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Effectiveness of Nigerian Bamboo Activated with Different Activating Agents on the Adsorption of BTX

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ABSTRACT: The effectiveness of Nigerian Bamboo activated with different activating agents on the adsorption of BTX was investigated. A series of activated carbons was prepared from Nigerian bamboo, carbonized at 400^{o}C – 500^{o}C and impregnated with different concentrations of four acids at 800^{o}C in a muffle furnace for 2 hours. The resultant products were further adsorbed into BTX in aqueous and vapour phases. The best activating agent for adsorption of BTX vapour was 0.143M trioxonitrate (v) acid, while the best activating agent for adsorption of BTX in aqueous solution was hydrochloric and trioxonitrate (v) acid. Adsorption of BTX was found to be more of chemisorptions than ordinary physical adsorption. The differences in the adsorption of the three bamboo type was not affected by the physical geometry of the bamboo but by the chemical composition of the bamboo and type of activating agent used. The activated carbon from bamboo with the best concentration was also found to adsorb BTX favourably and better than a commercial activated carbon with same particle size. @JASEM

Keywords: Nigerian bamboo, activated carbon, adsorption, BTX

Benzene, toluene and xylene are hydrocarbon compounds that are often found as pollutants in industrial waste water and effluent gases. One of the methods in water treatment to eliminate these pollutants is using a *bioregenarator*, which is a combination of adsorption technique and the degradation of the pollutant compounds using micro bacteria. However, the performance of the *bioregenerator* is expected to be better if we use an expanded bed system together with better selection of the activated carbon used. Several experimental studies have been conducted on the isothermal batch and fixed bed adsorption of benzene, toluene and para xylene vapours using different activated carbons (Villacanas *et al*., 2006, Negrea *et al*., 2008, Liang*, Yan-Jyun, 2010), but adsorption studies of BTX on activated carbon produced from Nigeria bamboo was not found. Ademiluyi *et al*., (2009a) had early worked on adsorption and treatment of organic contaminants using activated carbon from waste Nigerian Bamboo (activated with only hydrochloric acid) focusing only on waste water generated from a refinery. The need to further study the effectiveness of activated carbon from Nigeria bamboo in the selective adsorption of benzene, toluene and para xylene in the aqueous and vapours phase using different activating agents is therefore necessary.

Therefore the objective of this study is to investigate the effect of different activating agents on adsorption of BTX in vapour and aqueous phase. Also the effectiveness of activated carbon produced for Nigeria bamboo in the selective adsorption of benzene, toluene and para xylene in the aqueous and vapours phase will also be investigated.

MATERIALS AND METHOD

Materials and equipment: The materials used for this study were: Granular activated carbon produced from three Nigerian bamboo, distilled water, hydrochloric acid, phosphoric acid, trioxonitrate (v) acid, and tetraoxosulphate (vi) acid. The equipment used in the experiments were: two electronic weighing balance, Ohaus top loading Balance (+0.01) was used to weigh the bamboo before pyrolysis, while a more sensitive (+0.001) balance (Adams AFP 360L) was used for other analysis A laboratory electric oven , Laboratory electric muffle furnace (Type: OH85TR), locally fabricated pyrolysis reactor with thermocouple, mortar and pistol, P^H meter, spectrophotometer.

Carbonization: Carbonization (2000 grams of washed, cut and dried bamboo) was carried out in a pyrolysis reactor. The bamboo was carbonized at about 400-500^{o}C. Carbonization lasted for two hours after which the charred products were allowed to cool to room temperature. The charred material was crushed using mortar and pistol and sieved.

Chemical activation: 50g of carbonised bamboo was carefully weighed and poured in beakers containing know quantity of dilute hydrochloric acid, phosphoric acid, trioxonitrate (v) acid, and tetraoxosulphate (vi) acid with concentration ranging from 0.025M - 0.5M. The content of the beakers were thoroughly mixed until a paste is formed. The paste was then transferred to a crucible and the crucible was placed in a Muffle furnace and was heated to 800^{o}C for two hours. The activated sample was then cooled at room temperature, and washed with distilled water to a pH of 6 – 7, and dried in an oven at 105^{o}C for three hours. The final product was kept in an air tight polyethylene bag, ready for use.

