Pak. J. Agri. Sci. Vol. 39(3), *2002*

RECOVERY OF FURFURAL AND ACTIVE CARBON FROM SAWDUST

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Sawdust, an abundantly available waste material was utilized for the production of furfural and active carbon. The raw material was hydrolyzed with two different concentrations of (14% and 16%) HCl and H_2SO_4 for different time periods (100 and 140 minutes) with and without added salt catalysts ($NaCl$, $CaCl_2$, $ZnCl_2$, $AlCl_3$). The furfural was extracted by simple distillation and estimated calorimetrically. The residue left after the extraction of furfural was directly activated at 700°C to get active carbon. The adsorption efficiency of the resulting product was measured by using iodine and methylene blue.

Keywords: Saw dust, Furfural, Active carbon, Adsorption efficiency, Hydrolyzing agents, Salt catalysts, Pakistan.

INTRODUCTION

The level of progress and prosperity is associated with profitable specialization In agriculture and industry. Alarming increase in the industrial pollution and agro-wastes has challenged the experts to solve these problems through proper utilization of agro/industrial wastes to decrease pollution level and to get several economically important substances.

Pakistan is an agricultural country. A variety of agro-wastes are available which can be converted to several important chemicals like furfural and active carbon.

Furfural, belonging to furan family, is a five membered aromatic heterocyclic aldehyde having oxygen as hetero atom serving as ethereal linkage. The most recent and largest individual commercial role of furfural is as a chemical intermediate. It is a starting material of adiponitrile used in the manufacture of nylon. It is used as solvent in the refining of lubricating oils, separation of natural glyceride (fatty oils) into fractions and acetic acid recovery. It is also utilized for enhancing flavours in coffee. bread. beer., tobacco and pharmaceutical products.

Activated carbon is a powdered. granular and pelleted form of amorphous carbon characterized by very large surface area per unit volume, It is capable of adsorbing gases, liquids, or dissolved substances in solutions on the surface of its pores, selectively favouring non polar over polar substances. Compared with other commercial adsorbents, activated carbon has a broad spectrum of adsorptive activity, excellent physical and chemical stability and ease of production from readily available raw materials. Active carbon is useful for improving odour, taste and colour in potable water. beverages, sugar, proteins and different food products. It is used in nuclear reactors to adsorb radioactive gases. A number of successful attempts have been made by Chughtai *et al* (1989, 1990, 1992, 1996, 1999, 2000, 2001) to produce active carbon and furfural from various indigenous wastes. Present work is an extension of the previous efforts and it describes the optimal utilization of saw dust for the production of furfural and active carbon.

MATERIALS AND METHODS

Saw dust was collected from different saws in Faisalabad. It was sun dried for a week followed by oven drying at 105°C to a constant weight. The dried material was pulverized to a fine powder and was stored in a desiccator as a stock sample.

The stock samples (25 gram each) were refluxed with 75 ml. and 125mL HCl and H_2SO_4 for 100 and 140 minutes. respectively with and without added salt catalysts separately. The refluxed material was distilled and the furfural was extracted from the distillate. The extracted furfural was estimated colorimetrically by the method of Angel (1947). The residue obtained after the extraction or furfural was dried in an oven at 105°C and directly activated at 700°C for I hour in a muffle furnace, After cooling it to room temperature, it was ground to a fine powder. The active carbon thus prepared was checked for its adsorption efficiency using iodine and methylene blue index by a standard method (Beg and Usmani, 1985).

RESULTS AND DISCUSSION

Furfural

It is evident from Table I that furfural yield increased with increasing digestion period from 100 to 140 minutes at both concentrations of HCl in the prescence as well as in the absence of salt catalysts. Maximum yield of furfural (15,86%) was obtained with 16% HCl at 140 minutes in the presence of $ZnCl_2$ as catalyst. While the maximum yield of furfural (17.37%) with H_2SO_4 was obtained with 14% H_2SO_4 at 140 minutes digestion time using $AlCl_3$ as a catalyst.

