Active Carbons from Chemically Mediated Pyrolysis of Agricultural Wastes: Application in Simultaneous Removal of Binary Mixture of Benzene and Toluene from Water

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ABSTRACT: Active carbons were produced from bagasse, millet and sorghum straws by chemical activation with H_3PO_4. Carbon precursors with particle size of 1180 µm were used, in order to overcome difficulties caused by low density and high ash content. The influence of preparation conditions (temperature, residence time, and acid impregnation ratio) on the yield of the active carbons was examined. The impregnation ration which was controlled by varying the proportion of H_3PO_4 used for the activation had a strong influence on the yields of the carbons. The pyrolysis temperature was varied in the range 100-450 °C, but equilibrium yields of the active carbons were highest at 450C with optimum impregnation ratio of 13.6. The potential of the active carbons as efficient and economical means of removing mixture of aromatic hydrocarbon contaminants from water was indicated by the complete removal of objectionable odor from contaminated water samples containing 35.1348 mg/cm^3 benzene and 34.8534 mg/cm^3 Toluene, which are known carcinogens. Spectrophotometric determinations of the two solutes in the remediate water samples indicated slow but steady adsorption of the benzene/toluene mixture on the active carbons.

Key words: Binary mixture, Benzene, Toluene, Water, Active carbon, Agricultural waste

INTRODUCTION

Active carbons are carbonaceous materials with highly developed internal surface area and porosity for adsorbing chemicals from gases or liquids (Zanzi *et al*., 2001). Special emphasis on the preparation of active carbons from agricultural by-products has been given, due to the growing interest in low-cost active carbons from renewable safe copious supplies, especially for applications concerning environmental monitoring. Increased use of agricultural residues is an attractive addition to the utilization of wood and other carbonaceous materials for the production of active carbons. It is expected to help combat climate change, global warming and desertification. Production and use of active carbons from waste agricultural materials such as bagasse, millet and sorghum straws have been considered in this study, as an attractive solution to mitigate the third world environmental protection needs. Chemical

activation is one of the possible methods for the production of active carbons otherwise known as activated carbon (Guo *et al*., 2000; Hayashi *et al*., 2002; Baquero *et al*., 2003; Suarez-Garcia *et al*., 2004). The carbon precursors are pyrolyzed in presence of the chemical activating agent such as phosphoric acid (H_3PO_4), zinc chloride ($ZnCl_2$), potassium hydroxide (KOH) etc. Phosphoric acid functions as a dehydrating agent and inhibits the formation of tar (Su *et al*., 2003). The use of phosphoric acid is considered to be an environmentally benign technology, because of the ease of its recovery by washing with water (Baquero *et al*., 2003).

Previously, wood bark (Barkauskas *et al*., 2004); bagasse (Jaguaribe *et al*., 2005); maize cobs (Ekanem 1996); rice straws (Oh and Park 2002); rice husk (Imagawa *et al*., 2000); coconut shells (Gimba *et al*., 2001); oil palm shells, walnut shells (Hayashi *et al*., 2002) and coffee bean

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husks (Baquero *et al*., 2003) have been pyrolyzed to produce active carbon, but activation by ortho phosphoric acid impregnation of bagasse, millet and sorghum straws have not been studied to evaluate its possible influence on the quality and yield of carbon, as this method of producing active carbons may lower the energy cost. A number of precursors of vegetable origin have been activated with acid at 450 °C (Suarez-Garcia *et al*., 2002; Baquero *et al*., 2003), but the effects of lower pyrolysis temperatures with phosphoric acid activation were investigated in this study.The main objectives of this study therefore, were to prepare active carbons from bagasse, sorghum and millet straws by ortho phosphoric acid activation, examine the influence of preparation conditions (temperature, residence time and acid impregnation ratio) on the yields of the active carbons and investigate the potential of the active carbons for removal of benzene and toluene, which are known carcinogens present in the wastewater from petroleum refineries (Koh and Dixon 2001).

