attributed to the C-H2O reaction to remove some of carbon atoms and formation of micropores on the prepared activated carbon surface. Abbas and Darweesh, 2016 prepared activated carbon from date stones with 852 m²/g surface area. Amina, et al., 2015 prepared activated carbon from sawdust with 831 m²/g surface area.

3.2 FTIR spectroscopy

FTIR test exhibit better information on the quality of functional groups available into the surface of PAC and CAC. The abundance of functional groups has been define an effective adsorbed site for binding a furfural. IR spectra of PAC and CAC were shown in Figs.2 and 3. From Fig.2, 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 intermolecular 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 a carboxylic acid, carbonyl in ketone, the carbonyl group in quinone, an 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 difference in the charges between them. This agrees with Amina, et al., 2015 and Abbas and Darweesh, 2016.
3.3 Influence of pH
The adsorption of furfural from the wastewater solution was investigated at room temperature by changing the initial pH of the solution from 3.0 to 9.0. Initial pH values are considered the main factors affecting the adsorption capacity of furfural on activated carbon. Fig. 4 shows the effect of initial pH of wastewater on the removal percentage of furfural by PAC, CAC, and RSD. From this figure, it can be seen that the removal percentage expressing in terms of the furfural removal percent increased significantly with increasing the initial pH of the solution to reach a maximum value. The results showed that at PAC, CAC and RSD the removal percent of furfural 42.8, 39.3 and 21.2 at pH 2.0 and increased to 77.4, 72.1 and 37.2 respectively at pH 7.0. After that, the removal percent of furfural is relatively low with increasing the initial pH.
This phenomenon can be demonstrated as follows: activated carbon has active sites with negative charge while the furfural ion has active sites with a positive charge at low pH. The competition between furfural ion active site positive charge and hydrogen ions positive charge to combine with the activated carbon negative charge active site so the removal percent of furfural decreases with decreasing pH. With increasing pH, the concentration of hydrogen (H+) decreases giving more removal percent of furfural. Until the pH = 7.0 after that the increase in pH causes increase in the concentration of hydroxyl ion (OH-) negative charge which increases the hindrance for diffusion of furfural and activated carbon negative charge and thus reduces the removal percent of furfural, this agrees with Blazquez, et al., 2005. Therefore, the initial pH 7 is the best value and will be selected as for the next experiments to removal furfural ions from wastewater by using activated carbon.

3.4 Influence of agitation speed
The influence of agitation speed on the removal percent of furfural from 50 to 250 revolution per minute (rpm) and the results offered in Fig.5. The experimental results appear that the removal percent of furfural increased with increasing the shaking speed to extend maximum value. Furfural percent removal was 67.6%, 62.5 and 31.2% at 50 rpm and increased to 83.1%, 78.5% and 41.3% respectively at 150 rpm for PAC, CAC, and RSD. This phenomenon may be explained as follows: the increase of agitation speed increases the mobility of furfural which causes increases in the diffusion coefficients subsequently increase the mass transfer rate of furfural to the surface of adsorbent which increases the removal percent with increasing shaking speed. After that, the increasing of shaking speed from 150 to 200 rpm the removal percent decreased due to the fracturing of the bonding between the furfural and the surface site of PAC, CAC or RSD which causes desorbing the furfural from the surface site. An enhanced the probably physical adsorption is occurring rather than chemical adsorption. This agrees with Amina, et al., 2015 and Ghazi, 2012. However, the shaking speed 150 rpm will be selected for the next experiments.

3.5 Effect of contact time
The removal percent of furfural from wastewater was investigated in adsorption batch process at different contact time from 15 to 120 minutes. The relationship between removal percent of furfural and adsorbed time is shown in Fig.6. This figure shows that furfural removal will increase with increasing the adsorbed time until reaching a maximum value. Furfural percent removal was 83.1%, 78.5% and 41.3% at 105 min for PAC, CAC, and RSD respectively. After that, the removal percent of furfural ions approximately was constant with increasing the agitation time due to access to the equilibrium state which occurs when the saturation of the active centers and the inability to absorb more furfural molecules. This agrees with Liu, et al.,
2010 and Sulaymon, et al., 2014. For this reason, the time of 105 minutes was chosen for the later experiments.