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Methods: Adsorption experiments were conducted in three steps. First the effect of different concentrations of activating agents on adsorption of Benzene vapour was carried out to know the acid that give the highest benzene adsorption and secondly comp\red with a commercial activate carbon. Finally the adsorption of HTX in aqueous solution was also carried out

Effect of different concentrations of activating agents on BTX vapour adsorption using different type of bamboo: 0.2g of samples A, B and C (three bamboo species) activated with different acids at different concentrations were weighed into a crucible and were placed into desiccators. Benzene solution was poured in a Petri dish and placed inside the desiccators, After 1 hour the samples were weighed to know the mass of the samples after adsorption, until a constant weight was observed. Amount of benzene adsorbed were calculated in mg of benzene vapour adsorbed/g of activated carbon used. The best concentration from each activating agents was now use to study the rate of adsorption of benzene, xylene and toluene vapour. The adsorption of BTX vapour using bamboo activated carbon along with a commercial activated carbon was also carried out using the procedure above, but the activated carbons were sieved to same particle size before adsorption.

Adsorption of BTX in aqueous solution: 0.25% solution of benzene, toluene and xylene (BTX) were prepared. A certain amount of each solution was added to the Erlenmeyer flask containing 0.2 gram of activated carbons from different activating agents. Erlenmeyer flasks were closed and shaken intermittently at equal time. Solutions were separated from activated carbons and measured concentration of filtrates measured using calibrated UV spectrophotometer. BTX adsorbed in aqueous solution by activated carbon was expressed in percentage as concentration of BTX adsorbed by activated carbon compared with concentration of BTX before adsorption.

RESULTS AND DISCUSSION

Effects of different concentration of Activated Agents on the Adsorption of Benzene Vapour: The rate of adsorption of any adsorbents is affected by the type of activation carried out on the activated carbon hence, chemical activation of three bamboo types was carried out using four acids at different concentrations (Phosphoric acid, trioxonitrate (v) acid, and tetraoxosulphate (vi) acid and hydrochloric acid). Fig. 1 shows the benzene vapour adsorbed (mg/g) using different concentrations of tetraoxosulphate (vi) acid. More benzene were adsorbed at low (0.025-0.1M) concentration of tetraoxosulphate (vi) acid for all the bamboo types. The adsorption was optimum at 0.1M concentrations. At higher concentration of H_2SO_4 the adsorption rate of benzene reduced. This suggests a vigorous reaction between biomass components of bamboo (mainly hemicellulose, cellulose and lignin) which were gradually hydrolyzed as the concentration of H_2SO_4 increased. Tetraoxosulpahte (vi) acid must have promoted the breakdown of the 3-D structure of ligium and release of more water which could reduce benzene adsorption (McKay et al, 2010) at higher acid concentration as shown in equation (1):

$$C_nH_xO_y + H_2SO_4 \rightarrow H_2O + S_{element} + C_nH_xO_{y-3}$$

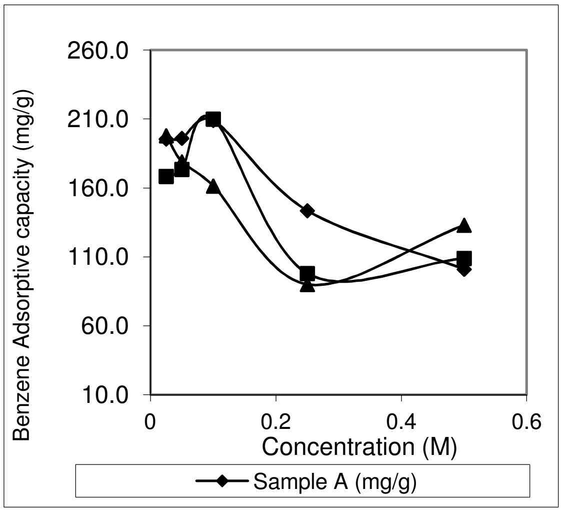

Fig. 1 Effect of activation with tetraoxosulphate (vi) acid on Benzene vapour Adsorption using activated carbon from Nigerian bamboo