Furfural yield increased by increasing acid concentration from 14% to 16% in case of HCl at all digestion times. But in case of H_2SO_4, it was observed that furfural yield increased with increasing acid concentration at 100 minutes except in case of 16% H_2SO_4 at 140 minutes. The decline in the furfural yield in case of 16%H_2SO_4 at 140 minutes may be due to the severe decomposition of the prpduct at longer digestion period in the presence of strong acid.

Table I. Comparison between average yield ('Yc,) of furfural and active carbon obtained from saw dust.

Catalysts	[illegible]	Acid	Digestion time (100 minutes)				Digestion time (140 minutes)			
			Solid Liquid ratio							
			1:3	1:3	1:5	1:5	1:3	1:3	1:5	1:5
			Yield of furfural (%)	Yield of active carbon (%)	Yield of furfural (%)	Yield of active carbon (%)	Yield of furfural (%)	Yield of active carbon (%)	Yield of furfural ('1..)	Yield of active carbon (%)
InCl$_c$	14	H_2SO_4	12,89	25.55	15.25	23.49	14.47	22.87	16.22	19.79
NaCI			13,65	24.22	15.86	[illegible]	14.62	21.09	16.53	20.33
Aiel;			14.83	22.27	16.84	20.02	15.55	20.15	17.37	18.78
Cae!$_2$			13.88	22.88	15.99	20.83	14.67	20.35	1686	19.13
Nil			11.22	28.5	13.23	26.10	11.78	2510	13IJ7	17.05
InCI,		HCI	9.18	34.71	1137	34.56	12.19	32,45	13.23	30.31
NaCI			8.86	37.13	11.05	35.10	/1.22	35.15	12.90	33.23
AICh			8.36	37.95	10.57	35.93	10.83	37.75	12.85	37.58
CaCI,			7.93	38.85	10,41	36.63	10.08	36.50	12,45	34.15
Nil			7.32	42.02	9.53	40.50	8.70	39.33	10.00	36.71
InCI,	16	H_2SO_4	15,45	22,48	16.63	19.33	10.16	19.10	12.52	18.92
NaCI			15.68	20.05	16.87	18.12	10.59	18.98	12.71	16.83
AIel;			16,47	18.47	17.22	16.29	11.72	16.81	14.23	15.93
CaCl,			16.16	19.84	16.36	17.83	10.88	18.10	1309	16.·1)
Nil			12,48	24.33	14.65	22.09	8.57	20.00	10.78	19.85
lnCI,		HCI	11.97	30.27	14.62	29.10	13.65	26.49	15.86	24,44
NaCI			11.78	31.90	13.93	29.65	12.97	27.16	14.92	25.0 I
AICI~			10.66	32.71	12.87	30.35	12.65	28.37	14.76	26.21
CaCl$_c$			10,46	33.90	12.17	31.73	I 1.98	29.90	13.82	27.93
Nil			10.26	35.55	10.48	33.49	10.65	32.27	12.21	29.22

The results obtained with different concentrations are in good agreement with the results obtained by Chughtai *et al.* (1985. 1(90) who observed that there was an increase in the yield of furfural with an increase in the acid concentration upto certain limit after which yield of furfural decreased.

Lower yields of furfural obtained at lower acid concentrations or H_2S0_4 may be due to incomplete hydrolysis of pentosans into pentoses, whereas. at higher acid concentration furfural yield seemed to be decreased due to destructive effect of concentration of acids or polymerization or chemical at low pH.

The catalysts showed remarkable positive effect on the percent yield or furfural at all experimental conditions shown in Table I. The maximum yield (15.86) of furfural was obtained with InC l_2 in case of HC I at all digestion times and acid concentrations. where as minimum yield (7.93) of furfural was obtained with $CaCI_2$. However in case of H_2S0_4 the maximum yield (17.37%) was obtained with AICI~ at all digestion limes and acid concentrations. where as minimum yield (10.16%) was obtained with lnCI,.

