Indian Journal of Fundamental and Applied Life Sciences ISSN: 2231– 6345 (Online)
An Open Access, Online International Journal Available at www.cibtech.org/sp.ed/jls/2016/01/jls.htm
2016 Vol. 6 (S1), pp. 481-493/Sedghi et al.
Research Article

OPTIMIZATION OF ACTIVATED CARBONS FABRICATED FROM AGRICULTURAL WASTES

Arman Sedghi[1], *Neda Mafifard[2] and Alireza Mahjobi[3]
[1]*Department of Materials Engineering, Imam Khomeini International University, Qazvin 34149-16818, Iran*
[2]*Department of Metallurgy and Materials Engineering, University of Tehran, Tehran, Iran*
[3]*Department of Materials Engineering, Islamic Azad University-Saveh Branch, Saveh, Iran*
**Author for Correspondence*

ABSTRACT
Fabrication of activated carbon from cheap raw materials and by fast method is vital for its commercial applications. Then in this paper agricultural wastes such as walnut and coconut shell were used as raw materials and chemical method was chosen to prepare activated carbon and fabrication parameters were optimized by characterization of product properties. To obtain a high quality product, some fabrication parameters such as activation agent concentration, impregnation ratio, particle size, soaking time, carbonization temperature and duration, activation temperature and duration were optimized by determining the Iodine number, specific surface area and activated carbon yield. Results showed that by optimization of fabrication parameters, activated carbons with specific surface area of 1139 and 1476 m^2/g and Iodine number of 985 and 1080 mg/g were achieved from walnut and coconut shell respectively. These results are comparable with commercial activated carbon properties.

Keywords: *Activated Carbon, Agricultural Wastes, Phosphoric Acid, Activation Treatment*

INTRODUCTION
Activated carbons have well-developed pore structures and high internal surface area which lead them to be used in wide range of industrial applications over the last few decades, including technologies for the gas purification, solvent extraction, removal of organic pollutants from water, catalyst or catalyst support in the catalytic processes and electrode materials in electrochemical devices (Li *et al.*, 2008).
Activated carbons have been prepared from a variety of precursors such as petroleum coke, straw, ash, peat, apricot stones, sugarcane bagasse, nutshells, rice husk, coconut shell, forest residues and tobacco stems but some of them were expensive or form dense and non-uniform pore structure after activation (Li *et al.*, 2008; Yahaya *et al.*, 2010). Agricultural wastes derived from some agricultural crops have been used as precursors for the preparation of activated carbon because of their low price, moderate carbon yield and good absorption properties (Martinez *et al.*, 2006). On the other hand, pore structure is heterogeneous and their properties directly related to processing parameters. In this respect, many investigations were focused on finding appropriate cheap raw materials as well as appropriate fast fabrication methods. It has been documented that the nature of the precursor, activation method and activation conditions determine the characteristics of porosity in activated carbons, including pore size distribution, shapes of the pores, and surface chemistry (Li *et al.*, 2008).
Two methods are used to prepare activated carbons; physical and chemical activation. In the physical activation method, a raw material is first carbonized at temperatures between 400 and 850 ºC and then activated by steam or carbon dioxide, air or their mixtures at higher temperatures around 600-900 ºC, i.e., there it was done in two carbonization and activation steps. In the chemical activation method, a raw material is impregnated with a chemical activation agent and the impregnated raw material is carbonized and activated simultaneously. Phosphoric acid activation is widely used for the production of activated carbon. The carbon yield of chemical activated carbon is higher than physical one because of the lower amount of by-products. One of the most important effective parameters on the quality of chemical produced activated carbon is type and amount of chemical additives. Chemical activation reduces the formation of tar and other byproducts, thereby increasing carbon yield on the other hand, type and the

amount of the chemical agents and processing parameters are drastically change the quality and quantity of fabricated activated carbon (Li *et al.*, 2006; Martinez *et al.*, 2006; Stavropoulos *et al.*, 2005; Puzy *et al.*, 2002).

Walnut is one of the most important agricultural products in Iran which produces large amount of waste walnut shell. In Iran, these shells are priceless and disposal of them are not only costly but also cause environmental problems. In contrast, due to excellent cellulosic structure and low ash content of walnut shell, it is suitable for preparing mesoporous-activated carbon. Conversion of walnut shells into activated carbons would increase their value, reduce the cost of waste disposal, and provide a potentially cheap commercial activated carbon (Li *et al.*, 2008).

In this study, activated carbons were fabricated from walnut and coconut shell by chemical method and effect of fabrication parameters such as activation agent concentration, impregnation ratio, carbonization temperature and duration, activation temperature and duration, as well as particle size and soaking time on adsorption properties and yields of them was studied and optimized. Also the optimized results were compared with commercially available activated carbons.

MATERIALS AND METHODS

The raw materials were walnut and coconut shell obtained from waste agricultural products of Iran (Semnan) and Sri Lanka (Negombo) respectively. The starting materials cleaned with deionized water, dried at 110 ºC for 24 h, and ground with a roller mill. Then, by using standard sieves the powder was classified to 5 groups in the range between 0.5-4 mm.

One of the most important factors in optimizing the fabrication conditions of activated carbon is activation agent. There are various kinds of activation agents such as H_3PO_4, H_2SO_4, HNO_3, HCl, $ZnCl_2$, NH_4Cl, K_2CO_3, $CaCl_2$, $MgCl_2$, NaOH, and KOH. Among these materials, phosphoric acid and zinc chloride have better properties. Using zinc chloride as an activation agent is decreasing nowadays because zinc residue in the activated carbons after activation process is harmful in some applications (Kostomarova *et al.*, 1988), therefore phosphoric acid was chosen as an activation agent in this study due to lower cost, good accessibility and desirable adsorption properties of achieved activated carbon. Food grade phosphoric acid (with 1.67 g/cm^3 density) was used as an activation agent. The concentration of activation agent was 80 wt. % for preparing initial samples.

Classified powders were mixed with phosphoric acid and the mixture was completely homogenized. In the next step, the samples carbonized at 100-250 ºC for 0.5-4 h. Then they activated in a furnace heated from room temperature up to 350-750 ºC for 0.5-4 h with the heating rate of 2 ºC/min. The heat treated activated carbons were washed with deionized water, to remove the probable amount of chemical agent or other components until the pH of the wash water became neutral (Suarez-Garcia *et al.*, 2003; Mcdowal *et al.*, 1990). Finally, samples dried at 120 ºC for 2 h, cooled at room temperature, and stored in hermetic–sealed containers for analysis. For optimization of activated carbons, processing parameters ranges must selected and in this range these parameters must be changed simultaneously or step by step. Processing parameters and their ranges in this study were shown in table 1 and optimization was done by changing parameters step by step.