MATERIALS & METHODS

Dry straws of sorghum and millet were collected from Rigasa farm center (non industrial area) in Kaduna State (Nigeria), in March 2006, after harvest. Sugarcanes were obtained from the same area and processed to bagasse. Cellulose absorbs large quantities of water and takes time to dry (F-tutor., 2007). The straws and bagasse were therefore air-dried for 3months on plastic mesh, to ensure adequate drying for easy milling and avoid the loss of carbon residue due to oven-dying. The straws were cut into pieces of approximately 3cm to obtain the samples for milling. The bagasse and chopped straw samples were milled with Christy and Morns miller at the National Animal Production Research Institute (NAPRI), Zaria. The milled bagasse and straw samples were sieved into a particle size of 1180 μm with Endecotts laboratory test sieve on Omron No. 17748 (manual timer) sieve shaker, as described by Lori *et al*., (2007). The sieved samples were packed into polythene bags and labeled accordingly. In porcelain crucibles, 0.5g of 1180μm grains of bagasse, sorghum or millet straws was impregnated with H_3PO_4, by adding drop wise, (while stirring the solid to facilitate homogeneous absorption of the acid) the amount

of the aqueous acid ($2.5cm^3$) necessary to produce swelling until incipient wetness (Baquero *et al*., 2003). Different concentrations of the H_3PO_4 corresponding to 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, and $7.0cm^3$ H_3PO_4 in aqueous solutions were used to vary the content of impregnation agent. After impregnation, the samples were dried for 1hr at 110°C in an oven, manufactured by Laboratory Thermal Equipment limited (Greenfield). The dried samples were transferred to digital thermo control, Gallenkamp electric furnace and heated at the various pyrolysis temperatures (100, 250, 350, 450°C) for the various heating periods (residence time) (16, 20, 24, 28, 30, 32, 36, 40, 45, 48, 52, 56, 59, 60, 65, 70, 75, 80, 85, 90, 95, 120, 150, 180, 220, 250, 280 min.). The solid pyrolysis residues were cooled at room temperature and later transferred to desiccators containing silica gel as desiccant. The carbonized samples were washed sequentially, several times with hot de-ionized water and finally with cold de-ionized water until the solutions were neutral to litmus paper. The washed samples were dried at 110°C to prepare the active carbons. The potential of the active carbons as efficient and economical means of removing mixture of aromatic hydrocarbon pollutants from water contaminated by petroleum processing activities was investigated in sealed flasks. Water samples containing 35.1348 mg/cm^3 benzene and 34.8534mg/cm^3 Toluene were remediate by suspension of 15g of the active carbon granules in 1 dm^3 of water samples for different contact time ranging from 10min. to 72hrs with initial shaking of the solution for 5min to simulate convenient, shaking time in field studies. The carbons were filtered off through 11cm filter paper. The residual concentrations of benzene and toluene were determined as binary mixture by measuring the absorbances of benzene and toluene in the remediate water, using Cole 7506 UV-VIS spectrophotometer at 250nm and 270nm for benzene and toluene respectively. The concentrations of benzene and toluene as binary mixture were calculated from the solutions of simultaneous equations (Eqs. 1 & 2) derived from Beer-Lambert's law for benzene and toluene.

$$A_{\lambda B} = {\lambda B}E_B \cdot C_B + {\lambda B}E_T \cdot C_T \qquad \text{Eq. 1}$$

$$A_{\lambda T} = {\lambda T}E_B \cdot C_B + {\lambda T}E_T \cdot C_T \qquad \text{Eq. 2}$$

where $A_{\lambda B}$ and $A_{\lambda T}$ are the measured absorbance at the two wavelengths λ_B and λ_T for benzene and toluene respectively. E_B and E_T are the absorption coefficients for benzene and toluene respectively. Solution of the simultaneous equations gave the concentrations of benzene (C_B) (Eq. 3) and toluene (C_T) (Eq. 4) expressed in mg/cm³ of water sample as follows:

$$C_B = \frac{\lambda_T E_T \cdot A_{\lambda B} - \lambda_B E_T \cdot A_{\lambda T}}{\lambda_B E_B \cdot \lambda_T E_T - \lambda_B E_T \cdot \lambda_T E_B} \qquad \text{Eq. 3}$$

$$C_T = \frac{\lambda_B E_B \cdot A_{\lambda T} - \lambda_T E_B \cdot A_{\lambda B}}{\lambda_B E_B \cdot \lambda_T E_T - \lambda_B E_T \cdot \lambda_T E_B} \qquad \text{Eq. 4}$$

The extent of odor removal was examined by momentary test on the sensory organ.

