Adsorption of Benzene on Activated Carbon from Agricultural Waste Materials

Akpa J.G.[1]* and Nmegbu C.G.J.[2]

[1]Department of Chemical/Petrochemical Engineering, Rivers State University of Science and Technology, Port-Harcourt, Rivers State, NIGERIA
[2]Department of Petroleum Engineering, Rivers State University of Science and Technology, Port-Harcourt, Rivers State, NIGERIA

Abstract

Activated carbon was produced from three carbon rich agricultural waste materials; bamboo, coconut and palm kernel shells by pyrolysis and chemical activation (using tri oxo nitrate (v) acid (HNO_3)). The activated carbons were characterized and used as adsorbent for the removal of benzene from aqueous solution. The effects of various parameters such as particle size, adsorbent dosage and initial benzene concentration on the adsorption efficiency of the activated carbons were investigated. Benzene adsorption decreased with increase in particle size of activated carbon, decrease was minimal with activated carbon produced from bamboo. Benzene adsorption increased with increase in adsorbent dosage. Increase in initial benzene concentration resulted in increased adsorption using activated carbon from coconut and palm kernel shells; a decrease in adsorption using activated carbon from bamboo.

Keywords: Activated carbon, benzene adsorption, chemical activation.

Introduction

Active carbon adsorption is a process[1] where the molecules of the contaminant are transferred from a dissolved state in the aqueous phase to the surface of active carbon. Carbonaceous adsorbents have been found[2] to be useful for the adsorption of different substances from gaseous and liquid phases due to their good kinetic properties and high adsorption capacities. In most applications, activated carbon is used for the removal of impurities from fluids, vapours or gases. Activated carbon is also used in gas purification, decaffeination, gold purification, metal extraction, water purification, medicine, sewage treatment, air filters in gas masks and respirators, filters in compressed air and many other applications.

The use of activated carbon for purification purposes (removal of unwanted components from streams) has been performed severally; removal of heavy metal ions such as copper[3], zinc and chromium[4] and mercury[5], in waste water treatment for purification, decolourization and the removal of toxic organics and heavy metal ions.

Activated carbon is produced by carbonization and activation[6] (enlargement of the pore structure, increases the internal surface area and makes it more accessible) of a "carbon rich material". Carbonization is the process of converting a carbon-rich material to pure carbon through pyrolysis – heating the carbon-rich material in a furnace in the absence of oxygen at extreme temperatures (600 - 900°C)[7]. The carbon produced is then activated to make it adsorbent. This can occur in one of two ways: physical or chemical treatment. In physical treatment, the carbonized material is exposed to oxidizing atmospheres (oxygen or steam) and heated between 600 - 1200°C[8]. In chemical treatment, it could be a one step process where carbonization and chemical activation occur simultaneously thus: prior to carbonization, a bath of a strong dehydration agent such as an acid, strong base or a salt[9] is prepared and the carbon rich material submerged. The bath is then heated to temperatures of 450 – 900 °C or the two step process where carbonization and chemical activation occur separately. Chemical Activation is often the preferred method[10] due to its shorter production time, lower production temperatures and higher purity of activated carbon produced.

Typical raw materials used for the production of activated carbon have high carbon but low inorganic contents like wood, lignite, peat and coal[11]; contain a minimum amount of organic material, have a long storage life, are hard enough to maintain their properties under usage conditions, may be obtained at a low cost, and are capable of producing high-quality activated product when processed[12].

The use of industrial waste, agricultural by-products[13] and residual wastes in the production of activated carbon abounds: paper mill sludge and peach stones[2], bagasses fly ash- a sugar industry waste[14], macadamia nutshell[15], rice husk[16], date stones[17], apricot stones[18], olive seed waste[19], oil palm wastes[20], palm kernel fibre[21], bagasse and rice husk[8] and bamboo[7,10]. The processing of these wastes for the manufacture of activated carbon has reduced the problems of disposal and management of these wastes and by products.

