

UTILIZATION OF PERICARP OF PEANUT (*Arachis hypogea*) FOR THE PRODUCTION OF FURFURAL AND ACTIVATED CARBON

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Carbonaceous materials can effectively and efficiently be converted into furfural and active carbon. For the present research work pericarp of peanut was hydrolyzed with 16% HCl and H₂SO₄ to produce furfural keeping solid-liquid ratio at 1:5, 1:8 and 1:10 for 100 and 140 minutes in the presence of salt catalysts (CaCl₂, ZnCl₂, AlCl₃ and NaCl). The residue left after the extraction of furfural was activated at 700°C to produce active carbon. Maximum yield of furfural and active carbon was 12% and 37%, respectively. For the evaluation of adsorption efficiency of prepared active carbon, iodine and methylene blue indices were used. Maximum value of adsorption efficiency with methylene blue and iodine was 48mg/g and 265mg/g of active carbon respectively.

Key words: Furfural, active carbon, pericarp of peanut, adsorption capacity, hydrolyzing agents, Pakistan.

INTRODUCTION

Investigations related to the effect of chemicals on flora, fauna, and the environment have focused almost exclusively on identifying their effects on human beings. As a result, environmentalists have selected natural resources that are particularly valued for food, shelter, medicine, recreation, or other uses. Only in the last few decades relationships have been recognized between these critical natural resources used for the production of valuable chemicals such as furfural and active carbon. The production of these chemicals also solved the problem of environmental pollution.

Furfural (an industrial solvent) is a colourless, inflammable, volatile, aromatic liquid (Vedernikov *et al.* 1993). It is used mainly as a selective extracting solvent in the lubricating oil of the petroleum industry. It is also used in polymer industry and takes part in the production of nylon 66 and resins used for moulding powders (Ali *et al.*, 2002). It is employed as an additive in syrup industry.

An amorphous form of carbon with high adsorption efficacy is called active carbon (Vila *et al.* 2002). Activated carbon removes organic and inorganic contaminants from water. Printing industry uses activated carbon to recover solvents. It is used in the production of consumer products such as water, sugar, wine, soup, gelatin and vinegar (Ahmedna *et al.* 1997). Pharmaceutical industry uses highly pure activated carbon, e.g. in the purification of vitamins and paracetamol.

A number of successful attempts have been made to produce furfural and active carbon from dhabb (*Typha angustata*), saw dust, corn cobs and bagasse (Chughtai *et al.*, 2000, 2001). In a quest for better raw material, present study was designed to produce furfural and active carbon by chemical treatment of pericarp of peanuts. Local production of these chemicals will not only solve the problem of waste treatment but will also save the foreign exchange spent on their import.

MATERIALS AND METHODS

Collection of raw materials:

The raw material (pericarp of peanut) was collected from Railbazar, Tandlianwala as well as dry fruit market Railbazar, Faisalabad.

Preparation of stock sample:

The material was sun dried for five days followed by drying at 110°C in a electric oven to constant dry weight. After grinding (2mm mesh) the dried material was stored in a desiccator as a stock sample.

Preparation of Furfural:

Stock samples (50g each) were refluxed with 16% (v/v) hydrochloric acid (commercial) and sulfuric acid (commercial) separately in various volumes (250cm³, 400 cm³ and 500 cm³) for 100 and 140 minutes in the presence of salt catalysts, i.e., ZnCl₂, CaCl₂, NaCl, AlCl₃. Control in each series of experiment (without salt catalyst) was also run. Simple distillation of the digested samples was carried out in round bottom flask of capacity, one litre. The process was continued until the distillate gave negative test with aniline acetate. The extracted furfural was estimated colorimetrically according to Angel (1947)

Preparation of Active Carbon:

The residue left after the extraction of furfural was used directly for the preparation of active carbon. The residue obtained from each treatment was air dried and activated in the absence of air for one hour in a muffle furnace at 700°C. It was then allowed to cool, weighed and ground to a fine powder (2mm).

Adsorption efficiency

Quality of prepared active carbon was checked by methylene blue and iodine index according to Beg and Usmani (1985). Active carbon was packed in plastic bottles and stored in a desiccator.