The data presented in table I shows that II,SO, furnished better percentage yields of furfural in the presence as well as in the absence of salt catalysts than IICI at all concentrations and digestion times proving it to be a better hydrolyzing agent as compared to HCI. This may be due to dehydrating nature of H_2S0_4. These results are in accordance with the results of Bains *et al.* (1977) who reported H_2SO_4 to be a better hydroiyzing agent than HCI.

Keeping in view the effect of solid liquid ratio on the yield of furfural. It is quite clear from the data given in table I that by increasing solid liquid ratio from 1:3 to 1:5 yield of furfural increased at all experimental conditions. This increase may be attributed to the fact that with lower solid: liquid ratio a direct contact between hydrolysing agent and carbonaceous material decreases thereby decreasing the yield. The results are in harmony to the findings of IJtomo (1970) who also noted an increase in furfural yield with an increase in solid: liquid ratio.

Comparing the effect of different acids (I!,S04 and IIel) at various concentration (14% and 16%), salt catalysts (NaC!, $AICI_J$, $CaCI_2$ $ZnCI_2$). digestion times (100 and 140 minutes) and various solid liquid ratios (1:3 and 1:5) it was observed that maximum furfural yield (17.37%) was obtained with 14% H_2S0_4 at 140 minutes with $AICI_J$ in the case of 1:5 ratio while the minimum furfural yield (7.32) was obtained with 14% Hel without any catalyst in 1:3 ratio. These results showed that H_2S0_4 is a promising hydrolyzing agent AICI, is better catalyst and 1:5 ratio is better than 1:3 ratio for the production of furfural. It was futher noted that furfural yield increased with the increase in digestion time from 100 to 140 minutes. with all concentration of Hel whereas in case of H"SO~ the furfural yield increased when digestion time was increased from 140 minutes with 14% H"SO~ while the yield of furfural slightly decreased with increasing digestion time with 16% H"S04 in the presence of salt catalysts.

Active Carbon

The residue left after the extraction of furfural from each experiment was activated at 700°C in the absence of air in a muffle furnace to get active carbon.

The average yield of active carbon decreased with increasing digestion time for both the acids with all catalysts (Table I). The maximum yield (42.02%) was obtained when the sample was hydrolyzed with 14% HCI for 100 minutes without any catalyst at 1:3 solid liquid ratio.

It is evident that the yield of active carbon decreased with increasing acid concentration with H_1S0_4, while the yield did not show any prominent difference with HCI.

The data in table I shows that in case of H"SO~ Zn'CI,- gave higher yields of active carbon while AICI, furnished the poor results. As for as HCI is concerned, maximum yield of activated carbon, i.e. (42.02%) was with 14% HCI without any catalyst. Moreover, all the four catalysts showed prominent positive effect on the yield than the yield obtained without any catalyst (Table I).

Results obtained regarding the effect of solid liquid ratio on the percentage yield of active carbon showed that higher percentage of active carbon were obtained at 1:3 solid liquid ratio for both the acids with catalysts

It is quite clear from the results that increase in acid concentration and digestion period resulted decrease in the percentage yield of the active carbon. Moreover, the catalysts improved the yield to a remarkable extent. Comparing the two acids it was noted that higher yields of active carbon were obtained with HCI as compared to H"SO~. Higher yield in case of HCI indicated that the raw material is less prone to decomposition or degradation with HCl as compared to H"S04 in 1:3 ratio.

The adsorption capacity of the prepared active carbon was evaluated with iodine and methylene blue (Beg and Usrnani, 1985). The results obtained are recorded in Table 2 for methylene blue and iodine. Commercial sample of active carbon (E. Merck) absorbed 663mg 1_1/g and 120mg methylene blue/g of active carbon.

Table 2: Comparison between average adsorption capacities expressed as mg of methylene blue and mg of iodine adsorbed by J g of active carbon.