Table 1: Processing Parameters for Fabrication of Activated Carbon and their Ranges

Primary Parameters	Variation
Chemical Agent Concentration	20-80%
Impregnation Ratio	0.25-3
Particle Size	0.5-4 mm
Soaking Time	0-24 h
Carbonization Temperature	100-250 ºC
Carbonization Time	0.5-4 h
Activation Temperature	350-750 ºC
Activation Time	0-3 h

Iodine number of samples was measured according to ASTM D4607 under different conditions. This number shows the amount of carbon activated porosity and in some cases can be an approximate amount of specific surface area.
Besides Iodine number, yield of samples calculated by using the following equation:
(1) Yield % $=W_4/W_1\times100$
After optimizing effective parameters, amount of weight loss ratio (W.L. %) and activation agent recovery (A.R. %) were determined by using equation 2 and 3 respectively.
(2) W.L. % $= [(W_1-W_4)/W_1] \times 100$
(3) A.R. % $= [(W_3-W_4)/W_2] \times100$
In equations 1, 2 and 3 W_1 is the weight of raw material, W_2 is the weight of final activated carbon, W_3 is the weight of the activation agent and W_4 is the weight of activated carbon before washing. Specific surface area of samples was measured by Nitrogen adsorption method (ASAP2000, Miromeritics) according to ASTM D819.

RESULTS AND DISCUSSION

In the first step, activated carbons were fabricated based on former research data (see table 2) (Toles *et al.*, 2000).

Table 2: Primary Processing Parameters of Initial Samples

Primary Parameters	Values
Phosphoric Acid Concentration	80%
Impregnation Ratio	2
Particle Size	2 mm
Soaking Time	24 h
Carbonization Temperature	200 ºC
Carbonization Time	2 h
Activation Temperature	450 ºC
Activation Time	1.5 h

Table 3 illustrates the properties of initial activated carbon samples. Based on this table, it reveals that Iodine number and yield reached 730 mg/g and 41% after activation for walnut shell which were lower than coconut shell's values. On the other hand properties of them are far from industrial products; therefore optimization of samples was necessary.

Table 3: Properties of Activated Carbons from Walnut and Coconut Shell Before Optimization

Sample	Phosphoric Acid Concentration (wt. %)	Iodine Number (mg/g)	Loss in Weight (%)	Yield (%)
Walnut Shell	80	730	59	41
Coconut Shell	80	900	56.7	43.3

As mentioned before, different effective factors should be optimized step by step in order to achieve the best quality activated carbons. Two factors which would be optimized first are concentration and impregnation ratio of activation agent. Concentration of activation agent affected the adsorption properties of activated carbon and also it is important from economical view. Figures 1 and 2 show the changes in Iodine number and yield respectively for both walnut and coconut shell samples. According to this data, the optimum concentration was considered 60 wt. % and 50 wt. % for walnut and coconut shell samples respectively. When the high density of phosphoric acid is used (i.e. 70 or 80 wt.%), the mixing of raw material and chemical agent is will be difficult, so to obtain a homogenous mixture, higher amount of acid should be used which is not economical. On the other hand, if the concentration is low, (i.e. 20 wt. %

or 30 wt. %), the activation process will not be done properly and the carbonization process needs more energy to evaporate water.

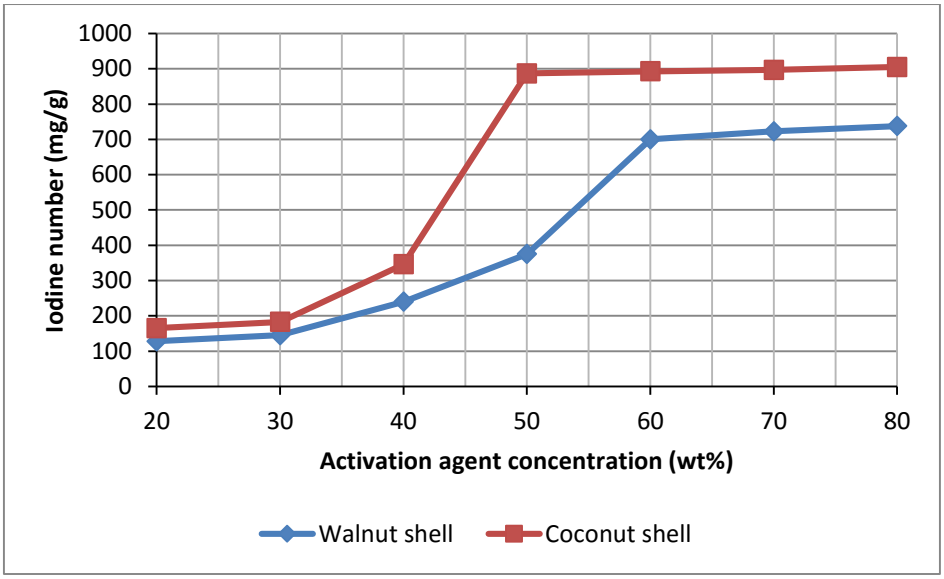

Figure 1: Effect of Activation Agent Concentration on Iodine Number of Walnut and Coconut Shell Based Activated Carbons

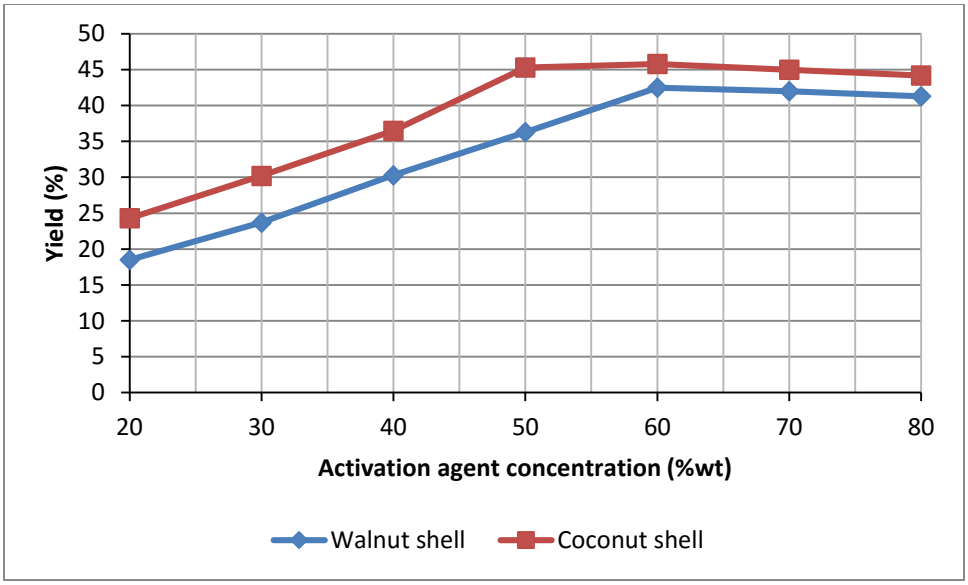

Figure 2: Effect of Activation Agent Concentration on Yields of Walnut and Coconut Shell Based Activated Carbons

