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Preparation and characterization of activated carbon derived from rubber wood sawdust *(Heavea brasiliensis)*: Textural and chemical characterization

COLLIN G. JOSEPH[1], LAWRENCE TEO KAH HOONG and FAUJAN B.H. AHMAD[2]

[1]Industrial Chemistry Program, School of Science and Technology, Universiti Malaysia Sabah, 88999 Kota Kinabahu, Sabah, (Malaysia).
[2]Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, Serdang 434 00, Selangor (Malaysia).

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ABSTRACT

Activated carbons from rubber wood sawdust (RW) were prepared by physical and chemical activation using potassium hydroxide as the dehydrating agent. A two-stage activation process method was used; with semi-carbonization stage at 200°C for 15 minutes as the first stage followed by an activation stage at 500°C for 45 minutes as the second stage. The precursor material with the impregnation agent was exposed straightaway to semi-carbonization and activation temperature unlike the specific temperature progression as reported in the literature. All experiments were conducted in a laboratory scale muffle furnace under static conditions in a self generated atmosphere covering process parameters such as impregnation ratios. We found that by using this method, the RW20% prepared with the impregnation ratio of 20% had the highest Iodine Number and Methylene Blue adsorption capacity which were 72.39 mg/g and 40mg/g respectively.

Key words: Activated carbon; two-stage activation process, physical and chemical properties.

INTRODUCTION

Activated carbons are carbons of highly microporous form with both high internal surface area and porosity, which find extensive use in the industrial sector for adsorption of pollutants from air and water streams. This material can be designed for adsorption of specific adsorbate, by using appropriate precursor[1-4], dehydrating agent and by optimizing the activation process conditions. Several activating agents have been reported for chemical activation process; however the most important and commonly used activating agents are zinc chloride, potassium hydroxide and alkaline metals. This agent, which has dehydrating properties, will influence the pyrolytic decomposition and retard the formation of tars during the carbonization process, increasing the carbon yield[5]. A number of activation methods have been reported in the literature using KOH as an activating agent. Chemical activation by KOH was first reported in the late 1970s by AMOCO Corporation[6] and these carbons were commercialized by the Anderson Development Company in the 1980s[7]. Since then, there have been many studies reporting on the activation of carbons using KOH[8-14]. The chemical nature of activated carbon significantly influences its adsorptive, electrochemical, catalytic, and other properties. However, few papers report on the effects on chemical preparation conditions and preparation methods on the carbon. Generally, activation methods can be classified as single-stage or two-stage activation process carried out either in inert medium or a self-generated atmosphere is shown in Table 1. This paper explains the effect of KOH impregnation to the precursors prepared by using as two-stage activation process method in a self-generated atmosphere. Trial and error methods were used to achieve a high surface area carbon with desired pore size by optimizing the process parameters such as the activation time, activation temperature and impregnation ratio. Table 1 summarizes efforts by researchers to prepare activated carbons using various methods with references to the precursors, experiment condition and results. Table 2 summarizes efforts by researchers to prepare activated carbons using KOH as the dehydrating agent.

Malaysia has been one of the main rubber producers and exporters in the Asian region for decades. As the demand for natural rubber started to decrease and Malaysian rubber plantations began to shift their activities towards other form of agricultural commodities, rubber trees from these rubber plantations were utilized for many other purposes, some of which are furniture-making, construction and pulp processing. This project currently undertakes the task to utilize rubber wood sawdust as a precursor for activated carbon. The preparation of activated carbon from rubber wood sawdust is one of the ways of adding value to rubber wood and this material can easily be sourced from the furniture industry wastes. This paper describes a study on the use of KOH as dehydrating agent and the effects of two stage activation process in self-generated atmosphere on the textural and chemical properties of the activated carbons prepared.

EXPERIMENTAL

Prior to the impregnation process, precursors were washed with distilled water and dried in an oven at 110°C for 24 hours. This was done to remove sand, branch fibers and dirt from contaminating the samples as explained in our previous paperes[1-4]. Impregnation process was done using KOH as the dehydrating agent. 5g, 10g, 25g and 25g of granular KOH were placed separately into 5 Erlenmeyer flask (250ml). 100ml of distilled water and 20g of precursor was added into each of the flask. The flask was then placed in orbital shaker

Table 1: Summary of earlier works by researchers to prepare activated carbons using various methods.