RESULTS & DISCUSSION

In preliminary studies, the effects of particle size on weight loss characteristics, rates of dehydration and volatile matter of the carbon precursors were used by Lori *et al.* (2007) to adjudge particle size of 1180 μm as appropriate for the carbonization of the bagasse, sorghum and millet straws. High contents of volatile matter ($64.52 \pm 1.18 – 66.65 \pm 3.07$), fixed carbon ($21.93 \pm 2.74 – 24.16 \pm 1.94$) and low ash ($2.27 \pm 0.15 - 3.80 \pm 0.17$) were also reported as favorable properties of the precursors for the production of active carbon (Lori *et al.*, 2007). The contaminated water samples were cloudy with characteristic pungent smell. Relatively high yield of active carbon is the goal of commercial carbon production. The yield of active carbon is defined as the ratio of the sample weight after pyrolysis or activation, to the weight of the raw material (Lua *et al.*, 2004). The effect of pyrolysis temperatures on the active carbon residues from bagasse, sorghum and millet straws are shown in (Figs. 1, 2, 3) respectively. The cellulosed carbon precursors burnt on carbonization to produce low yield of active carbons at high pyrolysis temperature (450 °C) (Table 1). This may be attributed to the large amounts of volatile matter that are released during pyrolysis and to a lesser extent, the dehydration of the precursors which was initiated by heating in an oven at 110 °C prior to carbonization in the furnace. For the pyrolysis process, equilibrium is defined as the point of attainment of approximate constant weight of
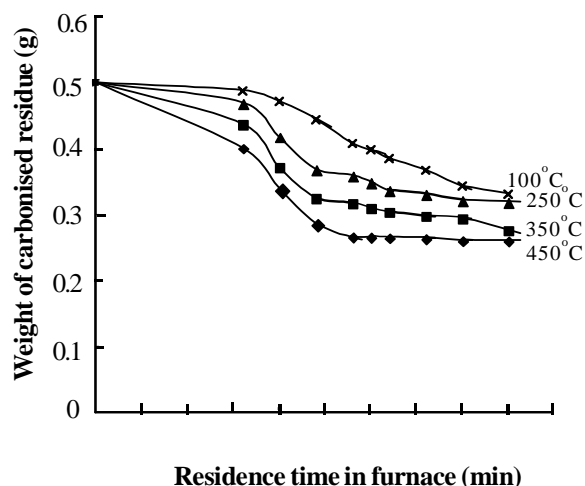

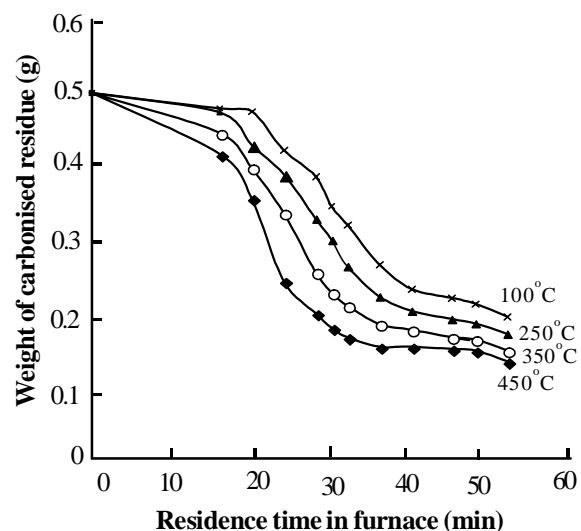**Fig. 1. Variation in weight of carbonized bagasse with residence time at different**

Fig. 2. Variation in weight of carbonized sorghum straw with residence time at different pyrolysis temperatures
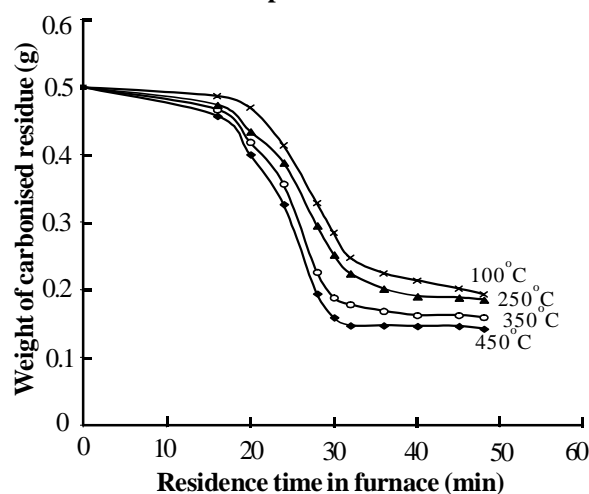