Next critical factor to reach the best activated carbon properties was impregnation ratio. This factor can be defined based on following equation:

$$Impregnationratio(R) = \frac{activating\ agent\ weight}{raw\ material\ weight}$$

As can be seen in Figure 3 and 4, Iodine number and yield increase with impregnation ratio up to a maximum and then become constant, after this threshold the impregnation ratio would not affect the

Iodine number or yield anymore. Theoretically and economically, minimum impregnation ratio at constant Iodine number and yield was considered as an optimum amount and it was found 2 and 1.5 for walnut and coconut shell samples according to Figure 3 and 4.

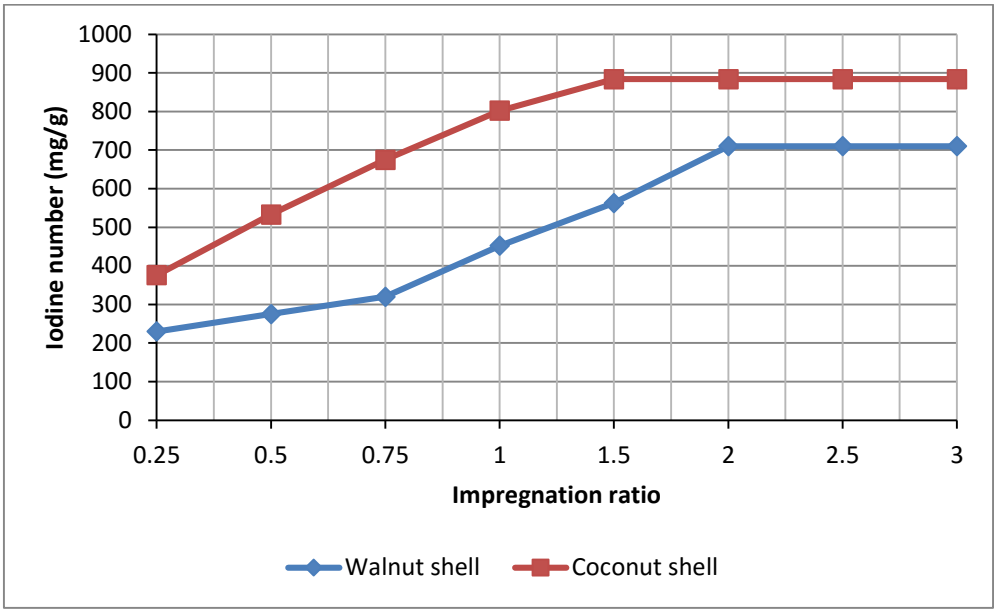

Figure 3: Effect of Impregnation Ratio on Iodine Number of Walnut and Coconut Shell Based Activated Carbons

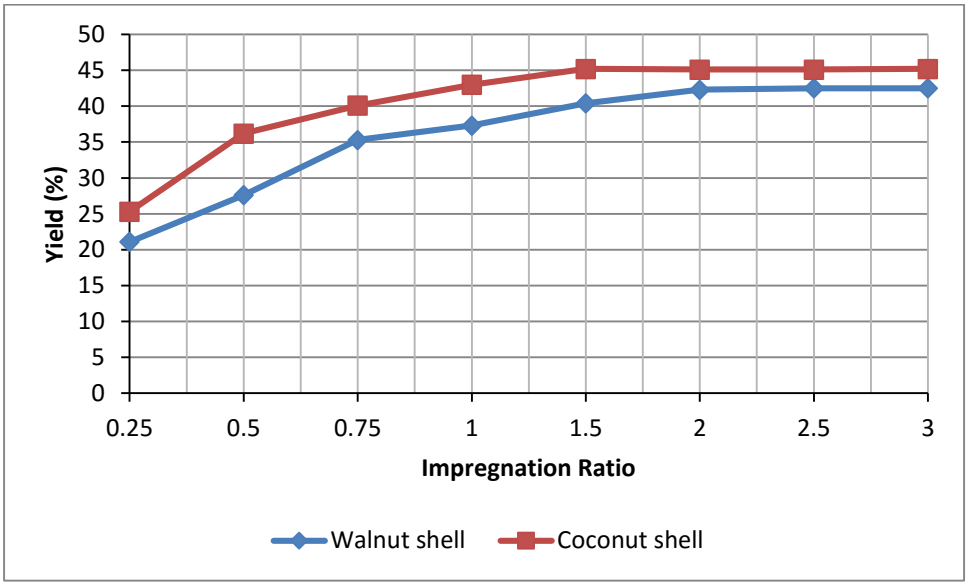

Figure 4: Effect of Impregnation Ratio on Yields of Walnut and Coconut Shell Based Activated Carbons

Particle size of raw material is another effective factor. As mentioned, by using standard sieves, the initial powder was classified into 5 groups in the range between 0.5-4 mm. According to data in Figure 5 and 6, by considering Iodine number and yield of samples, particle size of 1 mm for walnut shell and 2 mm for coconut shell were found the best value. Figure 6 shows that for these particle sizes, the yield has an acceptable amount around 42 % for walnut shell and 47.5 % for coconut shell. Martinez *et al.*, (2006)

reported the same relationship between particle size of raw material and adsorption properties in fabricating olive stone and walnut shell based activated carbons by using KOH as an activation agent.