Researcher	Precursor	Experimental Condition	Results
Kirubakaran *et al.*[15]	Coconut Shell	Two stage in N_2 atm;400 to 600°C; A time = 2m^2	S.A>1000m2/g at I.R.=1.5
Toles *et al.*[16]	Macadamia Shell, pecan, walnut and almond	Single and two stage; N_2 and self-generated atm; S.C.T=170°C; S.C. time= 30min; A.T.=450°C; A.time =1h	S.A=1100 to 1600m^2/g. Activation in self-generated atm gave the highest S.A.
Dastgheib and Rockstraw[17]	Pecan Shell	Three stage activation: 1) liquid-stage activation at 160°C 2) primary activation at 160-210°C 3) secondary activation at 300-500°C for 30min, I.R.=3	S.A=1071m^2/g.S.A increase until secondary A.T of 450°C and reduces when temperature increases above 450°C
Lafi[18]	Acorns and olive seeds	A single stage with self generated atmosphere. A.T. = 400-800°C. A.time=1h	A.T.=800°C produced the highest Methylene Blue no. of 130 mg/g

model 721 Protech for week. The samples were dried overnight in an over at 110°C. A muffle furnace model Carbolite RHF 1500 was used to semi-carbonized the samples at 200°C for 15 minutes as the first stage followed by and activation stage at 500°C for 45 minutes as the second stage.

The precursor material with the impregnation agent was exposed straightaway to semi-carbonization and activation temperature unlike the specific temperature progression methods as described in earlier work[1-4, 15-18]. After that, the activated refluxed in an acid solution (0.1M HNO_3) to remove metal ions, tar and ash followed by distilled water (10 times) to remove the acid. The activated carbons were dried in an oven at 110°C for a week, after which, yield percentage, moisture and ash content, pH[19], scanning electronic microscopy of the selected activated carbon were done. The scanning electronic microscopy was done using JEOL JSM 5610. Adsorption studies regarding the treatment of landfill leachate with the activated carbon, surface area and porosity studies with presented in our next paper.

RESULTS AND DISCUSSIONS

Temperature, heating period, materials, dehydrating agent and the method of carbonization and activation play an important role in determining the properties of the resulting activated carbon. Previous work in our laboratories[1-4] suggested that the temperature played an important role to produce optimum surface area for the carbons.

Percentage of yield pH, moisture and ash contents

The overall yield of the activated carbon was calculated based on the initial weight to the predried precursor. Relatively high yields of the final products are expected in manufacturing commercial adsorbents. Fig.1 shows the effect of KOH impregnations (wt %) on the percentage of yield, pH, moisture and ash content of rubber wood sawdust. The percentage of yield of rubber wood sawdust was between 48-77% with RW0% giving the highest percentage of 77%. Increasing the KOH-to-precursor ratio decreased the overall yield for rubber wood sawdust activated carbons. This was because the potassium ions attached onto the carbon surface, acting as catalyst to accelerate direct reaction between the carbon and KOH. These reactions contributed to the evolution of more volatile matter in the form of smoke and gasess[23]. Rubber wood sawdust is a typical carbonaceous biomass therefore, the following reaction occurred during KOH impregnation process.