This work investigates the use of activated carbon for the absorption of benzene. Benzene is a natural constituent of crude

oil and gasoline (and therefore motor vehicle exhaust). It is also an important industrial solvent and a precursor in the manufacture of some industrial chemicals including drugs, plastics, synthetic fibbers, lubricants, dyes, detergents, explosives and insecticides. Trace amounts of Benzene also result whenever carbon rich materials undergo incomplete combustion. It is a component of combustion products produced by the burning of PVC (polyvinyl chloride). These processes cause the release of benzene into the atmosphere, polluting the environment and causing health problems. Acute occupational exposure to benzene may cause narcosis (headache, dizziness, drowsiness, and loss of consciousness); while chronic exposure can cause cancer in humans, reduce the production of both red and white blood cells from bone marrow, resulting in anemia and damage of the immune system[22]. Hence it is necessary to reduce the benzene concentration in these processes/wastes and the environment to minimal levels that are not injurious to human health. One way of achieving this is by adsorbing benzene from these streams. The suitability of activated carbon for the absorption of benzene is therefore investigated. In this study, activated carbon was produced from three agricultural waste materials: coconut shell, bamboo and palm kernel shell and used to evaluate their adsorption rate of benzene (removal capacity of benzene from the aqueous phase). The effects of the particle size, the quantity (dose) of the adsorbent and initial concentration of the benzene on the adsorption capacity and efficiency of these activated carbons were also investigated.

Material and Methods

Materials: The agricultural waste materials – bamboo was obtained from used scaffold at a construction site at the Rivers State University of Science and Technology, while coconut and palm kernel shells were obtained from Ataba Town, a coastal town in Andoni Local Government area, Rivers State in the Niger Delta region of Nigeria. The various chemical reagents used in this experiment were analytical grades and purchased at a chemical shop at the industrial chemical section of Mile 3 market in Port-Harcourt, Rivers State.

The pyrolysis reaction was performed using the "pyrolysis set up" in the reaction kinetics laboratory of the Department of Chemical/Petrochemical Engineering, Rivers State University of Science and Technology, Port-Harcourt, Rivers State, Nigeria. The activation of the carbon, characterization of the produced activated carbons and batch adsorption experiments were also performed at the reaction kinetics laboratory.

Methods: The production of activated carbon from bamboo, coconut and palm kernel shells was performed as follows:

Preparation of Samples: The (carbon rich) raw materials: bamboo was cut to 2cm long with a cutting machine while coconut and palm kernel shells were size reduced using a crushing machine. The raw materials were washed with distilled water and sun dried.

Carbonization Process: A measured weight of each raw material was introduced into the reactor and pyrolized at 300°C - 350°C in the absence of air for two hours thirty minutes[20]. The distillates formed during the pyrolysis were collected by the receiver connected to the condenser to avoid air pollution, while the char materials were cooled at room temperature before discharging into containers.

Chemical Activation: The carbonated materials (carbon) from bamboo, coconut and palm kernel shells were crushed into powder using a crusher and sieved with a 1.88 mm sieve to obtain a uniform particle size. Measured weights of each carbonated materials were soaked in nitric acid of known concentration in a crucible. Each sample solution was stirred until the mixture turned to paste. The pastes were heated in a muffle furnace at 800°C for 2hrs in the absence of air to increase the surface area of the samples for adsorption purposes[23]. The activated carbons were cooled to room temperature, washed with distilled water until their pH approximates 7 (no change in colour when tested with a red litmus paper) indicating no trace of nitric acid, dried for 6hrs and stored in an air-tight nylon.

Characterization of Produced Activated Carbon: The physiochemical properties of the activated carbons such as the oil yield, Bulk Density, Porosity, moisture content, ash content and pH were determined using standard procedures. All results were the average of duplicate analysis.