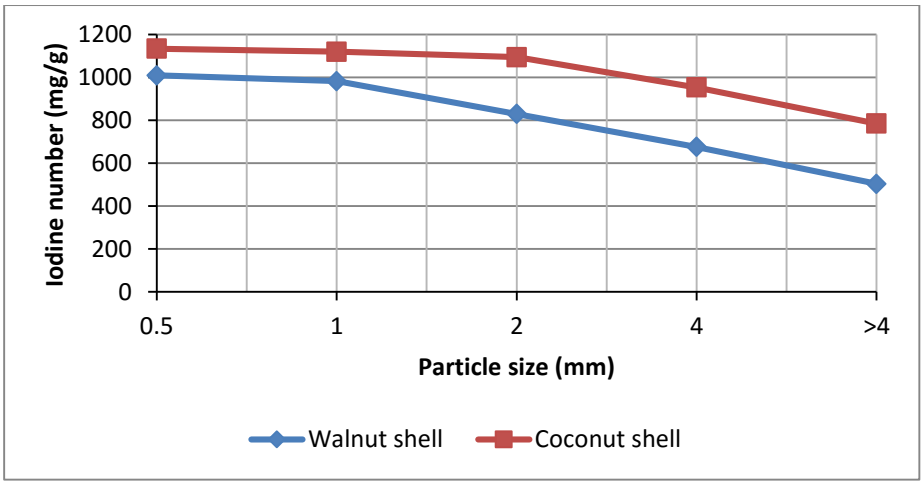

Figure 5: Effect of Particle Size on Iodine Number of Walnut and Coconut Shell Based Activated Carbons

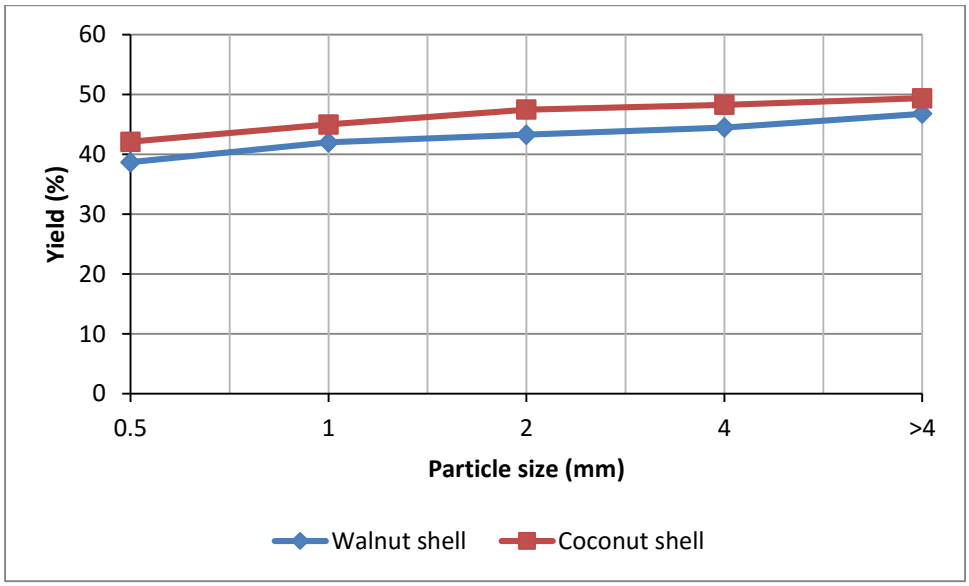

Figure 6: Effect of Particle Size on Activated Carbon Yields of Walnut and Coconut Shell Based Activated Carbons

Soaking time is another effective factor in fabricating activated carbon. It refers to a contact time between raw material and activation agent which is depends on mixing type, impregnation ratio and particle size of raw material. Soaking time was varied in the range mentioned in table 2 to find the optimum time. According to Figure 7 and 8 the best soaking time was considered 12 h and 6 h for walnut and coconut shell samples.

These figures show that by increasing the soaking time, the adsorption properties of the samples and the yield are improved, and when it is reached the maximum value, it becomes constant. As expected, it decreases with reducing the particle size because phosphoric acid needed lower time to penetrate into finer particle size. The best soaking time is the one that results in a homogenous mixture. In this regard, the raw material should be impregnated with activation agent completely.

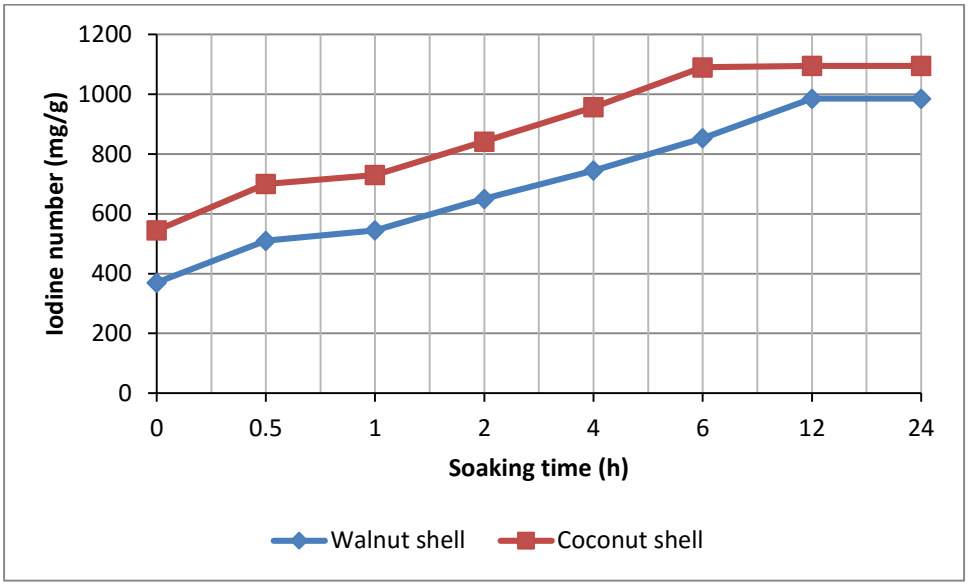

Figure 7: Effect of Soaking Time on Activated Carbon Iodine Number of Walnut and Coconut Shell Based Activated Carbons

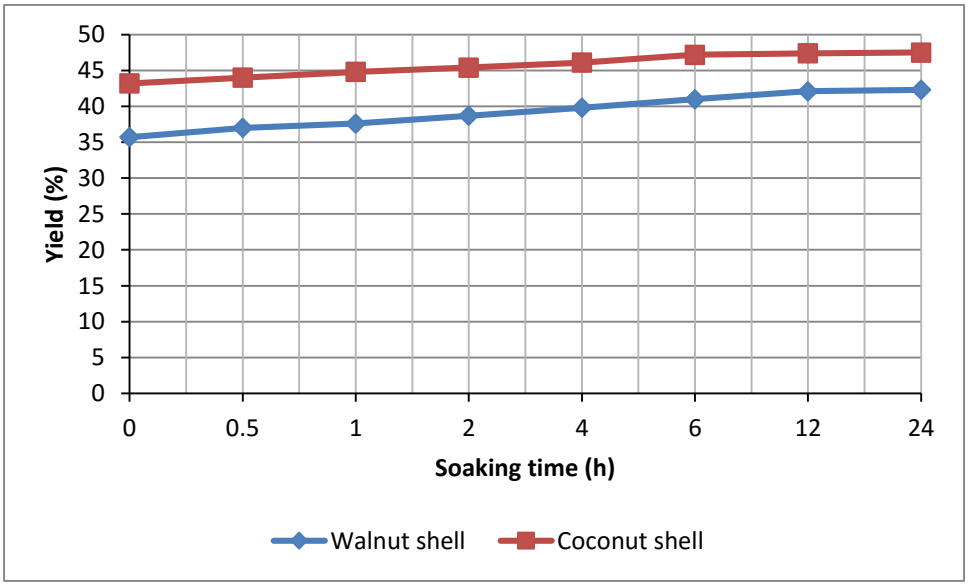

Figure 8: Effect of Soaking Time on Activated Carbon Yields of Walnut and Coconut Shell Based Activated Carbons