Fig. 2 shows the effect of phosphoric acid activation on benzene vapour adsorption. The highest benzene vapour adsorbed was obtained using phosphoric acid of 0.5M concentration. The sudden drop in the rate of adsorption for the bamboo types at 0.1 – 0.25M of Phosphoric acid may be due to fact that the activated carbons were not sieved to same particle size after activation with different concentrations of Phosphoric acid. Hence the activated bamboos were sieved (75 microns) and benzene adsorption was repeated for 0.1M and 0.5M of Phosphoric acid, to ascertain if 0.5M of Phosphoric acid is the best concentration to activate bamboo for BTX adsorption. This is presented in Table 1

Previous works carried out by Calafat and Labady (2003) showed that higher surface area and mesopore were favoured by increasing the concentration of phosphoric acid for activated carbon from coconut shell hence 0.5M concentration may be recommended as the best concentration for activate the activated carbon from bamboo using phosphoric acid. Unlike other acid, phosphoric acid and forms an ester when reacted with cellulose, as shown in equation 2. The esterification increases with increase in H_3PO_4 concentration. The combine cellulose ester can create another active reaction site with benzene to form an alkyl benzene–cellulose complex.

H_3PO_4 + HO – cellulose → cellulose – O – PO_3H_4..........2

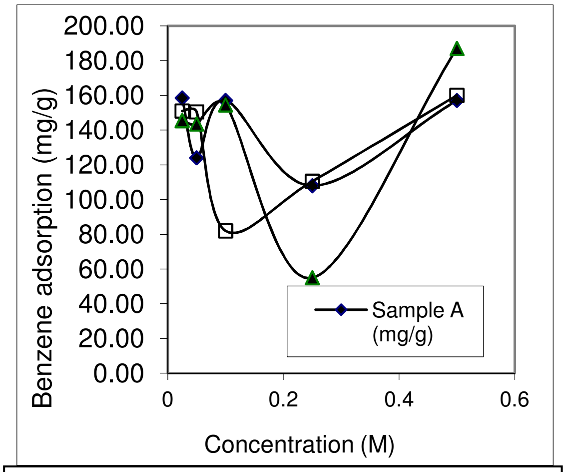

Fig. 2 Effect of activation with Phosphoric acid on benzene vapour adsorption using activated carbon from

Table 1 Properties of the Granular carbon locally made from three Nigerian based Bamboo activated with 0.1M and 0.5M of Phosphoric acid sieved to same particle size

Parameter	Unit	0.1M			0.5M		
		A	B	C	A	B	C
Yield	%	68.00	72.80	69.80	75.00	77.80	80.40
Benzene adsorbed	mg/g	346.0	290.0	310.0	414.5	365.0	372.0 0

Fig. 3 shows the effect of activated carbon activated with trioxonitrate (v) acid on benzene adsorption using activated carbon from bamboo. Adsorption of benzene increased with increase in concentration (0.025– 0.143M) and the reduced at concentration above 0.143M. High concentration of Nitric acid does not vapour adsorption of benzene. Increasing Nitric acid concentration increases the hydrolysis of cellulose in activated carbon. Setyadhi *et al* (2006) reported that the treatment with Nitric acid caused the introduction of significant number of oxygenated acidic surface groups on to the carbon surface when using commercial activated carbon (F400) and that activated carbon with low oxygenated acidic surface had the best benzene adsorption capacity.