3.6 Influence the initial concentration of furfural
The influence of the initial furfural concentration on the removal percent was examined at various concentrations between 50 and 250 mg/L which were patronized by the adsorption batch process, as shown in Fig.7. Experimental data indicate that the removal percent of furfural decreased with increasing the initial furfural concentration. Removal percent of furfural decreased from 83.1%, 78.5% and 41.3% when the concentration is 100 mg/l to 61.8, 57.1 and 31.6% when the furfural concentration increases to 250 mg/l for PAC, CAC and RSD respectively. This result improves the fact that the removal percent of furfural is strongly dependent on the initial concentration of furfural. This may be imputation to the reality that for all stable changeable of experiments, the amount of adsorbed material also constant. When increasing the furfural concentration the removal percent decreased due to the number of the available sites to adsorb material becomes lowest in comparison with the number of furfural molecules, subsequently the removal percent of furfural. This agrees with Amina, et al., 2015 and Mebrek and Derriche, 2010.

3.7 Influence of amount adsorbent
The amount of adsorbent is an important factor which has a significant effect on the removal percent of furfural from industrial wastewater by adsorption process. The removal percent of the furfural is constant if all the variables increase with increasing the number of adsorbents. These results are shown in Fig. 8. This figure shows that the removal percent of furfural increased from 83.1, 78.5 and 41.3 to 97.8, 94.4 and 55.9 with increasing the amount of PAC, CAC and RSD from 0.5 g to 1.5 g respectively. This result is due to the fact that increasing the amount of adsorbent material increases the surface area of its and thus increases the effective sites which have the ability to bind to the furfural molecules, subsequently increasing their removal percent. Thereafter the increase in the amount of absorbent material from 1.5 g to 2.5 g, the removal percent of furfural on PAC, CAC, and RSD remains approximately constant. This is due to the number of adsorbable ions that have been adsorbed, while the non-adsorbable ions (free ions) were not adsorbed, so the removal percent remains approximately constant. This agrees with Hamid, et al., 2016 and Ghazi, 2012.

3.8 Adsorption isotherm model
Adsorption isotherms are important to describe the adsorption mechanism for furfural transfer from the bulk of the solution to the interface than to the adsorbent surface. A two adsorption isotherm model were examined to characterize the case problem. The equilibrium data for adsorption of furfural into the prepared activated carbon was shown in Fig.9, from this figure it is clear that the Langmuir model fitted the data more than Freundlich isotherm. This agrees with Sulaymon, et al., 2014 and Mebrek and Derriche, 2010. The maximum adsorption capacity \(Q_m\) is 7.825 mg/g and adsorption equilibrium constant \(b\) is 0.648 with correlation constant \(R^2 = 0.987\). While for Freundlich isotherm \(K = 1.873\) and \(n = 0.203\) with \(R^2=0.804\).

\[
\text{Langmuir isotherm } q_e = \frac{Q_m b c_e}{1 + b c_e} \tag{3.1}
\]

\[
\text{Freundlich isotherm } q_e = K c_e^n \tag{3.2}
\]
4. CONCLUSIONS

The obtained results show that the prepared activated carbon from sawdust which was chemically activated by H₃PO₄ is an appropriate and an effective adsorbed material for the removal of furfural from refinery wastewater. The percent removal of furfural was affected by the initial pH of the solution, contact time, initial furfural concentration, and amount of adsorbed material (PAC, CAC, and RSD). The best removal percent of furfural was 97.8, 94.4 and 55.9% for PAC, CAC and RSD respectively, which were obtained at pH equal 7.0, agitation speed 150 revolutions per minute, agitation time 105 minute, furfural concentration 100mg/L, and adsorbent amount 1.5gm. Langmuir model fitted more the data than the Freundlich isotherm model.

5. REFERENCES

- Abbas A.S, and Darweesh T.M., 2016, Preparation and Characterization of Activated Carbon for Adsorption of Fluoroquinolones Antibiotics, Journal of Engineering, Vol.22, No.8, pp.140-157.

- Alsaqqar A.S, Salman M.S. Abood W.M, and Ali D.F., 2015, Furfural Degradation in wastewater by advanced oxidation process using UV/ H2O2, Iraqi Journal of Chemical and Petroleum Engineering, Vol.16 No.2 pp. 9-17.

- Amina A.A., Reham M.M., Soheir A. K., Ghada M.M., and Shaymaa E.E., 2015, The Effect of Activation Method on the Adsorption Performance of Saw-Dust Activated Carbon, British Journal of Applied Science & Technology, 7(3): pp. 302-315.

- Basheer H.D., Wan M.A., and Abdul Aziz A.R., 2011, Treatment technologies for petroleum refinery effluents: a review, Process Safety, and Environmental Protection, Vol.89, pp. 95-105.

- Blázquez, G., Hernáinz, F., and Calero, M., 2005, Removal of Cadmium Ions with Olive Stones: The Effect of Some Parameters, Process Biochemistry, Vol. 40, PP. 2649-2654.

