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Research Article

Agricultural Waste Conversion to Activated Carbon by Chemical Activation with Phosphoric Acid

Activated carbon is widely used in various processes as an inexpensive and effective adsorbent. The adsorption properties of activated carbon vary with the feed materials used and the method of activation. The use of an inexpensive material and performing a suitable production method may help to generate a low cost product. Agricultural wastes could be considered as suitable raw materials for the production of activated carbon. In this work, activated carbon was produced by chemical activation with phosphoric acid of agricultural wastes such as bagasse, hard shells of apricot stones, almond, walnut and hazelnut shells. The effects of various preparation variables on both yield and quality of the prepared carbon were studied. The results showed that the selection of final activation temperature, heating rate, activation time and impregnation rate of the chemical agent was important in determining the quality of activated carbon obtained. The surface area and ash content of the activated carbon produced were compared to those of imported commercial samples. According to the results obtained, activated carbon from the hard shells of apricot stones have the best adsorption properties and the highest surface area. This activated carbon could be used in the separation of metal ions from wastewaters.

Keywords: Activated carbon, Adsorption, Biomass, Chemical activation

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1 Introduction

Activated carbons are extremely versatile adsorbents with major industrial significance. The world consumption of activated carbons is steadily increasing and new applications are always emerging, particularly those concerning environmental pollution remediation, which should help to sustain demand for them. Important applications are related to their use in water treatment for the removal of flavor, color, odor and other undesirable organic impurities from water. Activated carbon is also used in industrial wastewater and gas treatment due to the necessity for environment protection and also for material recovery purposes. The food and pharmaceutical industries are also a major consumer of activated carbon [1–3].

Activated carbons are high surface area materials prepared from various amorphous carbon materials. In principle, the methods for production of activated carbon can be divided into two categories: physical and chemical activation. The physical activation method involves carbonization of a precursor at elevated temperatures (500–900 °C) in an inert atmosphere, followed by activation of the resulting char at high temperatures (800–1000 °C) in the presence of a CO_2 or steam atmosphere. In the chemical activation method, raw material is impregnated with an activating reagent and the impregnated material is heated under an inert atmosphere. The carbonization step and the activation step progress simultaneously in the chemical activation method. Different well-known chemical agents can be used in the chemical activation process and phosphoric acid and zinc chloride are most commonly used as activation reagents. The common feature of all substances used in the chemical activation process is that they are dehydrating agents which influence pyrolytic decomposition and inhibit the formation of tar, thus enhancing the yield of activated carbon [1, 2, 4]. The advantages of the chemical activation method can be summarized as follows:

– It uses lower temperatures for pyrolysis;
– Usually, it can be performed in one step;
– It produces a much higher yield than physical activation;

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– Very high surface area activated carbons can be obtained;
– If desired, microporosity can be well developed, controlled and maintained in a narrow range;
– There is an important reduction of the mineral matter content.

The literature also mentions some disadvantages of the chemical activation process, such as the corrosiveness of the process and the washing stage [5].

The physical and chemical properties of activated carbon (such as surface area, bulk density, ash content) vary with the nature of the precursors and the production process. These properties may not relate directly to their effectiveness in the applications of activated carbon, but they are important for commercial utilization [1, 2, 6].

The production of activated carbon must balance economic viability with performance. Process economics normally dictate the selection of easily available, low cost feedstock. Various carbonaceous materials such as coal, wood, lignite, and coconut shell are used in the production of commercially activated carbon [2]. High volumes of agricultural by-products are lignocellulosic wastes that may offer inexpensive and renewable sources of activated carbon. This option is particularly attractive since the yearly harvesting and processing of various agricultural crops grown in Iran yields considerable quantities of agricultural by-products. Moreover, the use of such eco-friendly starting materials may reduce solid waste pollution, while reducing the cost of the raw material for the production of activated carbon. Common examples of these wastes are fruit stones (apricot, peach and cherry stones), nutshells (almond, walnut and pecan), rice hulls, bagasse, grape seeds, olive waste, and corncob, etc. [7–12]. Agricultural wastes are widely available in Iran but few value-added uses exist for their disposal. The vast quantity of waste is generally dumped in landfills. All of the materials are renewable on an annual basis, unlike other carbon materials, e.g., coal, peat and wood, etc.