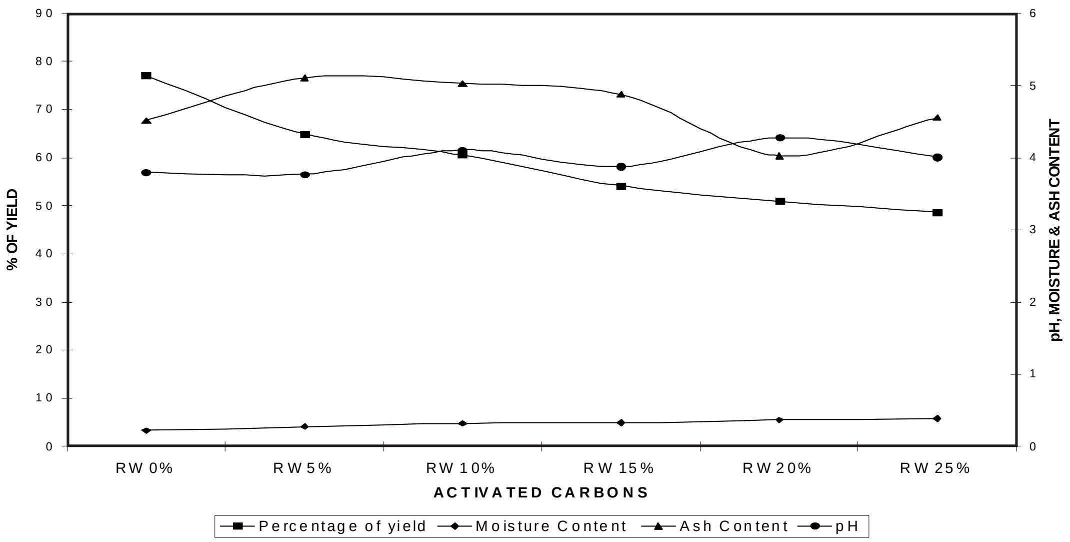


Fig. 1: The effect of KOH impregnations (wt%) on the percentage of yield, pH, moisture and ash contents of the rubber wood sawdust activated carbons

$$C_nH_xO_y + KOH \rightarrow (C_nH_{x-1}O_y\text{-}K) + H_2O\uparrow \qquad ...(1)$$

During semi-carbonization (1st stage) will result in the following products:

$$(C_nH_xO_y\text{-}K) \rightarrow \text{Char } (+K) + \text{Tars} + \text{Gases} \qquad ...(2)$$

Char usually contains a majority of carbon, C (~75-80%); some oxygen, O (~15-17%) and some hydrogen, H (<3%). Tar consist of phenol, CH_3COOH, C_3OH, and other high molecular weight hydrocarbons. Gaseous component include H_2O, CO_2, CO etc [20].

The following reaction during the activation (2nd stage) process.

$$C + 2KOH \rightarrow 2K + H_2\uparrow + CO_2\uparrow \qquad ...(3)$$
$$C + 2KOH \rightarrow 2K + H_2O\uparrow\text{-} + CO\uparrow \qquad ...(4)$$
$$CO_2 + 2KOH \rightarrow K_2CO_3 + H_2O\uparrow \qquad ...(5)$$

At activation temperature, metallic potassium intercalated with the carbon matrix, resulting in the widening and formation of new pores. Secondary reactions possibly took place as well between H_2O (eq3), C and KOH resulted in the formation of 'extra' K_2CO_3 as shown in the following equation:

$$H_2O + C + 2KOH \rightarrow K_2CO_3 + 2H_2\uparrow \qquad ...(6)$$

Potassium carbonate (K_2CO_3) is known to produce well-developed internal porosity on the activated carbon[21].

Our observation recorded that the pH of the activated carbons was about[4]. This is due to the washing process using nitric acid. Moisture and ash content for the activated carbon ranged from 3-6% and 4-5% respectively. The activated carbons showed a reducing pattern for the ash content and an increasing pattern for the moisture content as the impregnation ratio of KOH was increased. This was because higher concentration of KOH inhibits excessive burn-off, and lowering ash formation. KOH also has an affinity for adsorbing water, this accounted for the increasing pattern of the moisture content as the concentration of KOH increases in fig. 1.

Physical Appearance

The activated were photographed after activation, and these photographs showed an interesting physical appearance. Figure 3 shows the photograph of the untreated RW, RW0% and RW25%.

The untreated sawdust was light brownish in colour whereas the physically activated carbon, RW0%, was dark brown in colour. Chemically activated carbon, RW25%, was black in colour. The RW0% maintain the similar shape and structure as untreated sawdust but RW25% underwent remarkable physical change as shown in figure 2. The shape of the sawdust was completely lost and the RW25% took the shape of the crucible that was use as a reactor. RW25% had as sponge-like appearance and was very brittle. It is possible that KOH deposition on the surface of the material according to eq 1 during impregnation and eq 4 during activation contributed to extensive gasification that produced the sponge-like appearance. Morphological studies using scanning electron microscopy also corroborated this finding.