Table 1: Yield of furfural from the reaction of furfural with various catalysts at different solid liquid ratios.

Acid	Catalysts	Solid liquid ratio											
		1:5		1:8		1:10		1:5		1:8		1:10	
		Yield of furfural (%)	Yield of furfural (%)	Yield of furfural (%)	Yield of furfural (%)	Yield of furfural (%)	Yield of furfural (%)	Yield of furfural (%)	Yield of furfural (%)	Yield of furfural (%)	Yield of furfural (%)	Yield of furfural (%)	Yield of furfural (%)
16% H ₂ SO ₄	NaCl	3.7	4.5	8.2	3.3	23	4.8	7	30				
	CaCl ₂	3.2	3.6	7.8	3	22	3.4	23.8	6.7	27			
	ZnCl ₂	5.5	6.2	10	5.2	23	6	26	9	30			
	AlCl ₃	4.7	5.6	12	4.5	22	5.4	23	8.7	27			
	Nil	2.7	3.5	4.5	3	18	3.6	22	5.8	20			
16% HCl	NaCl	3.5	3.9	5.5	3.7	19	4.2	24	34				
	CaCl ₂	3	3.5	3.9	3.4	18	3.7	23	4.5	20			
	ZnCl ₂	5.3	5.9	6.7	7	22	9	24	11	28			
	AlCl ₃	4.2	5.2	6.9	6	20	7.5	24	30	28			
	Nil	2.5	3.2	3.7	3.4	17	3.7	20	24	24			

The yield of furfural increases with the increase in the solid liquid ratio for all catalysts. The highest yield was observed for ZnCl₂ at a solid liquid ratio of 1:10, which was 30%.

Acid	Catalysts	Solid liquid ratio											
		1:5		1:8		1:10		1:5		1:8		1:10	
		Yield of furfural (%)	Yield of furfural (%)	Yield of furfural (%)	Yield of furfural (%)	Yield of furfural (%)	Yield of furfural (%)	Yield of furfural (%)	Yield of furfural (%)	Yield of furfural (%)	Yield of furfural (%)	Yield of furfural (%)	Yield of furfural (%)
16% H ₂ SO ₄	NaCl	3.7	4.5	8.2	3.3	23	4.8	7	30				
	CaCl ₂	3.2	3.6	7.8	3	22	3.4	23.8	6.7	27			
	ZnCl ₂	5.5	6.2	10	5.2	23	6	26	9	30			
	AlCl ₃	4.7	5.6	12	4.5	22	5.4	23	8.7	27			
	Nil	2.7	3.5	4.5	3	18	3.6	22	5.8	20			
16% HCl	NaCl	3.5	3.9	5.5	3.7	19	4.2	24	34				
	CaCl ₂	3	3.5	3.9	3.4	18	3.7	23	4.5	20			
	ZnCl ₂	5.3	5.9	6.7	7	22	9	24	11	28			
	AlCl ₃	4.2	5.2	6.9	6	20	7.5	24	30	28			
	Nil	2.5	3.2	3.7	3.4	17	3.7	20	24	24			

RESULTS AND DISCUSSION

Yield of furfural: Percentage yield of furfural obtained with HCl and H₂SO₄ in the presence of various salt catalysts at different digestion times, acid concentrations and solid liquid ratios is recorded in Table 1.

Maximum yield of furfural with 16% H₂SO₄ and HCl was 12% and 11% in the presence of AlCl₃ and ZnCl₂ as catalysts, respectively (Table 1). Sulfuric acid furnished better percentage yields of furfural than HCl at both digestion times and solid-liquid ratios with a few exceptions proving it to be a better hydrolyzing agent as compared to HCl in the presence as well as absence of added salt catalysts. This effect may be attributed to the dehydrating nature of H₂SO₄.

Maximum yield (12%) of furfural was obtained with 16% H₂SO₄ at 100 minutes digestion time in the presence of AlCl₃ as a catalyst keeping solid-liquid ratio 1:10. Taking into consideration the effect of digestion period, it is evident from Table 1 that furfural yield increased with increasing digestion period at all concentrations of HCl keeping all other factors constant. The maximum yield (11%) of furfural with HCl as hydrolyzing agent was obtained with 16% HCl at 140 minutes in the presence of ZnCl₂ as catalyst. However, in case of H₂SO₄ yield decreased with increasing digestion time from 100 to 140 minutes as maximum yield (12%) was obtained at 100 minutes digestion time with AlCl₃ as a catalyst. This may be due to the reason that longer digestion time either caused degradation or polymerization of the product with H₂SO₄.

