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UTILIZATION OF HAZELNUT HUSKS, TEA AND TOBACCO WASTES, AS RAW MATERIALS

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ABSTRACT

In this study, moisture, ash, oil and cellulose of hazelnut husks, tea and tobacco wastes were analyzed. The amounts of pentosan, pentose and furfural were determined in the hazelnut husks, tea and tobacco wastes. Furfural was produced from each three waste products by a steam distillation method. IR spectra of each furfural product were measured and compared with standard furfural. Activated carbon prepared from the hazelnut husks at the different temperature, and organic and inorganic pollutants were removed by using the adsorbent obtained from hazelnut husk.

Key Words : Furfural production, Agricultural waste, Hazelnut husks

FINDIK KABUKLARININ, ÇAY VE TÜTÜN ATIKLARININ HAMMADDE OLARAK KULLANILMASI

ÖZET

Bu çalışmada, fındık kabukları, çay ve tütün atıklarındaki nem, kül, yağ ve sellüloz miktarları analiz edilmiştir. Ayrıca, fındık kabukları, çay ve tütün atıklarının içerdiği pentosan, pentos ve furfural miktarları belirlenmiştir. Furfural her üç atıktan destilasyon metoduyla ayrılmıştır. Atıklardan ayrılan furfural örneklerinin IR-spektrumları ile standart furfuralin IR-spektrumları karşılaştırılmıştır. Fındık kabuklarından farklı sıcaklıklarda aktif karbon elde edilmiştir. Bu aktif karbon kullanılarak organik ve anarganik atıklar adsorbsiyonla uzaklaştırılmıştır.

Anahtar Kelimeler : Furfural üretimi, Tarımsal atık, Fındık kabuğu

1. INTRODUCTION

Furfural is one of the most widely used solvents in the refining of lubricating oils as it is very effective in removing compounds containing oxygen or sulfur. It is also used as a feedstock in the production of furfuril alcohol tetrahydrofuran and furan resins (Coca and Diaz, 1980).

The production of furfural from agro-wastes has been known since 1830 when Döbereiner discovered furfural and was extensively reported in the literature. Every material containing pentosan is the source of furfural. Furfural is produced by hydrolysis to xylose of pentosans contained in wastes such as corncobs, rice hulls and hazelnut husks and other products, followed by dehydration of xylose to furfural. Among the most common catalyst employed in these reactions are acids (e.g. sulfuric, hydrochloric and phosphoric). Pentosan is a polysaccharide and gives pentoses after hydrolysis. Xylose is the most known pentose, which gives furfural by losing 3 moles of water (Duffey and Wells, 1955; Demirbaş, 1984; Mc Ketta, 1985; Sayılkan and Çetinkaya, 1991).

$$(C_5H_8O_4)_n + nH_2O \longrightarrow nC_5H_{10}O_5 \xrightarrow{-3nH_2O} nC_5H_4O_2 \quad (1)$$

Pentosan Pentose Furfural

It is possible to produce furfural using by some wastes of agriculture. The quality and availability of waste materials are important as well as collection, transport and handling. Collection, transport and handling pose measure problems and influence the economic viability of sources of raw materials. Therefore many researches have studied on the production of furfural using different raw materials (Duffey and Wells, 1955; Mc Ketta, 1985).

The hazelnut production is about 250 000 tons/year in Turkey. Whereas hazelnut husks which is 44-50 % of hazelnut is an important chemical raw material. Hazelnut husks are consumed as combustibles in the Black Sea region. Furfural and glucose are obtained as hydrolysis products; solid, liquid and gas products are obtained as prolysis products; oil is obtained as an extraction product from hazelnut husks (Onay et all., 1996). Active carbon is obtained from lignin of hazelnut husks (Güzel and Tez, 1993). Turkish hazelnut husks (Corylus Avellana type, Giresun) was examined by (Aşık et all., 1977). They obtained furfural and active carbon from the hazelnut husks. They also examined carbonization of the hazelnut husks.