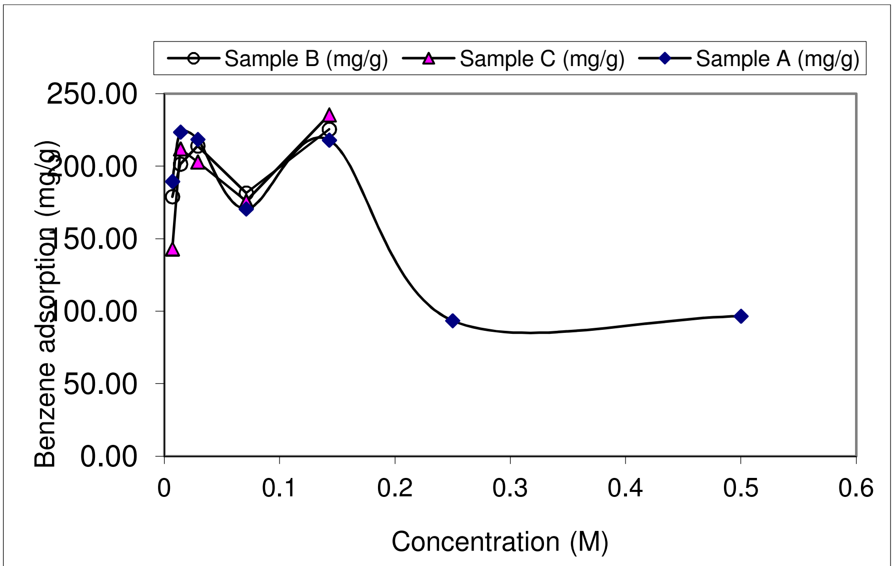

Fig 3. Effect of activation with Trioxonitrate (v) acid on benzene adsorption of activated carbon using activated carbon from Nigerian bamboo

The effect of effect of activated carbon activated with different concentration of hydrochloric acid on adsorption of benzene was not carried out because concentration of 0.1M has been established by Ademiluyi *et al*, (2009b) at the best concentration which produces activated carbon from bamboo with highest iodine number, and highest porosity. Hence 0.1M HCL was used to activated bamboo used for adsorption of BTX in aqueous solution

Effect of activated agents on adsorption of BTX in vapour and in aqueous phases: Fig. 4 shows Benzene-Toluene-Xylene (BTX) vapour adsorbed using activated carbon from bamboo activated with different activating agents. Activated carbon from bamboo activated with HNO_3 exhibit consistent increase in adsorption of BTX vapour, than other activating agents. HNO_3 was reported by Mckay *et al*., (2010) to produce a highly reactive product known as cellulose nitrite as shown in equation 3. Cellulose nitrite in turn reacts with benzene to produce an alkyl cellulose nitrate. NO_2^+ then forms a sigma complex with benzene as shown in equation 3

$$3HNO_3 + C_6H_{10}O_5 \rightarrow C_6H_7(NO_2)_3O_5 + 3H_2O \quad \text{.........3}$$

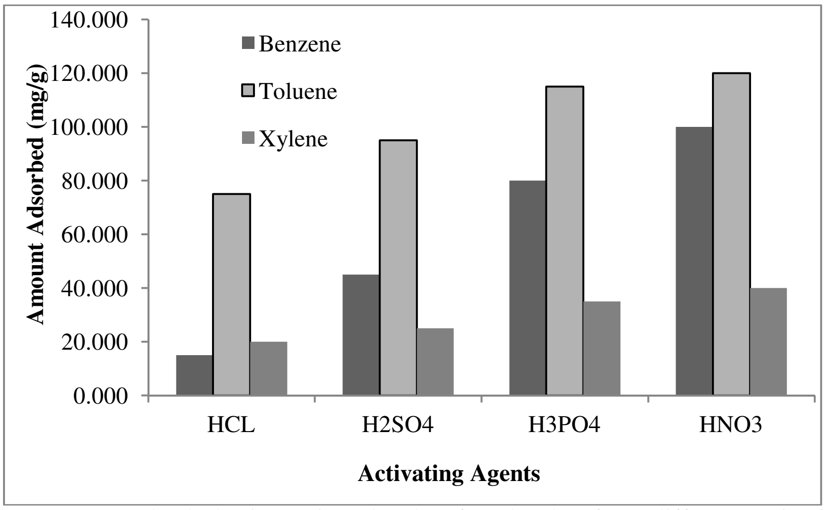

Fig 4 BTX vapour adsorbed using activated carbon from bamboo from different activating agent

More toluene vapour were adsorbed using activated carbon from bamboo than Benzene and xylene vapours for all activating agent. Toluene was reported to be 25 times more reactive than benzene (Wade, 2003). Toluene also forms a stronger complex with NO_2^+. than benzene and xylene. The methyl group is an activator.The product mix contains mostly ortho and para substituted molecules as shown in Fig 5. Yun *et al* (1997) also reported that toluene vapour was adsorbed more than benzene and xylene vapours during adsorption of BTX with a commercial fixed bed activated carbon.