The results are in good agreement with the results obtained by Chughtai *et al.* (1986) who observed that there was an increase in the yield of furfural with an increase in the digestion time for HCl and 100 minutes digestion time was proved to be best when H₂SO₄ was used after which yield of furfural decreased.

Keeping in view the effect of various salts added as catalysts, it can be seen from table 1 that catalysts have remarkable positive effect on the percentage yield of furfural with both the acids at all digestion times and solid liquid ratios. Aluminum chloride gave the highest percentage yield (12%) of furfural in case of H₂SO₄ while ZnCl₂ furnished maximum yield of furfural (11%) when HCl was used as hydrolyzing agent. The results are in good agreement to those of Chughtai *et al.* (1986) who found ZnCl₂ to be a promising salt catalyst with kai as a raw material. It was also clear from the data that better percentages of furfural are obtained in the presence of all the catalysts under all experimental conditions as compared to the samples when no catalyst was used (Table 1).

Yield of Active Carbon: Results presented in Table 1 indicate that yield of active carbon increased with increasing digestion time from 100 to 140 minutes with

few exceptions where either the yield remained unchanged or decreased for both the acids and solid; liquid ratios. Yield also increased with increasing solid liquid ratio from 1:5 to 1:8 and then to 1:10. Maximum active carbon was thus obtained at 1:10 solid liquid ratio for both the acids. Catalyst were also very effective in increasing the percentage yield, except for NaCl when 16% HCl was used keeping solid liquid ratio 1:5. Comparing the catalytic activity it was observed that CaCl₂ furnished maximum yield at 100 minutes digestion time and 1:5 and 1:8 solid liquid ratio, whereas AlCl₃ gave maximum yield at 1:10 solid liquid ratio. However, ZnCl₂ was more effective at 140 minutes digestion time under all sets of conditions. Comparing the two acids it was observed that HCl as compared to H₂SO₄ gave higher percentages of active carbon under all sets of conditions with few exceptions proving HCl to be a better hydrolysing agent. Maximum percentage yield of active carbon (37%) was obtained when the raw material was hydrolyzed for 100 minutes with 16% HCl in the presence of AlCl₃ as catalyst keeping solid liquid ratio 1:10.

Adsorption efficiency: Maximum adsorption efficiency was shown by the sample obtained with AlCl₃ at 140 minutes with 16% H₂SO₄ keeping solid liquid ratio 1:10. However, average results were better for ZnCl₂ than with AlCl₃ at both digestion time using HCl and H₂SO₄ (Table 2).

Active carbon obtained from H₂SO₄ hydrolysis- gave higher adsorption of methylene blue and iodine as compared to HCl under all sets of conditions. Maximum adsorption capacity in terms of methylene blue and iodine (48 mg/g and 265 mg/g, respectively) was obtained with 16% H₂SO₄ using AlCl₃ as catalyst at 1:10 solid liquid ratio.

Maximum adsorption capacity 48 mg/g for methylene blue and 265 mg/g for iodine with H₂SO₄ was obtained when AlCl₃ was used at 140 minutes keeping 1:10 solid liquid ratio. This increase in adsorption capacity of active carbon in the presence of AlCl₃ is in good agreement with the results of Nazli *et al* (1998) who reported AlCl₃ as a better salt catalyst.

The adsorption capacity of active carbon decreased with decreasing solid:liquid ratio according to the data presented in Table 2. Maximum adsorption capacity for methylene blue (48 mg/g) and iodine (265 mg/g) was obtained at 1: 10 solid:liquid ratio. This may be due to the reason that at lower solid:liquid ratio less amount of the hydrolyzing agent was unable to cause the complete activation of the product.

Taking into consideration the effect of digestion period, it is evident that increasing digestion time, increased adsorption capacity under all experimental conditions. We conclude that production of furfural and active carbon from agro waste not only reduces environmental pollution but also cater to the need of our industries.

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