Fig. 3. Variation in weight of carbonized millet straw with residence time at   different pyrolysis temperatures

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Table 1. Yield of active carbons at different pyrolysis temperatures and equilibrium residence times in furnace

Precursors	Active carbon yield (%)			
	100°C	250°C	350°C	450°C
Bagasse	81.8	72.0	63.6	53.6
Sorghum straw	53.2	44.4	36.8	30.6
Millet straw	49.6	45	35.8	29.6

carbon residue which corresponds to the point of complete carbonization, as indicated by the horizontal portion of the pyrolysis curves (Figs. 1, 2, 3). For bagasse, the equilibrium attained at 450°C also indicate that complete de-volatilization of the precursor which is a prelude to porosity evolution in the carbon residue, was achievable between 28-45 min. of heating. Carbon obtained from bagasse at the pyrolysis temperatures of 100-350°C is thus associated with low porosity as de-volatilization may be incomplete and on-going as indicated by (Fig. 1).

After the fast initial weight loss, carbonizations of sorghum straw at 100-450 °C was slowly accomplished by gradual de-volatilization, reaching an equilibrium after 36 min. at 450 °C (Fig.2). Beyond 48 min., the carbon residue from the sorghum straw became depleted at 450°C probably due to its interaction with CO_2 that may be produced during the pyrolysis. Despite the low yield at 450 °C, the carbon produced at this temperature may be more porous than the carbon residues obtained at 100-350 °C due to the incomplete de-volatilization at 100-350 °C. The carbonizations of millet straws at 100-450 °C were also accompanied by slow de-volatilization after the initial bulk de-volatilization that resulted in the initial sharp drops in weights of the carbonized residues (Fig. 3). The equilibrium attained between 32-45 min. of heating at 450 °C indicates complete de-volatilization of the millet straws. Although the carbon yield was lowest at this temperature, the steady nature of the equilibrium is a good index for predicting the pore quality of the carbon. Short lived equilibria were attained between 40-45 min. of heating at 250-350 °C. At 450 °C, production of active carbon from millet straw was completed in 45 min. Delay in the removal of the carbon residue from the furnace after 45 min. resulted in a decrease in carbon yield.

Generally, complete carbonization of 0.5 g of bagasse, sorghum or millet straws were achieved in 45 min. However, the times of commencement of carbonization as indicated by the respective equilibria are in the order bagasse < millet straw < sorghum straw but the various times taken to produce porous carbon from the cellulosic precursors at equilibrium, corresponds to different heating rates of 16.07, 14.06 and 12.5 °C/min for bagasse ,millet and sorghum straws respectively. Using the stated heating rates of the respective precursors, the rate of production of active carbon from bagasse (9.57 x 10^{-3}g/min) was more than double the rates of production of carbon from either sorghum (4.25 x 10^{-3} g/min) or millet straws (4.63 x 10^{-3}g/min). High yields of carbon residues were obtained from either precursor at lower temperatures of pyrolysis (Table 1). This may be attributed to the possible differences in the thermal stabilities of the pyrolysis products at the different pyrolysis temperatures. The similar trends shown in (Figs. 1, 2 and 3), may be indicating the similarity in the nature of the cellulose pyrolysis reactions at the different temperatures of carbonization of bagasse, sorghum and millet straws.

The percentage yield of active carbons using the respective residence time appropriate to the precursors were bagasse (53.6%) > sorghum straw (30.6%) > millet straw (29.6%) at 450°C. The carbon yield from bagasse was more than double the amount obtained in vacuum pyrolysis by Garcia-Perez *et al.*, (2002), at a heating rate of 12°C/min without activation. The higher yield obtained may therefore, be a consequence of the phosphoric acid activation, which may have hastened de-volatilization. The total burn-off ratio was obtained from the ratio of the weight loss during the whole heat treatment processes to the dry weight of the precursors. The total burn-off ratios were, millet straw (0.704) > sorghum straw (0.694) > bagasse (0.464). At 450°C bagasse and sorghum straw burnt completely to white ashes after heating for 80 minutes and the ashes decomposed into brown residues within 2hrs of heating. With millet straw, complete white ash was obtained after heating for 90minutes at 450°C and the ash also decomposed within 2hrs of heating. The general thermal behaviors of bagasse, sorghum and millet straws impregnated with ortho phosphoric acid are shown in (Fig. 4). The thermo-