Scanning electron microscopy

SEM was used to study the morphological structure on the prepared activated carbons. The surface structure of the untreated sawdust has dirt-covered, unclear and small pores. The surface structure of the physically activated carbon (RW0%) has clean and burnout pores with clear definition. The chemically impregnated activated carbon (RW25%) also showed similar traits but some of the pores were clearly enlarged with a lot of smaller pores surrounding the bigger pores. This clearly demonstrates that KOH helped to encourage pore enlargement. The pores were also elongated in shape. This is characteristically unique to KOH impregnated activated carbons. If the morphological structure area viewed as a whole (RW25%~overview), we can see that the structure is completely different as compare to RW0%.

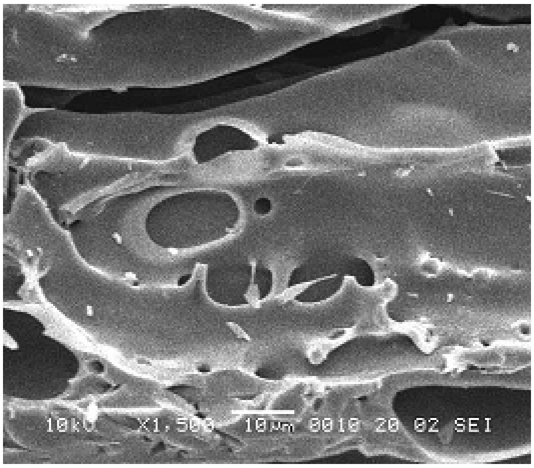
This was due to the reaction of KOH with the lignocelluloses material giving a burn-out sponge-like structure. These findings correspond with the physical appearance result of the activated carbons. Our results suggest that the chemical

Untreated Sawdust

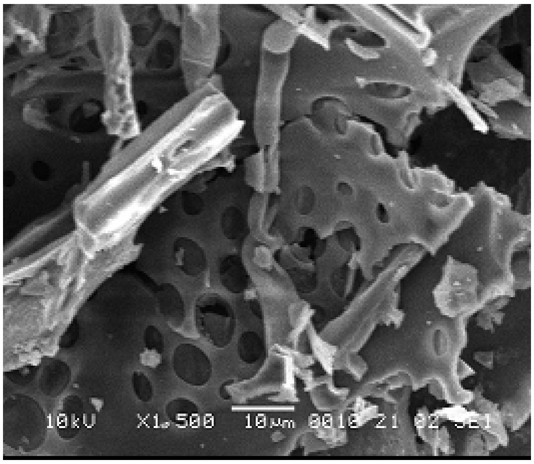
RW0%

RW25%

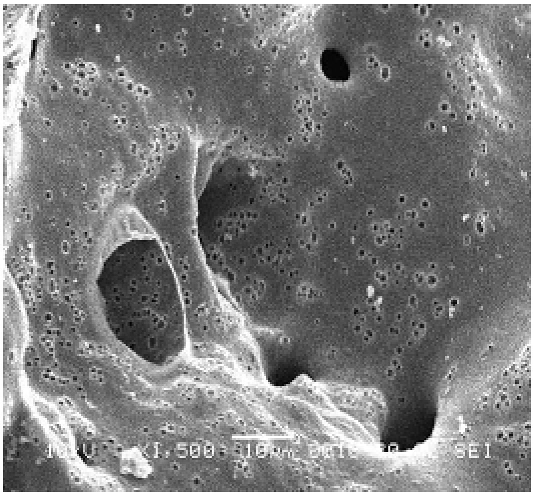
Fig. 2: Photographs of the untreated sawdust, physically activated carbon, RW0% and chemically activated carbon; RW25%.



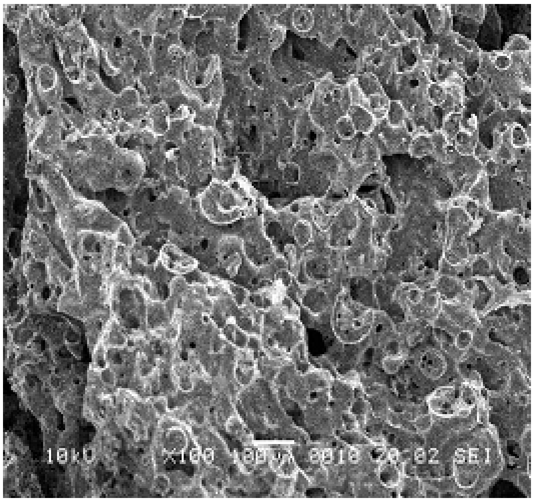
Untreated sawdust



OPS0%



RW25%



RW25%-overview

Fig. 3: The electron micrographs of untreated sawdust, RW0%, RW25% and RW25%-overview