The production wet tealeaves is about 600 000 ton/year in Turkey. The total black tea production is about 3-4 % of the wet tea leaves. A lot of chemicals such as caffeine, tannins, pectin, cellulose and coloring matter can be produced from tea waste. Tea seed oil can be used for edible purposes and is very similar to olive oil in composition. Caffeine, which has a percentage of 1.5-2.0 % in tea waste, is an important chemical in food and chemical industry (Yazıcıoğlu et all., 1977).

After China, India and Brazil, Turkey is the fourth country in tobacco production which is about 180 000 ton/year. Tobacco is consumed as cigarette, cigar, pipe, water pipe and chewing tobacco. Nicotine, which has a percentage of 1.0-1.5 % in tobacco waste, is an important chemical in the agricultural chemicals.

Activated carbons are used in treatment systems for adsorption and chemical recovery operations. Activated carbons can be produced from a number of raw materials such as coal, peat, agricultural wastes and these materials are exposed to various activation methods to produce activated carbon and adsorbent with the best qualities for different applications.

In our study, hazelnut husks, tea and tobacco wastes were chosen as raw materials to produce furfural. Hazelnut husks were also chosen to produce activated coal because of availability in our country and desirable physical characteristics as activated carbon precursors. Especially, tobacco and tea wastes can be regarded to have a negative value since they represent a waste disposal problem. Chrome and cobalt waste salts were chosen as inorganic pollutants and phenol, 4-choloro phenol, 2-4-diclorophenol, p-toluene sulphonic acid wastes were chosen as organic pollutant.

The aim of this study is to produce furfural by using some agricultural residues in our country. The second aim of this study is to produce activated coal for treatment systems.

2. MATERIALS AND METHODS

All the chemicals used in this study were obtained from Merck. Co. The hazelnut husks samples used in this study is *Corylus maxima Miller* (Foşa) type, which was brought from Trabzon (Araklı) in 1995, 1996 and 1997. All hazelnut fruits were picked up from trees during the first half of September. Hazelnut husks were stored at 4 °C and 60-65 % relative humidity. Tea wastes (by-product) were brought from Çay-Kur factories in Rize 1997 and tobacco wastes (by-product) were from Tekel cigarette factory in Samsun in 1997. Hazelnut husks were sieved in vibration sieves after being grind in a ball mill, and particles having a dimension of average 1.3 mm were used in this study. Tea and tobacco wastes, also sieved, and an average of 1.3 mm of particles were used in the experiments.

2. 1. Water content

Moisture was determined by weight loss after heating in an oven at 105 °C in accordance with AOAC method (Anon., 1965).

2. 2. Ash content

Ash content was determined by overnight heating at 550 °C in accordance with AOAC method (Anon., 1980).

2. 3. Cellulose content

Determination of cellulose was performed by gravimetric method, in accordance with AOAC method (Anon., 1990).

2. 4. Oil extraction

The samples (10 g) were extracted with hexane extraction for 6 h using Soxhlet apparatus. Oil was determined as the difference in weight of dried samples before and after extraction (Anon., 1980).

The experimentally determined chemical properties of the hazelnut husks and literature values are given in Table 1. The experimentally determined chemical properties of the tea and tobacco wastes are given in Table 2.

Table 1. The Average Values ($\bar{x}$) of Chemical Properties of Hazelnut Husks for Different Three Years Corp. (1995/1996 and 1997) and Their Comparison With Literature Values (%)

Analysis	Determined Values ($\bar{x}$)	Literature Values (Aşık et all., 1977)
Moisture	11.58	10-12
Ash	0.96	1.26
Oil	1.69	1.56
Cellulose	22.55	22.20
Heating value (cal/g)	4597	4410
Pentosan	25.13	25.30
Pentose	28.62	28.75
Furfural	14.53	14.80