gravimetric profiles of the precursors indicate pronounced weight losses even below 350 °C. These curves for the cellulosic precursors indicate faintly, three mass losses; one at 250°C and two others at 350 and 450 °C respectively. This may be attributed to a number of different thermal degradation reactions known to occur with cellulose at different temperatures. The degradation at lower temperatures (100 °C) is often predominantly thermo-oxidative and / or hydrolytic. At higher temperatures (>200 °C) water is lost, from that absorbed by the cellulose and then by β-elimination from the cellulose hydroxyls. At still higher temperatures (>250 °C), several competing pyrolytic reactions begin to take over. Following the initial degradation, the reactions can be categorized into de-polymerization of the cellulose chain; formation of an-hydro-glucose derivatives, volatile organic materials; tar and random bond cleavage of cellulose and intermediate decomposition products (F-tutor 2007).The thermo-gravimetric profiles also indicate that sorghum and millet straws presented similar thermal characteristics but bagasse appeared to have higher thermal stability.

Different concentrations of ortho phosphoric acid (H_3PO_4) in aqueous solution were used to vary the content of impregnating agent, expressed as impregnation ratio (Xp). Impregnation ratio is defined as gram H_3PO_4 per gram of precursor.
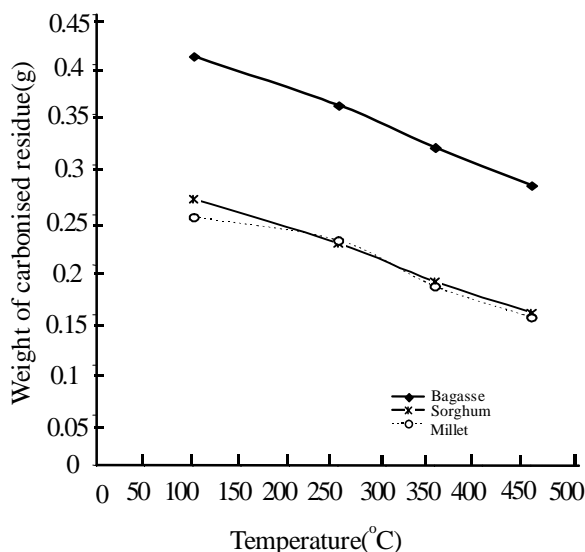
(Figs. 5, 6 and 7). show, that the impregnation ratio has a strong influence on the yields of active carbons from bagasse, sorghum and millet straws. Impregnated precursors exhibit continuous initial weight loss at 450°C up till a time when subsequent weight losses became stabilized and attained equilibrium. This is probably indicating different pyrolysis steps with different weight loss rates.
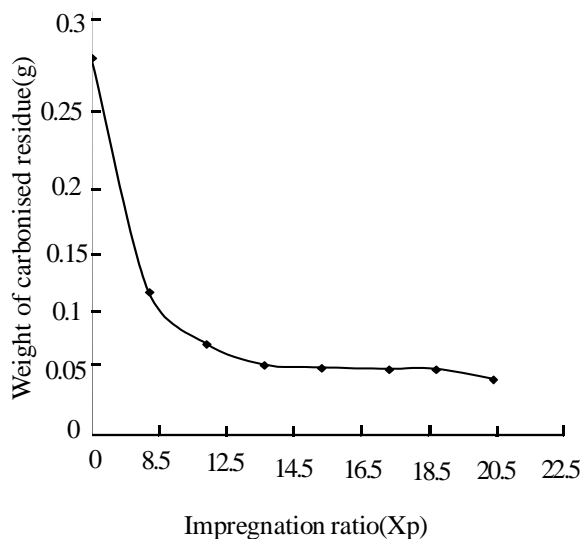

Fig. 5. Effect of phosphoric acid impregnation ratio on active carbon from millet straw