Yield of Carbon: The char material cooled after carbonization was weighed and used to obtain the percentage yield of carbon using the formula:

$$\% \text{ Yield of carbon} = \frac{\text{Weight of char}}{\text{Weight of raw material}} \text{ x } 100 \qquad (1)$$

Determination of Bulk Density: Clean dry empty 10ml centrifuge tube was weighed (W_1), the centrifuge tube was filled with the different activated carbon samples (tap tube as it is filled until sample fills to the mark) and weighed (W_2). The difference in the weights gives the weight of the activated carbon powder in the bottle. The bulk density of the activated carbon powder was calculated using the equation:

$$\text{Bulk Density} = \frac{\text{Weight of powder in the bottle}}{\text{Volume of bottle}} = \frac{W_2 - W_1}{\text{Volume of centrifuge tube}} \qquad (2)$$

Porosity Determination: The porosity of the activated carbon was obtained using the formula:

$$\text{Porosity} = \frac{\text{Pore Volume}}{\text{Total Volume (volume of centrifuge tube)}} \qquad (3)$$

The pore volumes of the activated carbons were obtained using the formula:

$$\text{Pore Volume} = \frac{\text{Bulk Density of activated carbon}}{\text{Density of Water}} \qquad (4)$$

Therefore the porosity is:

$$\text{Porosity} = \frac{\text{Bulk Density of activated carbon}}{(\text{Density of water}) \times (\text{Total Volume})} \qquad (5)$$

Determination of Moisture Content: The moisture content was determined using the ASTM D2867-09 method[24]. Clean empty crucible was oven dried at 110^oC, cooled in a desiccator and weighed (W_1). Known weights of each powdered air dried activated carbon powder was put into the crucible, weighed (W_2) and dried in an oven maintained at about 110^oC; the drying activated carbon was constantly reweighed at 30 minutes interval until the weight of the carbon became constant. The crucible was taken out, cooled in a desiccator and weighed again (W_3). The loss in weight of the activated carbon is used to calculate the moisture content (Xo) of the activated carbon from the relationship:

$$X_0 = \frac{W_2 - W_3}{W_2 - W_1} \times 100 \qquad (6)$$

Determination of ash content: The ash content of the activated carbons was determined according to the ASTM D2866-94 method[25]. Clean empty crucible was oven dried at 110^oC, cooled in a desiccator and weighed (W_1). Known weights of each powdered air dried activated carbon powder was put the crucible, weighed (W_2) and transferred into a preheated muffle furnace set at a temperature of 800^oC. The furnace was left on for one hour after which the crucible and its content was transferred to a desiccator and allowed to cool. The crucible and its content were reweighed (W_3). The percentage ash content of each activated carbon sample (dry basis) was obtained from the equation:

$$\text{Ash \%} = \frac{W_{ash}}{W_0} \times 100 = \frac{W_3 - W_1}{W_2 - W_1} \times 100 \qquad (7)$$

Where: W_{ash} = Weight of ash (grams).

Determination of pH: 1 g of each produced activated carbon was weighed and dissolved in 3 ml of de-ionized water. The mixture was heated and stirred for 3 minutes to ensure proper dilution of the sample. The solution was filtered and out and its pH was determined using a digital pH meter**.**

Liquid Phase Adsorption of Benzene: Batch experiments were performed to study the adsorption capability of the activated carbons produced for benzene in solution. 2g of each activated carbon sample was weighed into different 500ml conical flasks. 20ml of benzene was measured from the original mixture and poured into each 50ml conical flask and agitated at a stirring speed of 200 rpm to ensure intimate contact of the adsorbent and the solute in the solution. Each conical flask was observed for 20mins and filtered with a filter paper. A portion of the filtrate from each flask was poured into a cuvette and the concentration of benzene in the solution was measured using a spectrophotometer.

Effect of Process Parameters on Adsorption Rate: Batch experiments were performed to study the effects of certain process parameters such as particle size, adsorbent dose and initial benzene concentration on the adsorption process.

Particle Size: Various particle sizes of the produced activated carbons were used to conduct experiments to determine percentage removal of benzene at an initial concentration of 4ppm. The three different activated carbons produced were sieved into different particle sizes of 800 µm, 600µm, 300µm, 150µm and 75µm. 0.25gram of each particle size was weighed into a beaker. 25ml of benzene stock solution (4ppm) was measured into the beaker containing each activated carbon, stirred and agitated for 20mins. The solution was filtered using a filter paper and a conical flask. The filtrate was collected and the concentration of benzene in the solution was measured using a spectrophotometer.