Carbonization temperature was the next factor which must be optimized. Through this process, a series of destructive reactions occurs and volatile materials removed from raw materials and the porous carbon was performed (Kostomarova *et al.*, 1988). To optimize this parameter, the Iodine number and the yield were determined in walnut shell sample and also coconut one. Figure 9 shows that by increasing the carbonization temperature between 100-250 ºC, Iodine number for walnut and coconut shell increases up 700 mg/g and 850 mg/g respectively and then starts falling down. The same trend can be seen in curve related to activation yield in Figure 10. Although the reverse behavior can be seen in former researches done by Evbuomwan *et al.,* (2013) regarding yield trend, they found that the specific surface area reached a maximum and then decreased in preparing bamboo based activated carbon by KOH activation which indicates that the adsorption properties improved. This behavior may be related to incomplete

carbonization in lower temperatures. On the other hand, at higher temperatures the surface area decreases because of the burning of some cavities (Evbuomwan *et al.*, 2013). Therefore, the best carbonization temperature for both walnut and coconut shell was considered 200 ºC.

Besides carbonization temperature, carbonization duration is also important for achieving high quality activated carbon. Figures 11 and 12 show Iodine number and yield of activated carbon, from which an optimum carbonization time for walnut and coconut shell is obtained 2 h and 1.5 h respectively. In short carbonization time, some of destructive reactions will not be completed due to kinetics reasons and the produced activated carbon will not have desirable properties. In long carbonization time, although the destructive reactions do happen completely, but it would be possible that side reactions occur and affect the porous structure of the activated carbon (Puzy *et al.*, 2002). Therefore, there is an optimum value for carbonization time.

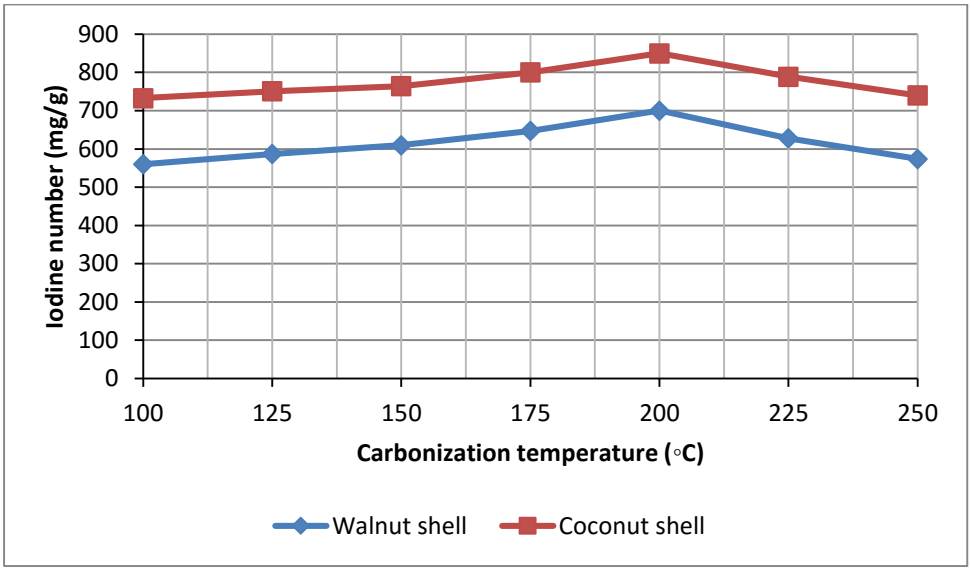

Figure 9: Effect of Carbonization Temperature on Iodine Number of Walnut and Coconut Shell Based Activated Carbons

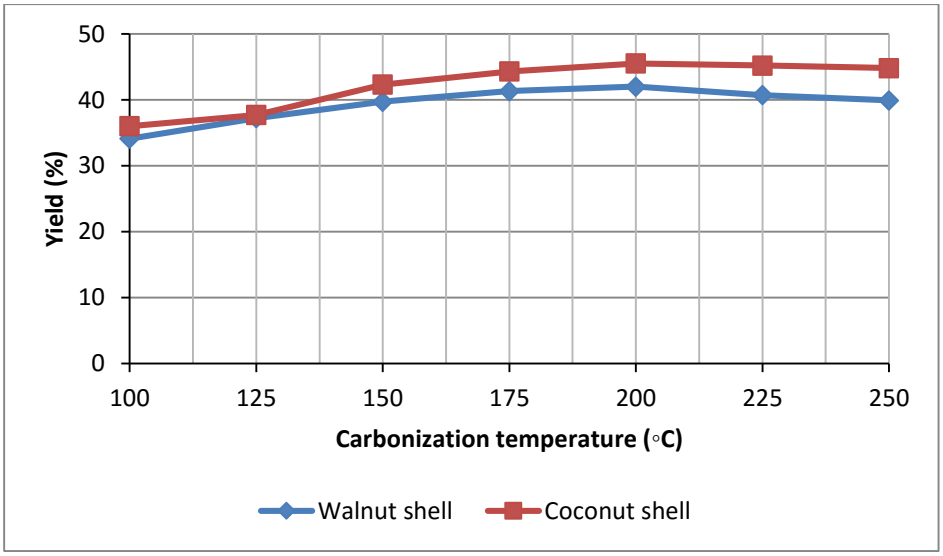

Figure 10: Effect of Carbonization Temperature on Activated Carbon Yield of Walnut and Coconut Shell Based Activated Carbons