In Iran, the activated carbon required for most industries (e.g., oil and gas, food, pharmaceutical, water and wastewater treatment, and gold recovery) is imported from countries such as China, Sri Lanka and the Netherlands at great expense. There is an opportunity to reduce the cost of these processes by producing activated carbon in Iran using domestically sourced raw material [13]. Residues from the agriculture and food industries are the non-product outputs from the growing and processing of raw agricultural products such as the hard shells of almond, apricot or pistachio, rice husk and olive wastes. In Iran, these low value biomass products are used inefficiently as fuel or discharged as wastes. The hard shell of fruit stones such as apricot stones and pistachio are very hard materials, a property that makes them an excellent alternative precursor for granular activated carbons since loss due to attrition of the particle is undesirable.

Limited research has been undertaken in Iran to produce activated carbon from agricultural waste [13–17]. However, there have been a considerable number of worldwide studies during the past decade on the production of activated carbon from these wastes [7–12, 18–22]. The objective of this work was to investigate the possibility of preparing activated carbon from domestic agricultural wastes by chemical activation. In this work, the chemical activation of these wastes such as bagasse, hard shells of apricot stones, almond, walnut and hazelnut shells for the preparation of activated carbon was performed. The activation was performed using phosphoric acid under different operating conditions.

2 Experimental

2.1 Raw Materials

Five kinds of agricultural wastes including bagasse, hard shells of apricot stones, almond, walnut and hazelnut shells were used as raw materials for the preparation of activated carbons. These wastes were selected as precursors because of their availability and desirable physical characteristics.

Elemental analysis of raw materials was performed by using a CHNS-O (Perkin Elmer series 2400II) elemental micro-analyzer. In order to assess the effect of the composition of the raw materials on the properties of the activated carbons, the content of lignin, cellulose, extractable materials and ash content were determined according to TAPPI standards (T264– OM 88, T222 and T211) [23–25]. The content of lignin and cellulose may be one of the criteria for the selection of appropriate raw materials in accordance with the requirements for the properties of the activated carbon [14, 15].

Tab. 1 shows the results of elemental analysis and chemical composition of these agricultural wastes. These raw materials appear to be very suitable starting materials for activated carbon production because of their low ash content. Bagasse has high ash content, whereas the hard shells of apricot stones have relatively low ash content. High ash content in the starting material is undesirable because it reduces the mechanical strength and adsorption capacity of the activated carbon produced. The ash content can result from the inorganic constituents of the raw material. The cellulose content is highest in bagasse and lowest in walnut shells. The elemental analysis data showed that the raw materials have a variation of composition. Hazelnut shells have the highest C content. Bagasse on the other hand, has the lowest C and H contents. Apricot stones and almond shells have rather similar elemental compositions.

Table 1. Chemical composition of the raw materials for activated carbon preparation.

Raw Materials	C (wt %)	H (wt %)	Ash (wt %)	Cellulose (wt %)	Lignin (wt %)
Almond Shell	50.30	6.05	1.54	39.25	27.00
Apricot Stone	50.50	6.03	0.20	39.75	34.50
Bagasse	46.00	6.00	3.40	42.80	15.80
Hazelnut Shell	51.40	5.95	1.20	40.50	27.20
Walnut Shell	49.00	5.75	1.70	34.50	33.30

2.2 Preparation of Activated Carbon

The chemical activation process was carried out by using phosphoric acid in seven stages, as follows [13]:

– Agricultural wastes were ground using a laboratory mill and sieved to obtain the desired size fractions using a conventional sieve-shaker;
– The selected particle size fraction was dried at 100 °C for 24 h;
– Samples were impregnated with phosphoric acid solution;
– The mixture was kept in an oven at 100 °C for 24 h;
– The mixture was subjected to carbonization and an activation process in a programmable electrical furnace (Nabertherm Labothem);
– The chemically activated carbon was washed extensively with hot distilled water until the pH of the wash water became neutral;
– The washed activated carbon was dried overnight at 100 °C in an air oven.