Adsorbent (Carbon) Dosage: The effect of activation carbon dose (quantity in weight) on the extent of solute adsorbed was investigated by varying the dose of 600 µm particle size activated carbon from 0.2 to 1.0g under the selected initial solute mass concentration (1ml of benzene in 250ml of distilled water, 4ppm) (concentration of benzene in solution). Different weight (0.2g, 0.4g, 0.6g, 0.8g and 1.0g) of each sample was weighed into a beaker. 20ml of the stock solution (4ppm) was measured into the beaker containing the sample, stirred and agitated for 20mins. The solution was filtered using a filter paper and a conical flask. The filtrate was collected and the concentration of benzene in the solution was measured using a spectrophotometer.

Initial Concentration of Solute: Two initial concentration of stock solution (1ml of benzene in 250ml of distilled water (4ppm) and 2.5ml in 250ml (10ppm)) were prepared. 0.25gram of 600 µm particle size of each activated carbon was weighed into three different beakers. 20ml of each initial concentration of stock solution was measured into each beaker, stirred and agitated for 20mins. The solutions were filtered using a filter paper into a conical flask. The filtrates were collected and the concentrations of benzene in the solution were measured using a spectrophotometer.

Results and Discussion

Characterization of Activated Carbon: The results of some physiochemical properties of the activated carbons produced from the three different raw materials are presented in table 1.

These properties affect the efficiency of the activated carbon in diverse ways, such as: The ash content[26] which is the inorganic, inert, amorphous and unusable part present in the activated carbon reduces the overall activity of activated carbon; while the porosity classified by the size of the diameter of the pores, describes the number of pores present in a sample enhances adsorption capacity of the adsorbent[27]. The overall effect of these properties is a combination of the individual effects.

Adsorption of Benzene using Activated Carbon: Effect of activated carbon Particle size on amount of benzene adsorbed: The effect of activated carbon particle size on the removal rate of benzene (% benzene adsorbed) is shown in figure 1. Figure 1 reveals that an increase in the particle size of the activated carbon results in an average corresponding decrease in the amount of benzene adsorbed for all activated carbon produced; however, the effect of particle size on the activated carbon from bamboo is very minimal.

The finer (smaller) the particles size of an activated carbon, the better the access to the surface area and the faster the rate of adsorption; also the smaller the particle size distribution, the smaller the pore spaces and the activated carbon particles tends to retain more benzene molecules. In contrast, a lager particle

size distribution implies larger pore spaces incapable of retaining benzene molecules seeping through[28]. These trends are show in figure-1.

Effect of Adsorbent dosage on amount of benzene adsorbed: The effect of activated carbon dose on the extent of benzene adsorption is shown in figure 2. Figure 2 shows that the amount of benzene adsorbed (removal efficiency) by the activated carbon from bamboo, coconut and palm kernel increases as the dose (quantity of activated carbon) increases. An increase in adsorbent dose increases the number of active sites available to the solute (benzene) for adsorption, thus increasing the rate of adsorption[29].