[illegible]	[illegible]	Acid	Digestion time (J00 minutes)				Digestion time (140 minutes)			
			Solid Liquid ratio							
			1:3	1:3	1:5	1:5	1:3	1:3	1:5	1:5
			Methylene blue	Iodine	Methylene blue	Iodine	Methylene blue	Iodine	Methylene blue	Iodine
ZᴛCr,-	14	H"SO~	46	256.15	52	287.43	53	291.83	57	316.33
NaCI			48	266.20	53	291.85	54	296.21	58	321.55
AICI₁			50	277.35	59	326.98	56	310.10	61	336.47
CaCl1			49	271.72	55	302.88	55	305.17	59	327.97
Nil			[illegible]	181,87	39	216.48	35	191,41	41	225.26
lnCI"		HCI	32	177.88	39	214.48	38	208.95	42	233.05
NaCI			30	165.65	36	198.60	36	199.67	43	227.53
AICI,			31	164.95	35	192.95	35	190.35	39	214.58
CaCI"			28	155.71	34	188.75	33	182.82	38	210.59
Nil			24	132.76	29	161,37	26	144.65	28	155.82
lnCl1	16	H1S0~	58	318.45	63	349.75	60	332.85	68	373.41
NaCI			60	331.55	64	354.61	61	337.21	69	382.35
AICI,			64	353.23	69	380.21	64	354.66	75	415.95
CaCI"			61	336.05	65	359.22	62	341.45	70	385.95
Nil			42	233.35	49	271.73	47	259.17	53	293.64
lnCI"		HCI	40	222.37	48	266.20	46	253.77	51	281.74
NaCI			38	208.97	44	244.1 I	43	237.88	49	273.13
AICl,			37	205.42	43	237.58	43	238.51	47	260.60
CaCI"			37	204.50	42	233.00	41	226.63	46	255.05
Nil			30	166.74	34	189.10	30	165.15	36	196.89

(I g of commercial active carbon adsorbed 120mg of methylene blue and 663 mg of I")

Data pertaining to the effect of acid concentration on the adsorption capacity of active carbon revealed that adsorption capacity (for both methylene blue and iodine) increased with increasing acid concentration from 14% to 16% in the presence as well as in the absence of salt catalysts for both the acids. The increase in the adsorption efficiency of the product may be due to the evolution of oxidising gases at higher acid concentration, leaving the mass more porous. This is in accordance with the findings of Chughtai *et at.* (1989, 1990. 1993) who also reported that the adsorption capacity of active carbon increased with increase in acid concentration. The maximum adsorption capacity of active carbon for methylene blue (75mg/g) and iodine (415.95mg/g) were recorded with 16% H2S0~ in 1:5 ratio.

The results showed that the adsorption capacity of active carbon increased with increasing digestion time from 100 to 140 minutes. Maximum adsorption value for methylene blue (75mg/g) and iodine (415.95mg/g) was obtained at 140 minutes digestion period.

The results further indicated that the catalysts helped a lot in improving the adsorption capacity of active carbon. Without using the catalysts, the maximum adsorption capacity was found to be 53 mg/g of methylene blue and 293.64 mg/g of iodine with 16% H_2S0_4 whereas the active carbon prepared with the same acid and concentration adsorbed 75 mg/gof methylene blue and 415.95 mg/g of iodine in the presence of AICI, as catalyst under identical conditions of concentration and digestion times. Moreover, AICI, was found to be the best catalyst when used with both H2S0~ and HCI.

The results also revealed that adsorption efficiency of active carbon is greater at 1:5 solid to liquid ratio than at 1:3 for almost all the catalysts and acids. This may be due to the reason that at 1:3 ratio less amount of hydrolysing agent was unable to cause the complete activation of the product..

It is obvious from the results that the maximum adsorption capacity of active carbon for methylene blue and iodine *(75mg/g* and 415.95 mg/g, respectively) was with 16% H2S0~ with AICI, as a catalyst at 140 minutes digestion time with 1:5 solid liquid ratio. Samples obtained with H_2S0_4 at 1:5 ratio gave higher adsorption of iodine and methylene blue at all concentrations and digestion times proving H_2S0_4 to be a better activating agent as compared to HCI and 1:5 ratio better than 1:3 ratio. Among the catalysts, the samples treated with AICI, gave better results than the other catalysts proving AICI, to be the best activating catalyst..

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