The surface area in activated carbon is mostly internal and microporous, and therefore, changes in particle size have little influence on the total surface area. Hence, in all experiments, the particle size of all raw materials was 0.5–1.2 mm. The effects of various preparation variables on both the yield and quality of the prepared carbon were studied. The variables investigated were final activation temperature, activation time, and impregnation ratio.

High yields are desirable in activated carbon production and help to reduce production costs. The activated carbon yield of this process can be determined from Eq. (1):

$$\text{Carbon Yield}(\%) = \frac{\text{activated carbon weight}}{\text{raw material weight}} \cdot 100 \quad (1)$$

The agent (H_3PO_4) recovery is also an important factor, and it is reused after concentration. The percent of H_3PO_4 recovery is calculated from Eq. (2):

$$\text{recovery} = \frac{\text{Activated carbon weight before washing} - \text{Activated carbon weight after washing}}{H_3PO_4 \text{ weight for impregnation}} \cdot 100 \quad (2)$$

2.3 Characterization of Activated Carbons

Activated carbons were characterized by selected physical and chemical properties. The Iodine number of prepared activated carbon was measured by titration at 30 °C based on the standard method (ASTM Designation D4607-860) [26]. This parameter was used to evaluate the activated carbon adsorption capacity. The activated carbons were ground until 95 wt % or more passed through a 325-mesh screen. From each sample, three small batches of dried activated carbons (0.1 g) were taken and were fully wetted with 10 mL of 5 wt % HCl. Then 100 mL of 0.025 M standard iodine solution was poured into the flask, and the contents were vigorously shaken for 30 s. After quick filtration, 50 mL of the solutions were titrated with standard sodium thiosulfate with starch as an indicator. The concentration of iodine in the solution was then calculated from the total volume of sodium thiosulfate used.

The BET (Brunaeur-Emmet-Teller) surface area (S_{BET}) of the activated carbons was determined from the adsorption-desorption isotherm of N_2 at 77 K. A Quantachrom NOVA 1000 surface area analyzer was used for determining this parameter by applying the 5-point BET isotherm. Before measuring the isotherm, the samples were heated at 473 K for 2 h, in vacuum, for degassing of the surface [27].

The apparent or bulk density is a measure of the weight of material that can be contained in a given volume under specified conditions. The volume used in this determination includes, in addition to the volume of the skeletal solid, the volume of the voids among the particles and the volume of the pores within the particles. A 10 mL cylinder was filled to a specified volume with activated carbon that had been dried in an oven at 80 °C for 24 h. Then the cylinder was weighed and the bulk density was calculated as [28]:

$$\text{Bulk density} = [\text{weight of dry material (g)} / \text{volume of packed dry material (mL)}] \quad (3)$$

The volume of this vessel was calibrated by measuring the volume of water at ambient temperature that the vessel can contain.

The ash content (Ash %) of an activated carbon is the residue that remains when the carbonaceous portion is burned off. The ash content of the activated carbons was determined by standard methods (ASTM Designation D2866-94, 1999) [29]. Approximately 1–2 g of powdered activated carbon was placed into weighed ceramic crucibles. The activated carbon and crucibles were dried for 24 h at 80 °C and reweighed to obtain the dry carbon weight. The samples were heated in an electrical furnace at 650 ± 25 °C for 3 h. The crucibles were cooled in a desiccator and the remaining solids (ash) were weighed. The percentage of ash was calculated by:

$$\%\,\text{Ash} = [\text{weight of solids remaining (g)} / \text{original weight of carbon (g)}] \cdot 100 \quad (4)$$

Finally, a comparison was made for the gold adsorption capacities of activated carbon produced from the hard shells of apricot stones and commercial activated carbons.