Table-1
Physiochemical Analysis of Produced activated carbons

| S/N	Activated carbon source	Parameter					
		Yield (%)	Bulk Density (g/dm^3)	Porosity	Moisture Content	Ash Content (%)	pH
1.	Bamboo	50	0.475	0.71	2.44	8.27	6.64
2.	Coconut Shell	51	0.55	0.82	5.18	6.13	6.34
3.	Palm Kernel Shell	50.5	0.65	0.96	2.35	6.44	6.1
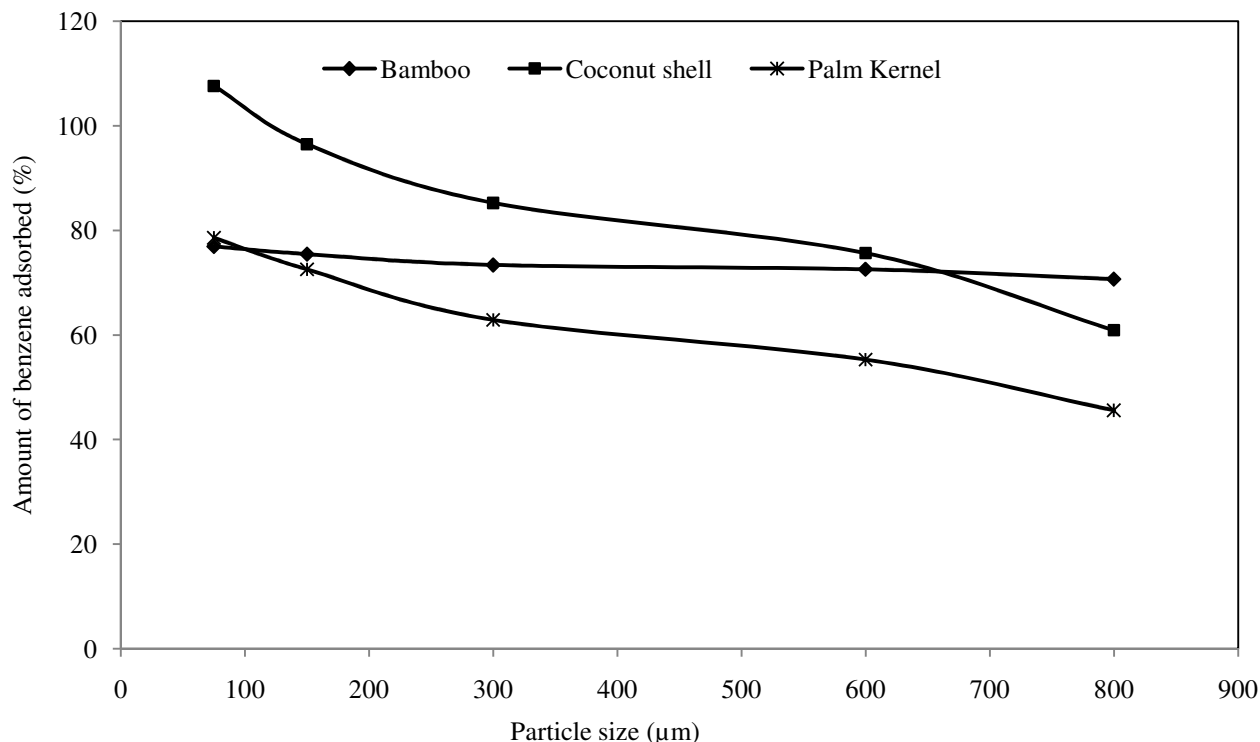
Figure-1
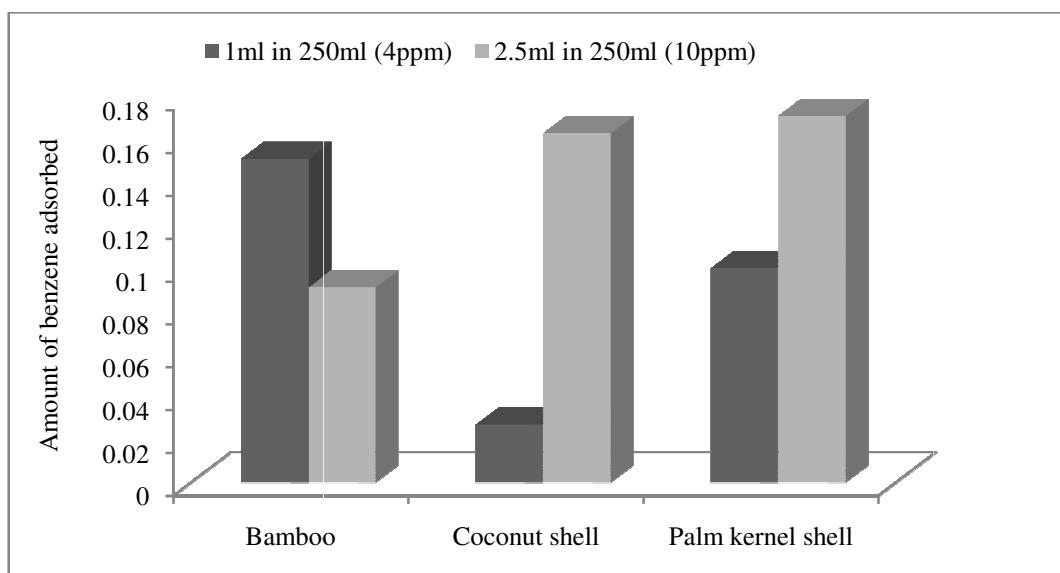**Variation of amount of benzene adsorbed with particle size**