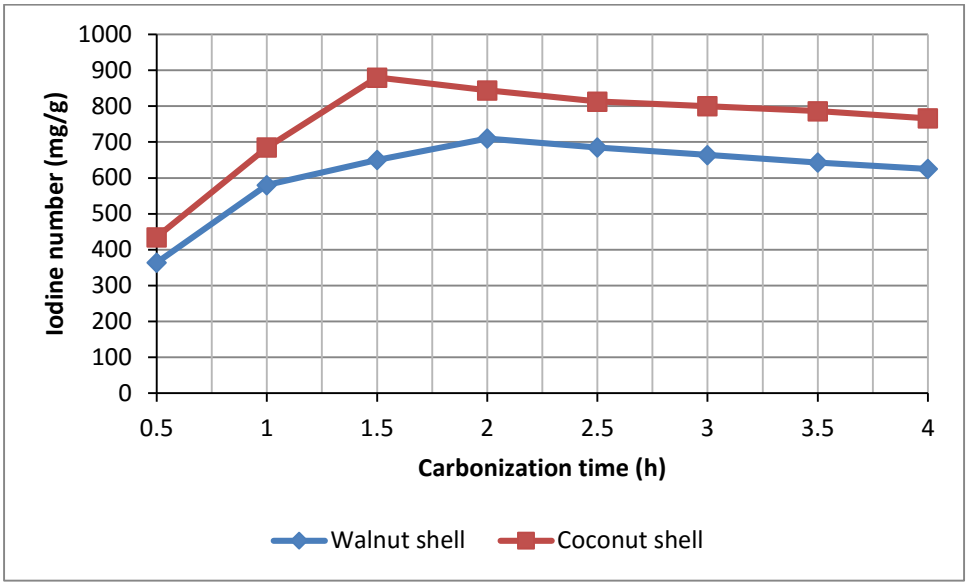

Figure 11: Effect of Carbonization Time on Iodine Number of Walnut and Coconut Shell Based Activated Carbons

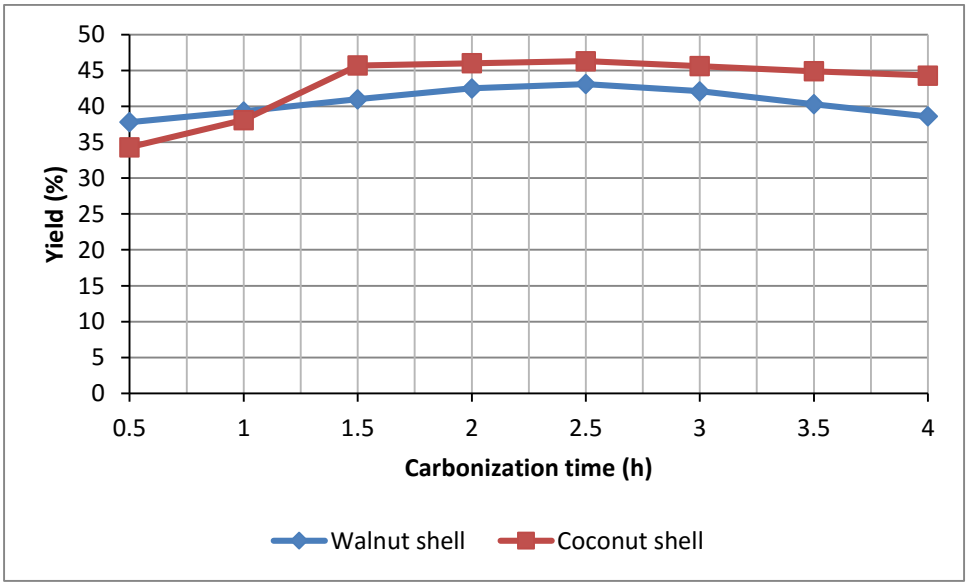

Figure 12: Effect of Carbonization Time on Activated Carbon Yield of Walnut and Coconut Shell Based Activated Carbons

Activation temperature is also important factor as the structure of porous material which was created in carbonization process was developed and the absorption properties improve (Anirudhan *et al.*, 2011). According to Figure 13 increasing activation temperature improves absorption properties of activated carbon up to a maximum value which may be due to more removal of volatile materials. At higher temperature, increasing the temperature not only causes a destruction of the porous structure, but also weight of activated carbon loses that result in weakening the adsorption properties of activated carbon (Girgis *et al.*, 1994). Figure 14 shows the inverse relation between activation temperature and yield. The same trend could be seen in preparing activated carbon by impregnation of styrene–divinylbenzene copolymer with phosphoric acid at various temperatures of 400-1000 ºC. Puzy *et al.*, (2002) found that the yield value was decreased by increasing the activation temperature due to separating components at

high temperatures. According to these two figures, the optimum activation temperature was considered 500 and 550 ºC for walnut and coconut shell respectively. The yield value for these temperatures is 40.7 % for walnut shell and 45.3 % for coconut shell.

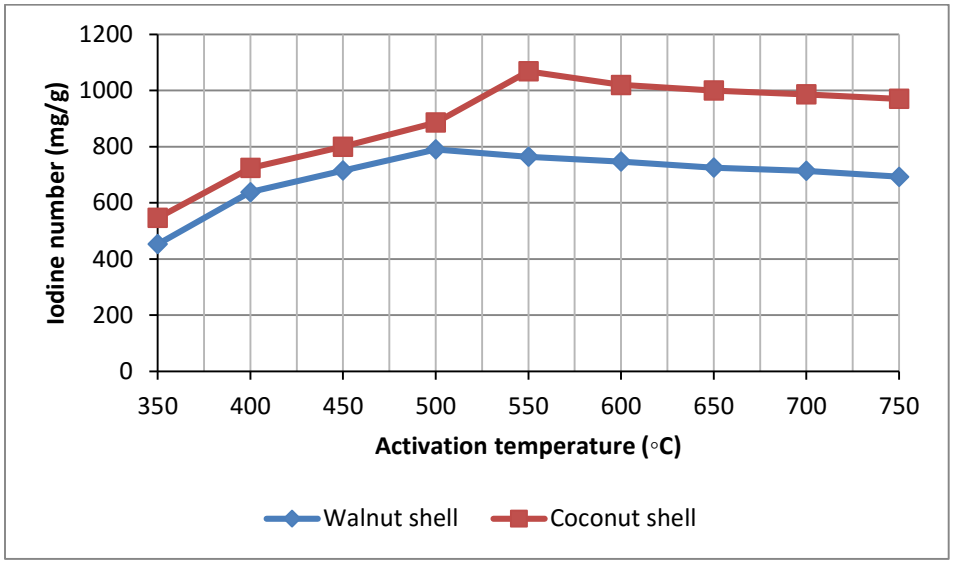

Figure 13: Effect of Activation Temperature on Activated Carbon Adsorption for Walnut and Coconut Shell