3 Results

3.1 Effect of Final Activation Temperature

The effect of final activation temperature on the production of activated carbon from different agricultural wastes is presented in Tab. 2. For these experiments, the activation time was 1.5 h and impregnation ratio was ca. 50 %[1)]. Based on the data in Tab. 2, the carbon yield did not change substantially. The highest yield was achieved when apricot stones were activated at 400 °C. It can be seen that increasing the temperature decreases the carbon yield and iodine number. Activated carbons prepared from hard shells of apricot stones had the highest iodine number and surface area.

1) Impregnation ratio = H_3PO_4 weight · 100/raw material weight

Table 2. Effect of final activation temperature.

Raw Material	Carbon Yield (%)	Recovery (%)	Iodine Number (mg I_2/g C)	Surface Area (m^2/g)
Final Temperature = 500 °C				
Almond Shell	24.9	71.2	412.0	169.1
Apricot Stone	30.0	76.2	450.0	251.1
Hazelnut Shell	21.4	76.1	440.0	229.5
Walnut Shell	29.4	69.4	420.0	186.3
Final Temperature = 400 °C				
Almond Shell	24.8	76.3	464.0	337.5
Apricot Stone	32.6	72.8	490.0	281.3
Hazelnut Shell	24.1	81.1	463.0	279.2
Walnut Shell	22.2	86.6	424.0	195.0

3.2 Effect of Activation Time

From the data in Tab. 3, it is clear that the activation time has a significant effect on the carbon yield, chemical activation agent recovery and adsorption properties. Increasing the activation duration from 1 h to 1.5 h, caused the iodine number to decrease, indicating that longer duration of activation time caused some of the pores to enlarge or even collapse.

3.3 Effect of Impregnation Ratio

In chemical activation with phosphoric acid, it is well known that the impregnation ratio is one of the variables that have a profound effect on the adsorption properties of activated carbon. The addition of different ratios of phosphoric acid to bagasse, hard shells of apricot stones, walnut shell and almond shell has been studied. The results are shown in Tabs. 4–7.

Table 3. Effect of activation time (Final activation temperature = 500 °C, Impregnation ratio = 50 %).

Raw Material	Carbon Yield (%)	Recovery (%)	Iodine Number (mg I_2/g C)
Activation Time = 1.5 h			
Almond Shell	24.9	71.2	412.0
Apricot Stone	30.0	73.4	450.0
Bagasse	14.8	64.8	387.0
Hazelnut Shell	21.4	76.1	440.0
Walnut Shell	29.4	69.4	420.0
Activation Time = 1 h			
Almond Shell	45.6	67.5	737.0
Apricot Stone	45.8	67.0	836.0
Bagasse	21.7	61.7	656.0
Hazelnut Shell	48.2	66.3	731.0
Walnut Shell	46.5	68.2	679.0

Table 4. Effect of impregnation ratio for activated carbon prepared from Bagasse (Final activation temperature = 500 °C, Activation time = 1 h).

Impregnation Ratio (%)	Carbon Yield (%)	Iodine Number (mg I_2/g C)
10	17.8	365
25	20.3	500
50	21.7	785
100	31.7	790

Table 5. Effect of impregnation ratio for activated carbon prepared from hard shells of apricot stones (Final activation temperature = 400 °C, Activation time = 2 h).

Impregnation Ratio (%)	Carbon Yield (%)	Recovery (%)	Iodine Number (mg I_2/g C)	Ash (%)
0	35.6	–	121	1.77
20	46.0	59.6	416	1.48
40	47.0	73.0	772	1.10
85	47.2	79.0	1082	1.05

Table 6. Effect of impregnation ratio for activated carbon prepared from walnut shells (Final activation temperature = 400 °C, Activation time = 1 h).

Impregnation Ratio (%)	Carbon Yield (%)	Iodine Number (mg I_2/g C)
100	40	318
150	46	460
200	48	924

Table 7. Effect of impregnation ratio for activated carbon prepared from almond shells (Final activation temperature = 400 °C, Activation time = 1 h).