However, the amount of benzene adsorbed using activated carbon from bamboo increased, reached a maximum value, decreased and became constant, this may be due to the establishment of equilibrium between the benzene adsorbed to the adsorbent and those remaining unabsorbed in the solution. The minimum amount of adsorbent corresponding to the maximum adsorption (the optimum dose) in the present study for bamboo is 0.42 g.

The amount of benzene adsorbed using the activated carbon from coconut and palm kernel increased continuously with increase in dose. No optimum dose was observed for activated carbon from coconut and palm kernel shells.

Effect of initial benzene concentration on amount of benzene adsorbed: The effect of initial benzene concentration on the removal of benzene by the activated carbon from the different sources is shown in figure 3.
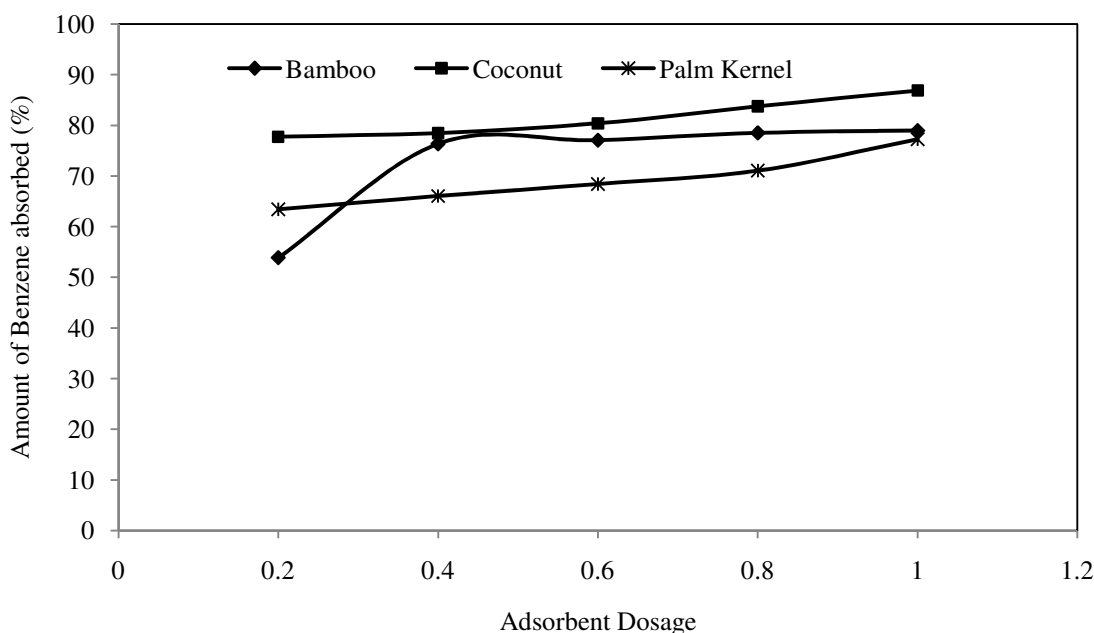
Figure-2
Variation of amount of benzene adsorbed with adsorbent dosage

Figure-3
Histogram of amount of benzene adsorbed by adsorbent for different concentrations of Benzene

The amount of benzene removed decreased with increase in initial benzene concentration using activated carbon produced from bamboo; that is the higher the initial concentration the lower the adsorption rate. This is due to the fact that the available sites are insufficient to adsorb proportionately the increased benzene in the initial aqueous solution. The active sites thus become saturated with adsorbed benzene[27], thus decreasing the amount of benzene subsequently adsorbed onto the activated carbon.

