

EFFECT OF METAL CHLORIDES ON THE YIELD AND QUALITY OF FURFURAL AND ACTIVE CARBON FROM CORN COBS

Arfa Sadaf, Fiyyaz Ahmad Chughtai, Zill-i-Huma Nazli & Nadia Jamil
Department of Chemistry, University of Agriculture, Faisalabad

This study was undertaken to determine the optimal utilization of corn cobs for the production of furfural and active carbon by digesting them with various hydrolyzing acids, in the presence of added metal chlorides. Corn cobs were refluxed with various concentrations of H_2SO_4 and HCl separately for 100 and 140 minutes in the presence of added metal chlorides ($NaCl$, $CaCl_2$, $AlCl_3$, and $ZnCl_2$). The refluxed material was distilled and furfural was extracted from the distillate. The maximum furfural yield was obtained with 14% H_2SO_4 and $AlCl_3$ at 140 minutes digestion time. The residue left after the extraction of furfural was activated directly at 700°C for one hour for the production of active carbon. The maximum yield of active carbon was obtained with 14% HCl at 100 minutes digestion time with $CaCl_2$. The active carbon was evaluated for its adsorption capacity using iodine and methylene blue by standard methods. The maximum adsorption capacity of active carbon for methylene blue and iodine was obtained with 16% H_2SO_4 with $AlCl_3$ at 140 minutes digestion.

Key words: active carbon, adsorption capacity, corn cob, furfural, metal chlorides

INTRODUCTION

Furfural—a five-membered heterocyclic aldehyde, is a degradation product of hemicellulose constituent of the plants. Hemicellulose is made up of chains of complex sugars called pentosans which can be easily hydrolyzed to pentoses. These are readily converted into furfural by acid hydrolysis in a complex process. Active carbon is a powdered, granular or pelleted form of amorphous carbon characterized by a very large surface area per unit volume. Any cellulosic and carbonaceous material of fossil fuel on carbonization and activation in the absence of air yields active carbon. A number of successful attempts have been made here to produce active carbon and furfural from various indigenous wastes. Among these are Kat, Sawdust, Bagasse, Sarkanda, Khabble grass, Pahari Kikar, Dhabb, etc. (Chughtai et al. (1986, 1987, 1989, 1990, 1991, 1993, 1996).

After wheat and rice, corn is the most important cereal grain in the world providing nutrients for humans and animals. A number of chemicals such as furfural, active carbon, xylose, etc. can be prepared from corn cobs. The present study was an extension of the previous work and it described the optimal utilization of corn cobs for the production of furfural and active carbon by digesting them with various hydrolyzing acids. However, the present work involved the addition of various metal chlorides along with hydrolyzing acids during digestion. The addition of metal chlorides improved the yield as well as the quality of the products.

MATERIALS AND METHODS

Corn cobs were collected from the Rafhan Maize Products Co. Ltd. Faisalabad. These were first sun-dried followed by oven drying at 105°C to a constant weight. The dried material was pulverized to a fine mesh and stored in a desiccator as stock samples. The stock samples (50 g each) were refluxed with 500ml of various concentrations (14%

and 16%) of H_2SO_4 and HCl for different time periods (100 and 140 minutes) with 2% added metal chlorides such as $NaCl$, $CaCl_2$, $ZnCl_2$, and $AlCl_3$. The refluxed material was distilled to get furfural which was extracted from the distillate and estimated colorimetrically by the method of Chuulua: et al. (1986). The residue left after the production of furfural was activated directly at 700°C for one hour to get active carbon. The carbonized mass was cooled to room temperature and then ground to a fine mesh. Adsorption efficiency of the resulting activated carbon was then tested by methylene blue and iodine decolourizing index using standard methods (Beg and Usmani, 19X5). The data thus obtained were analyzed using analysis of variance technique as described by Steel and Torrie (1984).

RESULTS AND DISCUSSION

The furfural yield obtained with H_2SO_4 and HCl having different concentrations and for different digestion periods, using various metal chlorides is shown in Table I. The study revealed that with increasing digestion time and acid concentration, furfural yield first increased up to a certain limit and then declined. These results are in accordance with the results of Chughtai et al. (1986, 19X9). The study showed that the maximum yield of furfural was obtained with $AlCl_3$ in case of H_2SO_4 at both concentrations and digestion times, and with $ZnCl_2$ in case of HCl . It was observed that the maximum yield of furfural (17.X%) was obtained with 14% H_2SO_4 at 140 minutes digestion time with $AlCl_3$. The yield of furfural in this study was higher than that of the previous study when the sank raw material was hydrolyzed using the same concentrations of these two acids at different digestion times but without added metal chlorides (Nusrat, 1997). This increase in yield of furfural appeared to be due to the addition of metal chlorides.

The results of average percentage yield of active carbon have been presented in Table 2. Yield of active carbon decreased with increasing digestion period and with increasing concentration of both the acids. The maximum yield of active carbon in case of H_2SO_4 was obtained with $AlCl_3$, while in case of HCl it was with $CaCl_2$. It was observed that the maximum yield (32.0%) was obtained with 14% HCl at 100 minutes digestion time with $CaCl_2$. Yield and quality of active carbon in this study is better than that of the previous study when the same raw material was hydrolysed using different concentrations of acids for different digestion times without adding metal chlorides (Nusrat, 1997). This again seemed to be due to the addition of metal chlorides.