Impregnation Ratio (%)	Carbon Yield (%)	Iodine Number (mg I_2/g C)
100	37	546
150	40	569
200	47	888

The data in Tabs. 4–7 indicates that the iodine number of prepared activated carbon was substantially influenced by the phosphoric acid concentration in the impregnating solution, whereas the carbon yield did not change greatly. According to these data, the iodine number of activated carbon from bagasse increased from 365 to 790 mg I_2/g carbon with an increase of impregnation ratio from 10 % to 100 %, the iodine

number of activated carbon from hard shells of apricot stones increased from 121 to 1082 mg I_2/g carbon with an increase of impregnation ratio from 0 % to 85 %, the iodine number of activated carbons from walnut and almond shells increased from 318 to 924, and 546 to 888 mg I_2/g carbon, respectively, with an increase of the impregnation ratio from 100 % to 200 %.

3.4 Comparison of Gold Adsorption with Different Activated Carbons

The gold adsorption from dilute solution with produced activated carbon from apricot stones was compared to three types of imported industrial activated carbon samples. These imported commercial activated carbons are:

– C2: activated carbon used in gold recovery processes in Iran;
– C3: activated carbon used in gas-phase separation processes;
– C4: activated carbon from CECA company.

The details of gold adsorption can be found elsewhere [30–32]. In summary, a measured volume of gold solution (50 mL) was contacted with a given weight of activated carbon in glass bottles. Samples were shaken at room temperature for 6 h. In all experiments, the pH of the solutions was kept constant at 10.5. The properties of these activated carbons and percentage of gold adsorption are listed in Tab. 8. It was found that the activated carbon produced from apricot stones has the same recovery efficiency as other imported commercially activated carbons.

Table 8. Comparison of properties and gold adsorption with different activated carbons.

Activated Carbon	Density (kg/m^3)	Surface Area (m^2/g)	Iodine number (mg I_2/g C)	Ash (%)	Gold Adsorption (%)
Apricot Stones	451.50	1387.30	668.00	0.20	98.15
C2	487.60	1078.00	590.00	7.72	97.69
C3	477.00	678.40	617.00	7.15	96.29
C4	448.20	1477.70	836.00	6.78	97.92

4 Conclusions

The physical and chemical properties of activated carbon (such as surface area, bulk density, ash content) vary with the feed material used and the method of activation. These properties do not relate directly to the effectiveness of their application, but they are important for commercial utilization.

Agricultural wastes could be considered as suitable raw materials for the production of activated carbon. In this work, the production of activated carbon from these wastes such as bagasse, hard shells of apricot stones, almond, walnut and hazelnut shells has been studied. The activation was performed using phosphoric acid under different operating conditions. The agricultural by-products used in this study have different physical and chemical properties. It was seen that all of them react with phosphoric acid to make effective activated carbon. The results showed that the selection of final activation temperature, heating rate, activation time and impregnation rate of the chemical agent was important in determining the quality of the activated carbon.

Based on the results obtained, it appears that the type of raw material affects the properties of activated carbon produced. According to the results, the highest yield of activated carbon was related to hard shells of apricot stones. High ash content in activated carbons is undesirable because it reduces the mechanical strength and adsorption capacity of activated carbon produced. The ash content can result from the inorganic constituent of the raw material. The lowest ash content of raw material was related to the hard shells of apricot stones.

The surface area of activated carbons obtained seemed to depend on their ash content – the higher the ash content, the lower the N_2 surface area. Thus, bagasse had the lowest N_2 surface area and iodine number. The highest iodine number and surface area were obtained in activated carbon produced from hard shells of apricots.

The surface area and iodine number of the prepared activated carbons were also compared to those of imported commercial ones.

According to the results, activated carbon from hard shells of apricot stones had the best adsorption properties and the highest surface area. This activated carbon could be used in the separation of metal ions (such as gold) from wastewaters.