2. 5. Determination of the Amounts of Pentosan, Pentose and Furfural

10 g sample was put in a 1 litter three necked-flask with 100 ml HCl (12 W/W %), mixed and heated until 360 ml distillate was collected. The heating rate was regulated by a variac. 300 ml HCl was dropped slowly from a dropping funnel into the flask to keep the flask's volume constant. The acidic solution of floroglusin (HCl 12 W/W %) and the distillate were mixed in a flask. After 14 hours, the furfural-floroglusin derivative was filtered from 1 G4 Nordan crucible, and the amounts of pentosan, pentose and furfural were calculated from this furfural-floroglusid derivative (Goldstein, 1981; Sayılkan, and Çetinkaya, 1991). The amounts of pentosan, pentose and furfural of the hazelnut husks are given in Table 1. The amounts of pentosan, pentose and furfural of the tea and tobacco wastes are given in Table 2.

Table 2. The Average Values ($\bar{x}$) of the Chemical Properties of tea Waste and Tobacco Waste (%), in 1997

Analysis	Tea Waste ($\bar{x}$)	Tobacco Waste ($\bar{x}$)
Moisture	6.54	12.06
Ash	4.89	20.77
Oil	1.13	2.83
Cellulose	20.05	19.62
Pentosan	11.83	7.70
Pentose	13.44	8.61
Furfural	6.91	4.90

2. 6. Production of furfural by distillation method

100 g sample was mixed with 475 ml H_2SO_4 (2.90 M) in a 1 litter flask. Upon the distillation of this mixture, 360 ml of distillate was collected. After saturating the distillate with NaCl, it was redistilled and 235 ml of the distillate was collected. This product was saturated with NaCl and furfural was extracted with 30 ml ether. After drying the organic phase by Na_2SO_4, ether was separated. Furfural was distilled by fractional distillation.

2. 7. Preparation of activated carbon from hazelnut husks

The active carbon was prepared from hazelnut husks by using N_2 and CO_2. 30 gram crushed samples with particle size of 1.3 mm were subjected to carbonization at 400 °C, 500 °C and 600 °C with a period of times for 1, 2 and 3 hours at each temperature. The products obtained from carbonization process were activated by CO_2 at 850 °C. The surface area of the products was measured by N_2 adsorption method (Monosorb Quanta Chrom). The values of surface area are given in Table 3.

Table 3. The Surface Area of Activated Carbon Samples at the Different Temperatures

Carbonization Time (hour)	Surface (m^2/g) (400 °C)	Surface (m^2/g) (500 °C)	Surface (m^2/g) (600 °C)
1	510	580	610
2	595	650	670
3	625	690	720

2. 8. Adsorption Experiments

Adsorption studies were performed by placing fixed amount of adsorbent in 100 cm^3 of solution containing inorganic or organic pollutant at different concentration. The solutions were shaken to reach equilibrium at 20 °C. The adsorbent and adsorbate were separated by centrifugation at 6000 $rev.min^{-1}$ for 8 minutes. Concentrations of the solutions were determined spectrofotometerically.

3. RESULTS AND DISCUSSION

In this study, moisture, ash, oil and cellulose of hazelnut husks, tea and tobacco wastes were analyzed. The amounts of pentosan, pentose and furfural were determined in the hazelnut husks, tea and tobacco wastes. Aşık et all., (1997) reported that the chemical properties of hazelnut husks (Corylus Avellena type). Similar chemical properties were found for the hazelnut husks (Corylus Maxima miller type). Experimental results and literature values of the hazelnut husks were given in Table 1. Chemical properties of the Turkish tea and tobacco wastes have not previously been reported in anywhere. In this work the amount of moisture, ash, oil, cellulose, pentosan, pentose and furfural values are determined and listed in Table 2. The percentage of the cellulose of the hazelnut husks seems to be almost the same with cellulose of the tea and tobacco wastes. The percentage of pentosan, pentose and furfural of the hazelnut husks is two times more than found in tea waste and three times more than in tobacco waste. The percentages of ash of the tea and tobacco wastes are found to be four times more and twenty times more than hazelnut husks respectively. These are given in Table 1 and Table 2.