- Foo, K.Y. and Hameed, B.H. 2011, Preparation and characterization of activated carbon from pistachio nut shells via microwave-induced chemical activation, biomass, and bioenergy, 35, pp. 3257-3261.

- Ghazi Aidan, 2012, Agricultural wastes and activated carbon from them for furfural removal from water solutions, Life Science Journal, Vol.9, No.3, pp. 2501-2505.

- Hamid N.S., Malek N.F. Mokhtar H., Mazlan W.S, Tajuddin R.M., 2016, Removal of oil and grease from wastewater using natural adsorbent, Jurnal Teknologi (Sciences & Engineering), 78:5–3 pp. 97–102.

- Hassan H., Nima A.G., Alirez and Shahram A., 2012, Using activated sludge system to reduce furfural concentration in refinery wastewater, Advance in Environmental Biology, Vol.6, No 8, pp. 2378-2383.
• Klasson T.K., Minori U., Isabel M.L., and Larry L.B., 2011, *Feasibility of removing furfurals from sugar solutions using activated biochars made from agricultural residues*, Bioresources, Vol.6, No.3, pp. 3242-3251.

• Kun X., Yuhe S., Fangfang D., Yingmin Y., Qingsong L., 2016, *Liquid-liquid equilibria for the extraction of furfural from aqueous solution using different solvents*, Fluid Phase Equilibria, 425 pp.393- 401.

• Liu, Q-S, Zheng, T., Wang, P., and Guo, L., 2010, *Preparation And Characterization Of Activated Carbon from Bamboo By Microwave-Indesed Phosphoric Acid Activation*, Industrial Crop and Products, Vol. 31, PP. 233-238.

• Mebrek O.R. and Derriche Z., 2010, *Removal of Furfural from Aqueous Solutions by Adsorption Using Organobentonite: Isotherm and Kinetic Studies*, Adsorption Science & Technology, Vol. 28 No. 6.

• OSHA, 2000, *Occupational Safety and Health Administration of Furfural*, U.S.Dept. of labor.

• Samarghandi M.R, Leili M, Godini K, Mehralipour J and Harati R., 2015, *Furfural removal from synthetic wastewater by persulfate anion activated with electrical current: energy consumption and operating costs optimization*, Der Pharma Chemica, Vol.7, No 7, pp. 48- 57.

• Sulaymon A. H. and Hayfaa L. Swadi, 2014, *Adsorption/ biosorption of furfural and mercury onto granular activated carbon/granular dead of anaerobic sludge*, Journal of Chemical and Pharmaceutical Research, Vol. 6, No. 2, pp. 570-579.

• Tyagi, D. K., Sarita, Y., and Yadav, O. P., 2011, *Equilibrium And Kinetic Studies On Adsorption Of Aniline Blue From Aqueous Solution Onto Rice Husk Carbon*, International Journal of Chemistry Research, Vol. 2, NO. 3, PP. 0976-5689.

• Wang, T., Tan, S., and Liang, C., 2009, *Preparation and Characterization Of Activated Carbon From Wood Via Microwave-Induced ZnCl_2 Activation*, Carbon, Vol. 47, PP. 1880-1883.

• Yagmu, E., Ozmak, M., and Aktas, Z., 2008, *A Novel Method for Production of Activated Carbon From Waste Tea By Chemical Activation With Microwave Energy*, Fuel, Vol. 87, PP. 3278-3285.
Figure 1. Diagram illustrating the steps of preparation of activated carbon.

Figure 2. FTIR of Prepared Activated Carbon.
Figure 3. FTIR of Commercial Activated Carbon.

Figure 4. The influence of pH alteration on the removal percent of furfural [Agitation speed= 100 rpm, time =120 min, C_0=100mg/L, dose = 0.5g].
Figure 5. The influence of agitation speed on the removal percent of furfural \([\text{pH} = 7, \text{time} = 120 \text{ min}, C_0 = 100 \text{ mg/L}, \text{dose} = 0.5 \text{ g}]\).

Figure 6. The effect of the contact time on the removal percent of furfural \([\text{pH}=7, \text{agitation speed}=150 \text{ rpm}, C_0=100 \text{ mg/L}, \text{dose} = 0.5 \text{ g}]\).
Figure 7. Effect of initial concentration of furfural on the removal percent [ pH=7, agitation speed=150 rpm, time =105 min, dose = 0.5g].

Figure 8. The effect of the adsorbent amount on the removal percent of furfural [ pH=7, agitation speed =150 rpm, time =105 min, C₀=100mg/L ].
Figure 9. The Langmuir and Freundlich isotherm model for the furfural removal by Prepared activated carbon.