Fig.4. Thermal behaviors of the phosphoric acid impregnated bagasse, sorghum and millet straws
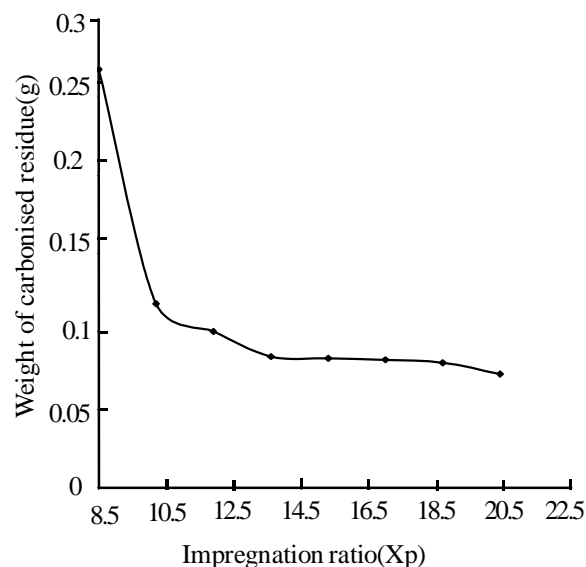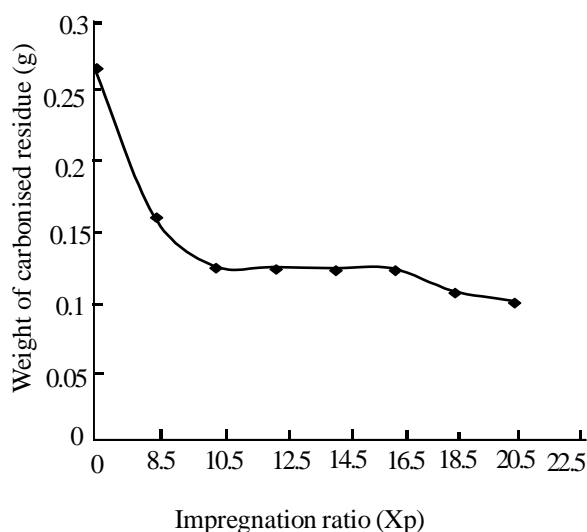

Fig. 6. Effect of phosphoric acid impregnation ratio on active carbon from sorghum straw

Fig. 7. Effect of phosphoric acid impregnation ratio on active carbon from bagasse

The equilibrium points in Figs. 5, 6 and 7 correspond to the optimum yields of the porous solid products (carbon) of the pyrolysis of the cellulosic precursors. Optimum activation of sorghum and millet straws to enhance porosity evolution was achieved with 13.6-18.7g H_3PO_4 per gram of the precursors as indicated by the equilibria in their impregnation profiles (Figs. 6 and 7). With bagasse, optimum activation was achieved with 13.6-17g H_3PO_4 /g bagasse. Impregnation coefficients greater than 18.7 decreased the weight of active carbon produced from millet straws.Similar decreases in carbon yields from bagasse and sorghum straws were observed with impregnation ratio greater than 17. Much higher impregnation coefficients burnt the carbon residues to ash.The potential of the active carbons as efficient and economical means of removing mixture of aromatic hydrocarbon pollutants from water was indicated by the complete removal of objectionable odor from contaminated water samples containing 35.1348mg/cm³ benzene and 34.8534mg/cm³ Toluene. This result indicates the suitability of the active carbons in detoxifying hydrocarbon contaminated water. It is consistent with the removal of compounds, such as phenol (Uddin *et al.*, 2007) from water. Spectrophotometer determinations of the two solutes in the remediate water samples indicated slow but steady adsorption of the benzene/toluene mixture on the active carbons from the cellulosic materials.