Table 2: Summary of earlier works by researchers to prepare activated carbons using KOH impregnations

Researcher	Precurson	Experimental Condition	Results
Kirubakaran *et al.*[15]	Esparto grass *(Stipa tenaci ssima)*	N_2, atm; K_2CO_3 used as reference; I.R. 0.2-4.0;A.T. 400°C, 600°C, 800°C; A time 30min,	Highest S.A. of 1960m²/g obtained at 800°C KOH activation more effective than K_2CO_3. K_2CO_3 enchances mesopore formation
Lillo-Rodenas *et al.*[23]	Anthractie	N_2CO_2 steam and atmcomb varying gas flow rate; comb. NaOH Na_2CO_3 used as activating agent I.R.3.0 -4.0; A.T. 760°C; A. time 1 h:	Highest S.A. of 2193 as m2/g obtained at N_2 flow effective under CO_2 atmosphere. Na_2CO_3 not an activating agent. Reaction between NaOH and C begins at ~ 570°C, for KOH/C at 400°C
Ganan et al24	Mesophase Coal pitch	N_2atm; 1&2-step activation I.R.: 1.0-60; A.T.: 375-900˜C 450°C, A time : 1-2 hrs. Air gasification conducted	Highest S.A. for 1 step activation 638m²/g at I.R.=3. Highest S.A. for 2 step activation: 2346m²/g at IR=3. Air gasification at 300°C no significant improvement in carbon texture.
Carvalho *et al*[25]	Cork Waste	N_2atm.: 1&2-step activation A.T. 300°C and 500-900°C, A. time. 0-16h	Highest S.A.=1415m²/g. Increase of I.R. has positive effect initially but opposite situation is observed at high I.R.

S.A= Surface area; S.C.T.=Semi-carbonization temperature, S.C. time=semi-carbonization time, A.T.= Activation tempearture, A time= activation time., I.R.=impregnation ratio.

activator played an important part in clearing, restructuring and producing better pores. These findings are consistent with the findings by other researchers. Potassium compounds are effective catalyst for activation[21].

Conclusion

In conclusion, this study showed that the use of dehydrating agent and the two-step activation process in self-generated atmosphere played a major role in shaping and transforming precursors into activated carbons. Granular KOH was used as a dehydrating agent, produced a very different activated carbon, changing not only the pore structure and morphology of the activated carbon but also giving the sponge-like physical appearance of the precursor itself. The precursor, rubber wood sawdust, was changed from its natural form to take the shape to the reactor. It is our opinion that extensive gasification coupled with activation temperature of 500°C contributed to this change.