The IR spectra of the furfural samples were measured with Unicom Mattson 1000 FT IR Spectrometer and compared with standard IR spectra of furfural (Figure 1). Aromatic C-H bands at 3130.77 (cm^{-1}), aliphatic C-H bands at 2853.85-2930.77 (cm^{-1}), C = O bands at 1676-1684.62 (cm^{-1}) and substitute aromatic bands 761.54-769.23 (cm^{-1}) were determined from each three spectra.

The boiling point of the furfural samples was measured as 158-159 ^{0}C (literature value = 161 ^{0}C); melting point of 2.4-Dinitro phenyl hydrazone derivatives was 227 ^{0}C (literature value = 229 ^{0}C) (Shriner et all., 1980).

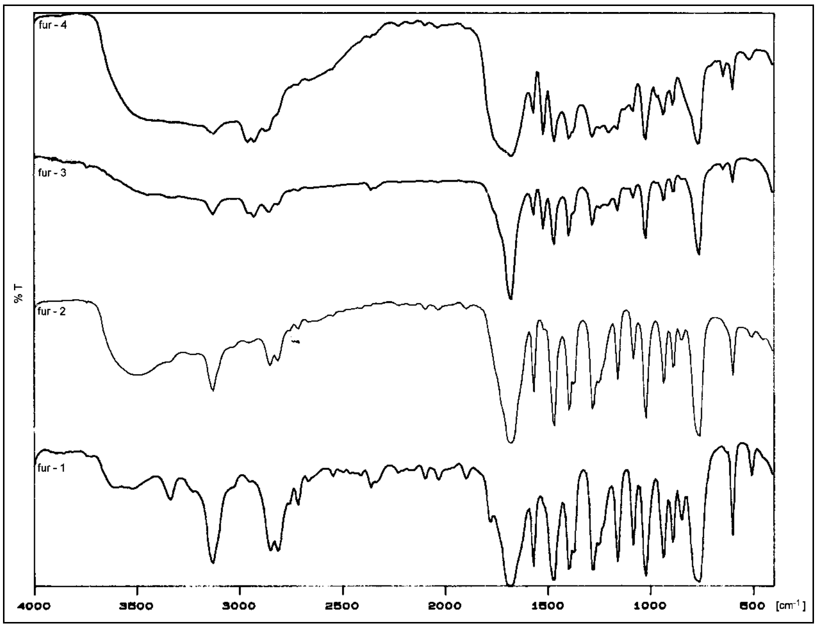

Figure 1. IR spectra of the furfurals (standard furfural (fur-1), hazelnut husks furfural (fur-2), tea waste furfural (fur-3) and tobacco waste furfural (fur-4)) are given respectively

Plantation of these three raw-materials in Black Sea region will supply the need of raw material for furfural factories (500 tons /day capacity). The hazelnut husks (125 000 tons), tea waste (23 000 tons) and tobacco waste (3 000 tons) are produced by-product of the hazelnut, tea and tobacco factories annually.

The surface area of the active carbon was changed with carbonization temperature and time. The greatest surface areas were obtained at 600 °C.

Activated carbon produced from hazelnut husks was used to remove some organic and inorganic pollutants from aqueous solutions. Experimental data were fitted to the Langmuir model. Langmuir model is described by the equation

$$q = \frac{QbC}{1 + bC} \qquad (2)$$

Where Q and b are the Langmuir constants showing the adsorbtion capacity of the adsorbent and energy of the adsorbtion process, respectively.

This equation can be linearized as

(3)

The values of Q and b were calculated by using Least Square Method and given in Table 4.

The Langmuir constants calculated from the experiments for inorganic and organic pollutants show that the activated coal produced from hazelnut husk is very effective in removing pollutants for treatment systems.

Table 4. Langmuir Constants for Inorganic and Organic Pollutants

Pollutants	Q ($mg.g^{-1}$)	b ($dm^{-3}.g^{-1}$)
Phenol	175	0.082
4-chlorphenol	172	0.075
2.4-diclorophenol	185	0.094
p-toluene sulphonic acid	97.22	0.0092
Cr (VI)	171	0.0122
Co	121	0.0145

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