However, the amount of benzene removed increased with increase in initial benzene concentration using activated carbon produced from coconut and palm kernel shells. The initial concentration provides the necessary driving force to overcome the mass transfer resistance of benzene between the aqueous and the solid phases[26]. Hence an increase in initial benzene concentration will increase the mass transfer of benzene and ultimately enhance the adsorption rate of benzene by the activated carbon.

Conclusion

Activated carbon was produced in the laboratory from three local agricultural waste materials; bamboo, coconut shell and palm kernel shell. The materials were carbonized at a temperature of $300 - 400^{o}C$ and activated with tri oxo nitrate (v) acid.

The produced activated carbons were characterized (determination of physico-chemical properties such as: percentage yield, bulk density, porosity, ash content and pH) and used for adsorption of benzene to ascertain their efficiencies. The effects of particle size, carbon dosage of the activated carbon and initial benzene concentration of benzene on adsorption rate of the activated carbon were investigated.

Benzene adsorption decreased with increase in particle size of activated carbon, decrease was minimal with activated carbon produced from bamboo. Benzene adsorption increased with increase in adsorbent dosage. Increase in initial benzene concentration resulted in increased adsorption using activated carbon from coconut and palm kernel shells; a decrease in adsorption using activated carbon from bamboo.

References

1. Rajoriya R.K., Prasad B., Mishra I.M. and Wasewar K.L., Adsorption of Benzaldehyde on Granular Activated carbon: Kinetics, Equilibrium and Thermodynamics, *Chem. Biochem. Eng. Q* **21(3)**, 219-226 **(2011)**

2. Arriagada Y.T., Activated Carbon, *Journal of Science and Technology, Elsevier Pub*, **5(2)**, 81–87, **(2001)**

3. Yantasee W., Lin Y., Fryxell G.E., Alford K.L., Busche B.J. and Johnson C.D., Selective removal of Copper (II) from aqueous solutions using Fine Grained Activated Carbon Functionized with Amine, *Ind. Eng. Chem. Res.,* **43**, 2759-2764 **(2004)**

4. Monser L. and Adhoum N., Modified activated carbon for the removal of copper, zinc, chromium, and cyanide from wastewater, *Separation and Purification Technology*, **26(2-3)**, 137-146 **(2002)**

5. Budinova F.N., Production and Characterization of Activated Carbon, *Chem. Int'l*, **4(12)**, 200-209 **(2006)**

6. Eddleston D.D., The Use of Granulated Activated Charcoal, *World Science*, **46(6)**, 528-533, **(2008)**

7. Awoyale, A. A., Eloka-Eboka, A. C. and Odubiyi, O. A., Production and Experimental Efficiency of activated carbon from local waste bamboo for waste water Treatment, *International Journal of Engineering and Applied Science*, **3(2)**, 8-17, **(2013)**

8. Kalderis, D., Bethanis, S., Paraskeva, P. and Diamadopoulos, E., Production of activated carbon from bagasse and rice husk by a single-stage chemical activation method at low retention times, *Bioresource Technology*, **99(15)**, 6809-6816, **(2008)**

9. Romanos J., Beckner M., Rash T., Firlej L., Kuchta B., Yu P., Suppes G., Wexler C. and Pfeifer, P., Nanospace engineering of KOH activated carbon, Nanotechnology, **23(1)**, 15401, **(2012)**

10. Cobb, A., Warms, M., Manner, E. P. and Chiesa, S., Low-Tech coconut shell activated charcoal product, *International Journal for Service Learning in Engineering*, **7(1)**, 93-104, **(2012)**