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REFERENCES

1. Anuar, K., Collin, G.J., Zulkarnain, Z., Hussein, M.Z., Haron, M.J. dan Abdullah, A.H., "Surface area and porosity studies of activated carbons prepared from oil palm shells (*Elaeis Guineensis*) using physical and chemical activators such as CO_2,H_3PO_4, K_3PO_4 and KOH" *ASEAN J. of Sci. and Tech for Dev.,* **20**(2): 149-158 (2003).
2. Anuar, K., Collin, G.J., Zulkarnain, Z., Hussein, M.Z., Haron, M.J. dan Abdullah, A.H., "Activated carbons prepared from oil palm shell: application for column separation of heavy metals" *Indian Chem. Soc.,* **81**(2): 946-949 (2004).
3. Anuar, K., Collin, G.J., Ahmad F.B.H., Zulkarnain, Z., Hussein, M.Z., dan Abdullah, A.H., "Preparation and characterization of activated carbon from Resak wood (*Vatica Hulletti*) : Surface area and porosity studies" *Oriental J. of Chem.,* **81**(1): 43-46 (2002).
4. Anuar, K., Collin, G.J., Ahmad F.B.H., Zulkarnain, Z., Hussein, M.Z., Dan Abdullah, A.H., "Preparation and characterization of activated carbon from Resak wood (*Vatica Hulletti*) " *Res. J. of Chem. Environ.,* **5**(3): 21-24 (2001).
5. Gergova, K., Petrov, N., Eser, S. "Adsorption properties and microstructure of activated carbons produced from agricultural by-products by steam pyrolysis" *Carbon.,* **32**: 693-702 (1994).
6. Marsh, H., Crawford, T.M., O'Grady, T.M., Wennerberg, A.N., "Carbons of high surface area. A study by adsorption and high resolution electron microscopy" *Carbon.,* **20**: 419-426 (1982).
7. O'Grady, T.M., Wennerberg, A.N., Petroleum-Derived Carbons, High-Surface-Area Active Carbon, in: ACS Symposium Series, 303 *Amercan Chemical Society.,* 302 (1986).
8. Otawa, T., Nojima, Y., Miyazaki T., "Development of KOH activated high surface area carbon and its application to drinking water purification" *Carbon.,* **35**: 1315-1319 (1997).
9. Otawa, T., R., Itoh, M. "Production and adsorption characteristics of MAXSORB: High-surface-area active carbon" *Gas Sep. Purif.,* **7**: 241-245 (1993).
10. Ahamadpour, A., Do, D.D., "The preparation of active carbon from coal by chemical and physical activation" *Carbon,* **34**: 471-479 (1997).
11. Ahamadpour, A., Do, D.D., "The preparation of activated carbon from macadamia nutshell by chemical activation" *Carbon.,* **35**: 1723-1732 (1997).
12. Hu, Z.H., Vansant, E.F., "Chemical activation of elurtlithe producing carbon-aluminosilicate composite adsorbent" *Carbon.,* **33**: 1293-1300 (1995).
13. Laine, J., Calafat, A."Factors affecting the preparation of activated carbons from coconut shell catalized by potassium" *Carbon.,* **29**: 949-953 (1991).
14. Hu, Z.H., Srinivasan, M.P. "Preparation of high-surface-area-activated carbons from coconut shell" *Micropor. Mesopor. Mater.,* **27**: 11-18 (1999).
15. Kirubakaran, J.C., Krishnatah, K., Sheshadri, S.K., *Ind. And Eng. Chem. Res.,* **30**: 2411 (1991).
16. Toles, C.A., Marshall, W.E., Johns M.M. *J. Chem. Tech.,* **72**: 255 (1998).
17. Dastgeib S.A., Rockstraw D.A. "Pecan Shell activated carbon: synthesis characterization, and application for the removal of copper from aqueous solution" *Carbon*., **39**: 1849-1855 (2001).
18. Lafi W.K., "Production of activated carbon from acorns and olive seeds" *Biomass and Bioenergy* **20**: 57-62 (2001).
19. SIRIM., Specification of powdered activated carbon MS 873: Standard and Industrial Research Institute Malaysia., (1984).
20. Jankowaka, H., Swiatkowski and Choma *J., Active Carbon Elis.* Horwood Ltd. (1991).
21. Annuar, K., Collin, G.J., Dzulkefly, K., Zulkarnain, Z., Hussein, M. Z., Haron, M.J. and Abdullah, A.H. and Jamaluddin D. "Activated Carbons from oil palm shells (*Elaeis Guineenis*)- preparation and characterization" *Mal. J. of Anal. Sci.,* **8**(1): 130-134 (2004).

22. Diaz-Teran, J., Nevskaia, D.M., Fierro, J.L.G., Lopez-Peinado, A.J., and Jerez, A., "Study of chemcial activation process of a lignocellulosic material wiht KOH by XPS and XRD" *Micro. and Meso. Mat.,* **60**(1-3): 173-181 (2003).
23. Lillo-Rodenas, M.A., Cazorla-Amoras, D., Linares-Solano, A., "Understanding chemical reactions between carbons and NaOH and KOH: An insight into the chemical activation mechnaism. *Carbon,* **41**(2): 267-275 (2003).
24. Ganan, J., Gonzalez-Garcia, C.M., Gonzalez, J.F., Sabio, E., Macias-Garica, A., and Diaz-Diez, M.A., "Preparation of activated carbon from bituminous coal pitches" *App. Sur. Sci.* (In press) (2004).
25. Carvalho, A.P., Cardoso, B., Pires J., and Brotas de Carvalho, M., "Preparation of activated carbons from cork waste by chemical activation with KOH" *Carbon.* **41**(14): 2873-2876 (2003).