There were no appreciable adsorptions of the mixture on the tested active carbons within 1/2-16hrs (Figs. 8 and 9). The rapid increases in total adsorption after 16hrs may be explained in terms of the total number of molecules of the hydrocarbons approaching the carbon pores as a result of the sudden rush following the drenching of the active carbons in the water samples. Without the usual continuous shaking that enhances interactions, the number of the hydrocarbon molecules entering the pores before the expiration of the time for incipient wetness of the active carbons is less. Therefore, the saturation of the active carbon bed is delayed and occurs in relatively longer time (Figs. 8 and 9). Thus indicating a nonlinear adsorption over the selected time frame. This form of non linear adsorption was reported to follow Sips isotherm under steady state when there is no apparent change in surface concentration of adsorbed species (Das *et al.*, 2004).
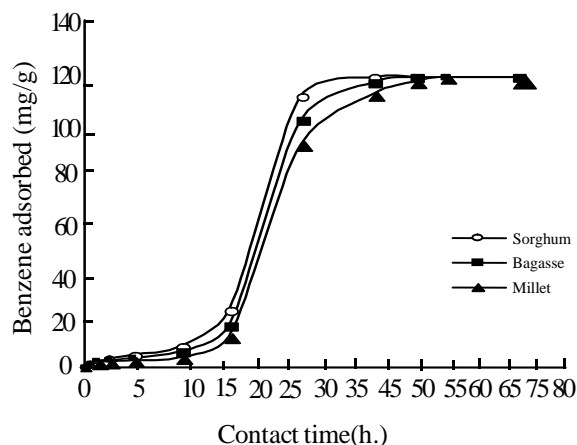
Fig. 8. Aqueous phase adsorption of benzene on active carbons from bagasse, sorghum and millet straws
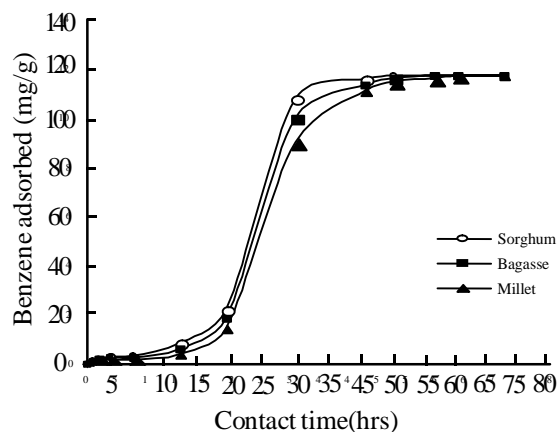
Fig. 9. Aqueous phase adsorption of toluene on active carbons from bagasse, sorghum and millet straws

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However, linear adsorption became apparent after 24 h. (Figs. 8 and 9). From 16 h. of adsorption contact time, values from spectrophotometer determinations in the binary mixture indicate, benzene was adsorbed faster than toluene. This observation conforms to the competition of organic moieties for the adsorption sites on hydrophobic active carbons (Haghseresht *et al.*, 2003) and may be related to the molecular diffusion. The differential sorption capacities of aqueous phase benzene and toluene on to the active carbons does not appear to be related to the trend in hydrophobic of benzene and toluene, probably because the difference in water solubility of benzene (0.188%) and toluene (0.067%) at the adsorption temperature is small. Similar report was made on the sorption of benzene and toluene on organo-minerals (Koh and Dixon 2001). More than 77% of either benzene or toluene was removed from the water samples at 36 h. The time taken to complete the population of benzene molecules on the various active carbon beds follows the sequence sorghum straw (48 h.) > bagasse (55 h.) > millet straw (60hrs). Complete removal of toluene molecules by the active carbons also follows the same sequence in total adsorption times of 53, 60 and 64 h. for carbons from sorghum straw, bagasse and millet straw respectively.

CONCLUSION

An optimum H_3PO_4 impregnation ratio of 13.6 produced active carbon yields of 53.6, 30.6 and 29.6% from bagasse, sorghum and millet straws respectively, at an optimum temperature of 450 °C, with furnace residence times of 28, 36 and 32 minutes respectively. The potential of the active carbons as efficient and economical means of removing mixture of aromatic hydrocarbon pollutants from water was indicated by the complete removal of odor from contaminated water samples containing 35.1348 mg/cm^3 benzene and 34.8534 mg/cm^3 Toluene. This result indicates the suitability of the active carbons in community water remediation protocols to detoxify hydrocarbon- contaminated ground water. Without the usual continuous shaking in adsorption experiments, the 5minutes initial shaking time was found to be adequate for the complete deodorization of the water samples in less than two and half days by mere suspension of the active carbons. The critical factor being the ratio of weight of carbon to volume of contaminated water. From this study, 15 g: 1 L is adequate for effective remediation to remove hydrocarbon contaminants up to 35.1348 mg/cm^3.

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