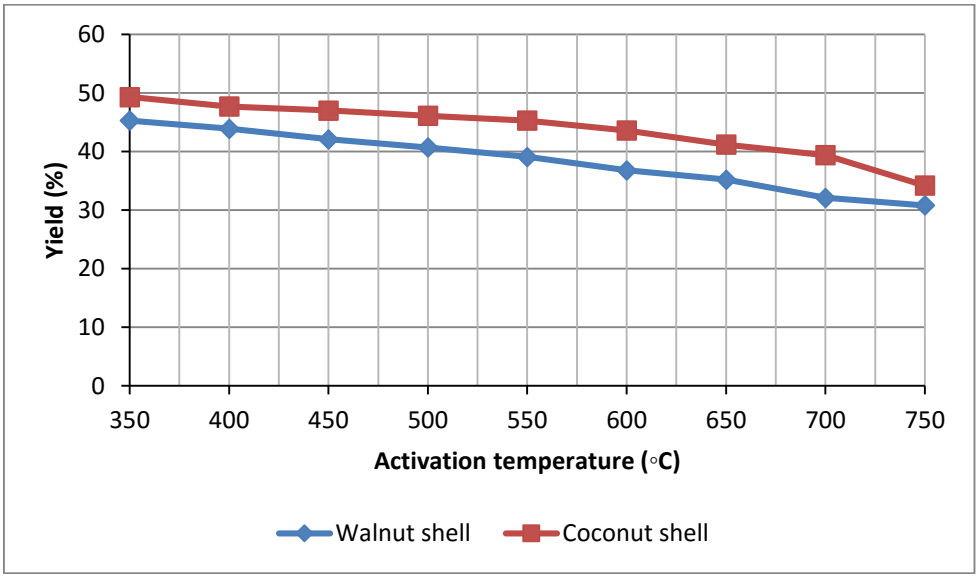

Figure 14: Effect of Activation Temperature on Activated Carbon Yield of Walnut and Coconut Shell Based Activated Carbons

The last effective parameter is activation time. Based on Figure 15 and 16, the optimum activation time is 1 h for walnut shell and 1.5 h for coconut shell. Higher activation time leads to lower yield (same as activation temperature behavior) which is in agreement with the study done by Yahaya *et al.,* (2010) that showed the reverse relation between yield and activation time on preparing activated carbon from rice husk. By increasing the activation time, volatile materials have enough time to remove and form a porous structure so the Iodine number increases up to a maximum point. Finally, as there are not any more volatile components, it becomes constant.

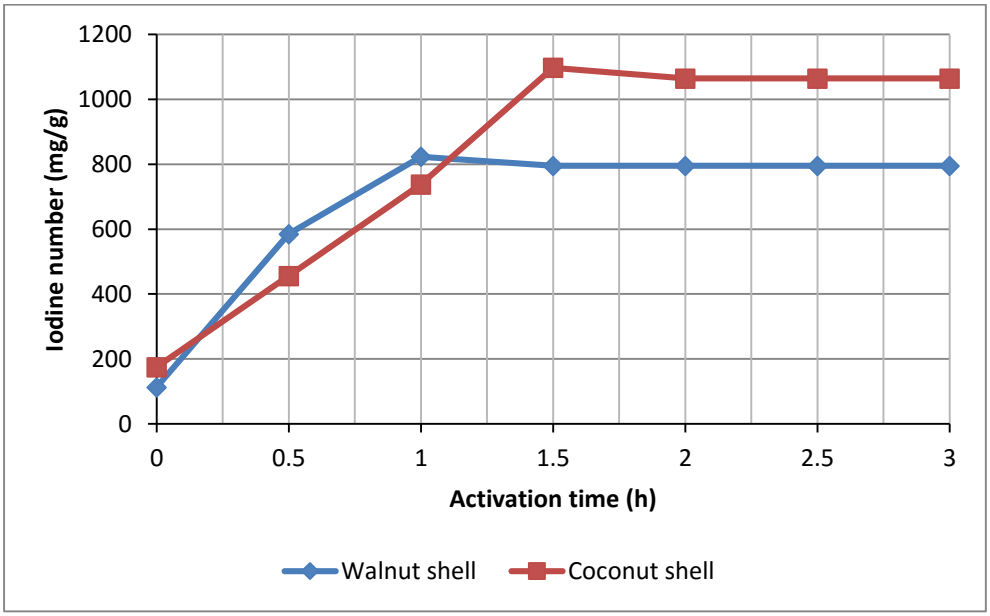

Figure 15: Effect of Activation Time on Activated Carbon Iodine Number of Walnut and Coconut Shell Based Activated Carbons

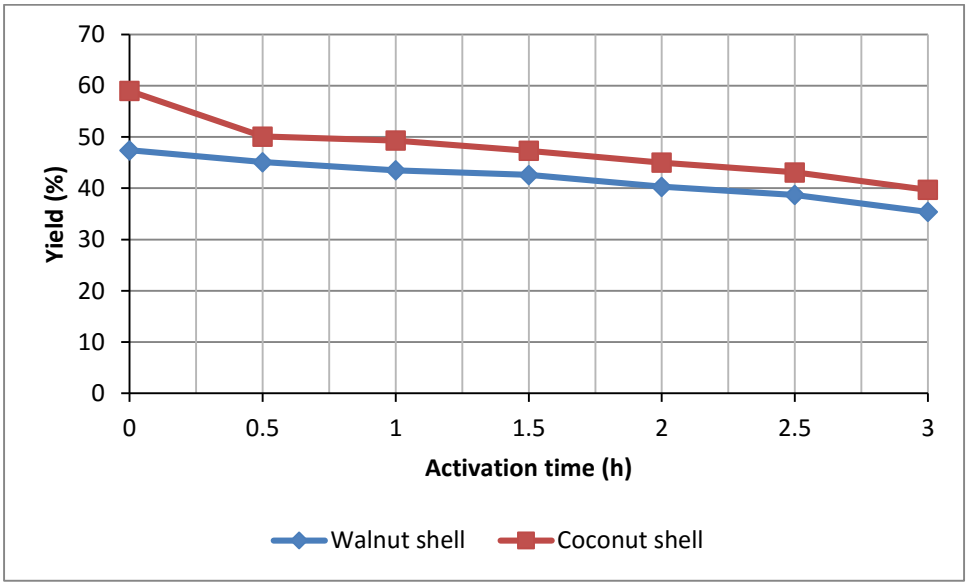

Figure 16: Effect of Activation Time on Activated Carbon Yield of Walnut and Coconut Shell Based Activated Carbons

The amount of optimized parameters for activation of walnut and coconut shell which were found from our research is collected in table 4. Based on applying these parameters, properties of activated carbons fabricated from these two shells such as weight loss, activating reagent recovery, ash content, moisture content, Iodine number, specific surface area and yield were measured and have shown in table 5. In order to compare optimized samples properties with commercial ones, the specific surface area and Iodine number of them were compared with properties of some commercial activated carbons and results were plotted in Figure 17. Based on this figure, its reveals that Iodine number and specific surface areas of our samples are in the range of best commercial activated carbons also this property has been found from cheap raw materials and fast fabrication methods.