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References

[1] R. C. Bansal, J. B. Donnet, F. Stoeckeli, *Active Carbon*, Marcel Dekker Inc., New York **1988**.
[2] J. F. Byrne, H. Marsh, *Porosity in Carbons: Characterization and Application* (Ed: J. W. Patric), Ch. 9, Edward Arnold London, Melbourne Auckland, New Zealand, **1995**.
[3] R. Zanzi et al., in *Proc. 6th World Congress of Chemical Engineering,* Institute of Chemical Engineers in Australia, Melbourne, Australia, **2001**.
[4] C. Moreno-Castilla, F. Carrasco-Marn, M. V. Lopez-Ramon, M. A. Alvarez-Merino, *Carbon* **2001**, *39 (9)*, 1415.
[5] H. J. Teng, H. C. Lin, *Am. Inst. Chem. Eng.* **1998**, *44 (5)*, 1170.
[6] C. A. Toles et al., *Bioresour. Technol.* **2000**, *71 (1)*, 87.
[7] W. Heschel, E. Klose, *Fuel* **1995**, *74 (12)*, 1786.
[8] J. Hayashi et al., *Carbon* **2002**, *40*, 2381.
[9] M. M. Johns, W. E. Marshall, C. A. Toles, *J. Chem. Technol. Biotechnol.* **1998**, *71*, 131.
[10] W. K. Lafi, *Biomass Bioenergy* **2001**, *20*, 57.
[11] K. Gergova, N. Petrov, V. Minkova, *J. Chem. Technol. Biotechnol.* **1993**, *56*, 77.
[12] R. R. Bansode et al., *Bioresour. Technol.* **2003**, *89*, 115.
[13] M. Soleimani, T. Kaghazchi, *5SCCE & 3SCPE Conference*, Tehran, Iran, **2005**.

[14] T. Kaghazchi, M. Soleimani, *7th Asia Pacific Int. Symp. on Combustion and Energy Utilization*, Hong Kong **2004**.
[15] M. Maddadi Yeganeh, T. Kaghazchi, M. Soleimani, *Chem. Eng. Technol.* **2006**, *29 (10)*, 1247. DOI: 10.1002/ceat.200500298
[16] S. Arjmand, T. Kaghazchi, S. Mehdi Latifi, M. Soleimani, *Chem. Eng. Technol.* **2006**, *29 (8)*, 986. DOI: 10.1002/ceat.200500325
[17] T. Kaghazchi, M. Madadi Yeganeh, M. Soleimani, in *Proc. of CHISA 2006* (Ed: Jan Novosad), Czech Society Chemical Engineers, Prague, Czech Republic, **2006**.
[18] E. Genceli et al., *Fuel Process. Technol.* **2002**, *75*, 97.
[19] J. Hayashi et al., *Carbon* **2002**, *40*, 2381.
[20] D. Savova et al., Biomass Bioenergy **2001**, 21, 133.
[21] C. A. Toles, M. M. Johns, W. E. Marshall, *Carbon* **1997**, *35 (9)*, 1407.
[22] T. Yang, A.C. Lua, *Microporous Mesoporous Mater.* **2003**, *63*, 113.
[23] *Preparation of Wood for Chemical Analysis*, TAPPI Standards, T 264 om-88, **1988**.
[24] *Acid-Insoluble Lignin in Wood and Pulp*, TAPPI Standards, T 222 om-88, **1988**.
[25] *Ash in Wood, Pulp, Paper and Paperboard: Combustion at 525 °C*, TAPPI Standards, T211 om-93, **1993**.
[26] *Standard Test Method for Determination of Iodine Number of Activated Carbon*, ASTM Standard, Designation D4607-94, **2000**.
[27] S. B. Brunauer, P. H. Emmett, F. Teller, *J. Am. Chem. Soc.* **1951**, *73*, 309.
[28] *Encyclopedia of Industrial Chemical Analysis* (Eds: F. D. Snell, L. S. Ettre), Vol. 8, Interscience, New York **1968**.
[29] *Standard Test Method for Total Ash Content of Activated Carbon*, ASTM standard, Designation D2866-94, **2000**.
[30] T. Kaghazchi, M. Soleimani, *3rd Int. Conf. on Advances in Strategic Technologies*, Kuala Lumpur, Malaysia, August **2003**.
[31] M. Soleimani, T. Kaghazchi, *Amirkabir J. Sci. Eng.* **2004–2005**, *15 (60)*, 139.
[32] M. Soleimani, T. Kaghazchi, *Int. Congress of Chemistry and Environment*, Indore, India, December **2005**.