The adsorption capacity of active carbon evaluated with iodine and methylene blue is given in Tables 3 and 4. The adsorption capacity of each sample was compared with the adsorption capacity of commercially available sample (E-Merck) having values 663 mg iodine/g and 120 mg methylene blue/g of active carbon. The adsorption capacity of the active carbon increased with increasing digestion time. This is in accordance with the findings of Chughtai et al. (1989, 1990, 1993). However, adsorptive power of the product increased with increasing concentration of both the acids. The maximum adsorption capacity was obtained with $AlCl_3$ in case of H_2SO_4 and with $ZnCl_2$ in case of HCl . It is obvious from the results that the maximum adsorption capacity of active carbon for methylene blue and iodine was 65.00 and 368.78 mg/g respectively, obtained with 16% H_2SO_4 with $AlCl_3$ at 140 minutes. It may therefore be stated that 16% H_2SO_4 in the presence of $AlCl_3$ (2%) is a better hydrolyzer/activator.

Table 1. Comparison between average yield (%) of furfural at various concentrations of H_2SO_4 and HCl , digestion periods and metal chlorides

Metal chloride (2%)	Acid Cone.	Acid used	Digestion time in minutes	
			100	140
NaCl	14%	H_2SO_4	15.35	17.50
$CaCl_2$			15m	17.25
$AlCl_3$			15.46	17.80
$lnCl_2$			14.75	17.m
NaCl	14%	HO	11.11	13.50
$CaCl_2$			11.m	13.00
$AlCl_3$			11.25	13.25
ZnO			11.35'	13.75

NaO	16%	H_2SO_4	11.50	125.
$CaCl_2$			10.30	12.73
$AlCl_3$			10.XO	12.12
ZnO			15X5	12.10
NaO	16%	HO	11.1	1.7
$CaCl_2$			11.50	1.71
$AlCl_3$			11.X	1.70
$lnCl_2$			12.m	1.15

Table 2. Comparison between average yield (%) of active carbon at various concentrations of H_2SO_4 and HCl , digestion periods and metal chlorides

Metal chloride (2%)	Acid Cone.	Acid used	Digestion time in minutes	
			111	1-11
NaO	14%	H_2SO_4	1X,7	15.1
$CaCl_2$			11.7	11.7
$AlCl_3$			175	1-1A
$lnCl_2$			21.11	17.0
NaO	14%	HO	11.14	2KX
$CaCl_2$			11.0	2.1
$AlCl_3$			11.0	28.1
$lnCl_2$			10A	2(d
NaCl	16%	H_2SO_4	11.1	11.1
$CaCl_2$			11.4	11.0
$AlCl_3$			12.0	10.7
$lnCl_2$			1-10	11.8
NaCl	16%	HO	11X	2U
$CaCl_2$			25.5	22.5
$AlCl_3$			2-10	22.0
$lnCl_2$			23.1	20.X

Table 3. Comparison between average adsorption capacities expressed as mg of iodine adsorbed by 1g active carbon (powder form) obtained from residue left after distillation with commercial H_2SO_4 and HCl , at 700°C

Metal chloride (2%)	Acid Cone.	Acid used	Digestion time in minutes	
			11111	1411
NaO	14%	H_2SO_4	21157X	287.20
$CaCl_2$			21110	28175
$AlCl_3$			211712	211210
$lnCl_2$			25120	27K3-1

Yield and quality of furfural and active carbon

NaCl		Ha	195.12	202.56
CaC~		Ha	193.30	200.73
Ala,		Ha	196.85	205.75
ZE0,		Ha	198.34	20734
NaCl		H ₂ SO ₄	330.12	357.63
Can		H ₂ SO ₄	322.63	362.20
AlCl ₃		H ₂ SO ₄	335.30	368.78
lnCl ₂		H ₂ SO ₄	32157	353,17
NaG	16%	Ha	223,12	242.90
eaq	16%	Ha	219,12	239.50
AlCl ₃	16%	Ha	225.59	238.50
lnCl ₂	16%	Ha	226.63	247.85

Standard adsorption capacity of active carbon
(E. Merck) = 663 mg iodine/g.

Table 4. Comparison between average adsorption capacities expressed as mg of methylene blue adsorbed by 1g active carbon (powder form) obtained from residue left after distillation with commercial "2S04 and HCl, at 700°C

Metal chloride (%)	Acid Cone.	Acid used	Digestion time in minutes	
			100	140
NaG	14%	H ₂ SO ₄	50	58
CaCl ₂			49	56
AlCl ₃			52	59
ZOO,			48	55
NaCl	14%	Ha	26	31
Caq			25	30
AlCl ₃			27	32
ZE0,			29	33
NaO	16%	H ₂ SO ₄	61	64
CaCl ₂			61	64
AlCl ₃			62	65
lnCl ₂			60	63
NaCl	16%	Ha	36	45
CaC~			35	43
AlCl ₃			37	44
lnCl ₂			39	46

Standard adsorption capacity of active carbon
(E. Merck) = 120 mg methylene blue/g.

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