Table 4: Optimized Processing Parameters for Fabrication of Activated Carbon from Walnut and Coconut Shells by Chemical Activation Method

Raw material	Walnut Shell	Coconut Shell
Activation Agent Concentration	60%	50%
Impregnation Ratio	2	1.5
Particle Size	1 mm	2 mm
Soaking Time	12 h	6 h
Carbonization Temperature	200ºC	200ºC
Carbonization Time	2 h	1.5 h
Activation Temperature	500ºC	550ºC
Activation Time	1 h	1.5 h

Table 5: Some Properties of the Activated Carbon Produced from Walnut and Coconut Shell by Optimized Processing Condition

Raw Material	Walnut Shell	Coconut Shell
Loss in Weight	57.9%	52.8%
Activating Reagent Recovery	68.7%	66.4%
Ash Content	1.4%	1.2%
Moisture Content	1.8%	1.5%
Iodine Number	985 mg/g	1080 mg/g
Specific Surface Area	1139 m^2/g	1476 m^2/g

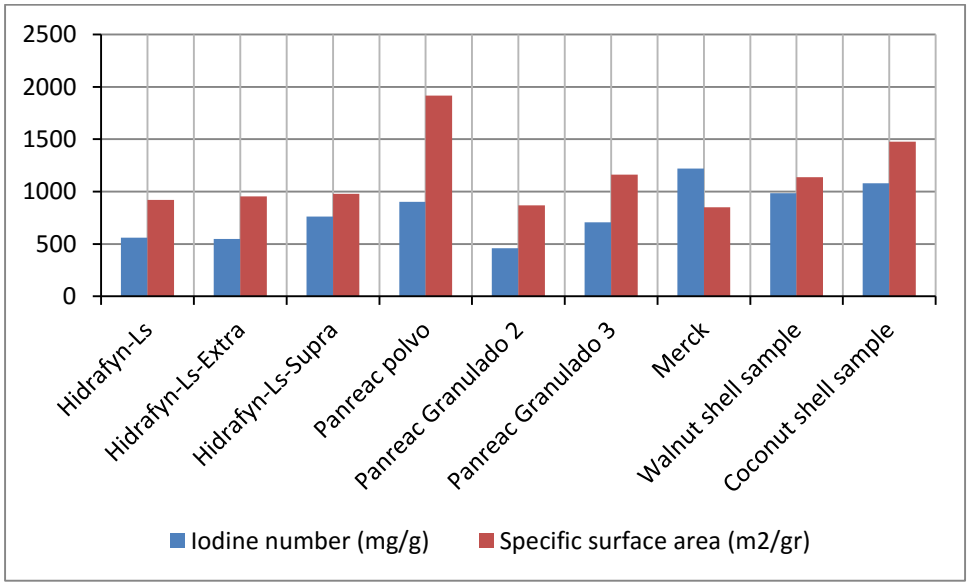

Figure 17: Comparison of Commercial Activated Carbons Properties with Optimized Results of this Research

Conclusion

1. Chemical activation method has been applied on walnut and coconut shells in order to prepare activated carbon and it reveals that without optimization, properties activated carbons are not well enough for commercial applications.
2. The most important processing parameters for optimization of activated carbons were activation agent concentration, impregnation ratio, particle size, carbonization temperature and duration and activation temperature and duration which were varied based on raw materials type and were found for walnut and coconut shells.

3. By applying the optimized parameters, Iodine number of 985 mg/g and specific surface area of 1139 m^2/g was achieved for walnut shell based activated carbon. Also specific surface area of coconut shell based activated carbons was reached up 1476 m^2/g which is comparable with best commercial activated carbons.

REFRENCES

Anirudhan TS and Sreekumari SS (2011). Adsorptive removal of heavy metal ions from industrial effluents using activated carbon derived from waste coconut buttons. *Journal of Environmental Science* **12**(23) 1989-1998.

Evbuomwan BO, Abutu AS and Ezeh CP (2013). The Effects of Carbonization Temperature on some Physicochemical Properties of Bamboo Based Activated Carbon by Potassium Hydroxide (KOH) Activation. *Greener Journal of Physical Science* **3**(5) 187-191.

Girgis BS, Khalil LB and Tawfik TAM (1994). Activated carbon from sugar cane bagasse by carbonization in the presence of inorganic acids. *Journal of Chemical Technology Biotechnology* **61** 87-92.

Kostomarova MA and Surinova SI (1988). Adsorbents, their production, properties and application. *Proceedings of all Russian Conference on Adsorbents*, Nauka, Leningrad 58.

Li W, Yang K, Peng J, Zhang L, Guo Sh and Xia H (2008). Effects of carbonization temperatures on characteristics of porosity in coconut shell chars and activated carbons derived from carbonized coconut shell chars. *Industrial Crops and Products* **28** 190-198.

Martinez ML, Torres MM, Guzman CA and Maestri DM (2006). Preparation and characteristics of activated carbon from olive stones and walnut shells, *Industrial Crops and Products* **23**(1) 23-28.

Mcdowal JD (1990). Method of producing granular activated carbon, *United States Patent* 5,162,286.

Puziy AM, Poddubnaya OI, Martinez-Alonso A, Suarez-Garcia F and Tascon JMD (2002). Synthetic carbons activated with phosphoric acid I. surface chemistry and ion binding properties, *Carbon* **40** 1493-1505.

Stavropoulos GG and Zabaniotou AA (2005). Production and characterization of activated carbons from olive-seed waste residue, *Microporous and Mesoporous Material* **82** 79-85.

Suarez-Garcia F, Martinez-Alonso A and Tascon JMD (2003). Synthetic carbons activated with phosphoric acid III. Carbons prepared in air, *Carbon* **41** 1181-1191.

Toles CA, Marshall WE and Johns MM (2000). Activated nutshell carbons from agricultural waste. *United States Patent* 6,033,573.

Yahaya NKEM, Latiff MFPM, Abustana I and Ahmad MA (2010). Effect of Preparation Conditions of Activated Carbon Prepared from Rice Husk by $ZnCl_2$ Activation for Removal of Cu (II) from Aqueous Solution, *International Journal of Engineering Technology* **10**(6) 28-32.