11. Lua, A. C. and Guo, J., Preparation and characterization of activated carbons from oil-palm stones for gas-phase adsorption, *Colloids and Surfaces A*, **179(2-3)**, 151-162, **(2001)**

12. Ahmedna M, Marshall W.E. and Rao R.M., Granular activated carbons from agricultural by –products: preparation properties and application in cane sugar refining, Bulletin of Louisana state University Agricultural centre, 54 (**2000)**

13. Khalil H.P.S.A., Jawaid M., Fiwoziam P., Umar R., Aminal I. and Hazizan Md. A., Activated carbon from various Agricultural wastes by chemical activation with KOH: Preparation and Characterization, *Journal of Biobased Material and Bio energy*, **7(5)**, 1-7, **(2013)**

14. Gupta V.K. and Imran A., Removal of lead and chromium from waste water using bagasses fly ash – a sugar industry waste, *Journal of colloid Interface Science*, **271(2)**, 321-328, **(2004)**

15. Ahmadpour A. and Do D.D., The preparation of activated carbon from macadamia nutshell by chemical activation, *Carbon*, **35**, 1723-1732. **(1997)**

16. Guo Y., Yu K., Wang Z. and Xu H., Effects of activation conditions in preparation of porous carbon from rice husk, *Carbon*, **41**, 1645-1648, **(2003)**

17. Haimour N.M. and Emeish S., Utilization of date stones for production of activated carbon using phosphoric acid, *Waste management*, **26 (6)**, 651-660, **(2006)**

18. Sentorun,-Shalaby C., Ucak-Astarlioglu M.G., Artok L. and Sarici C., Preparation and Characterization of activated carbon by one-step stem pyrolysis/activation from apricot stones, *Microporous and Mesoporous Materials*, **88(1-3)**, 126-134, **(2006)**

19. Stavropoulos G.G. and Zabaniotou A.A., Production and Characterization of activated carbons from olive-seed waste residue, *Microporous and Mesoporous Materials*, **82(1-2)**, 79-85, **(2005)**

20. Lua A.C. and Guo J., Preparation and characterisation of chars from oil palm waste, *Carbon*, **36**, 1663-1670, **(1998)**

21. Evbuomwari B.O., Agbede A.M. and Atuka M.M., A Comparative Study of the physio-chemical properties of Activated Carbon from oil palm waste, *International Journal of Science and Engineering Investigations*, **2(19)**, 75-79 **(2013)**

22. Huff J., Benzene-induced cancers: abridged history and occupational health impact, *Int. J Occup. Environ. Health*, **13(2)**, 213–221, **(2007)**, PMID 17718179

23. Ademuliyi T., Production of Activated Carbon from Agricultural Wastes, *AIChE*, **34**, 59-62 **(2008)**

24. ASTM D2867 – 09, Standard Test method for Moisture in Activated Carbon, www.astm.org/standards/D2867.htm, **(2009)**

25. ASTM D2866 – 94, Standard Test method for Total ash Content of Activated Carbon, www.astm.org/Data Base, **(2004)**

26. Ariyadejwanich P., Tanthapanichakoon W., Nakagawa K., Mukai S.R. and Tamon H., Preparation and characterization of mesoporous activated carbon from waste tires, *Carbon*, **41**, 157-164, **(2003)**

27. Narbaitz R.M. and Karimi-Jashni A., Electrochemical regeneration of granular activated carbons loaded with phenol and natural organic matter, *Environmental Technology*, **30(1),** 27–36, **(2009)**

28. Yao S., Liu Z. and Shi Z., Arsenic removal from aqueous solutions by adsorption onto Iron oxide/activated carbon magnetic composite, *Journal of Environmental Health Science & Engineering*, **12**, 58 **(2014)**

29. Bazrafshan E., Faridi H., Kord M.F. and Mahvi A.H., Arsenic removal from aqueous environments using *moringa peregrina* seed extract as a natural coagulant, *Asian J Chem.,* **25,** 3557-3561 **(2013)**