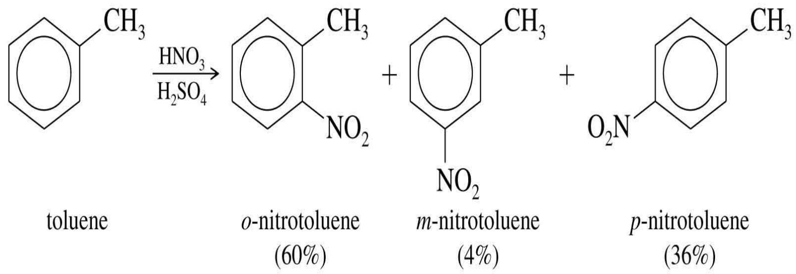

Fig 5 Showing toluene forming a stronger complex with NO_2^+

The BTX adsorbed in aqueous solution using activated carbon from bamboo from different activating agent is presented in Fig. 6. Bamboo activated carbon activated with HNO_3 and HCl adsorbed BTX significantly more than other activated agents (H_2SO_4 and H_3PO_4) in the aqueous phase.

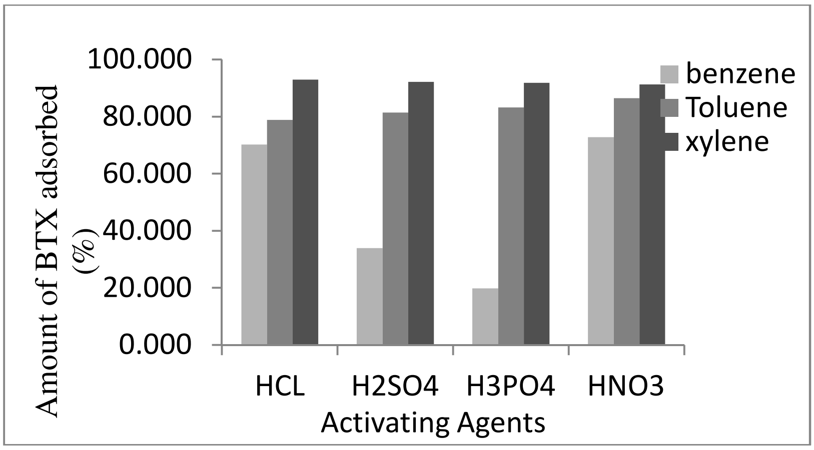

Fig 6 BTX adsorbed in aqueous solution using activated carbon from bamboo activated with different activating agent

Comparing Fig 5 and 6, activated carbon activated with HCI adsorbed more BTX in aqueous solution than in vapour phase. It should also be observed from Fig. 6 that Toluene and xylene adsorbed by the different activated carbons for the entire activating agent are not as significant different for BTX in aqueous solution than vapour. It seem more chemically active sites are created for BTX adsorption in aqueous than in vapour phase. There is more of chemi-sorption than ordinary physical adsorption.

Fig 7 shows the effect of activating agent on benzene adsorption using different Nigerian bamboos. HNO_3 still adsorbed more benzene vapour than other activating agent. Sample A and B has the same adsorption rate though the thickness and outer diameter before carbonization and activation are not the same from Table 2. Sample A and C is a upland bamboo while sample B is a riverine bamboo. Significant variation observe in sample C from the benzene adsorption rate of the different activating agent shows that the sample C is greatly affected by activation. Hence adsorption is not affected by the physical geometry of the bamboo but by the chemical composition of the bamboo and type of activating agent.

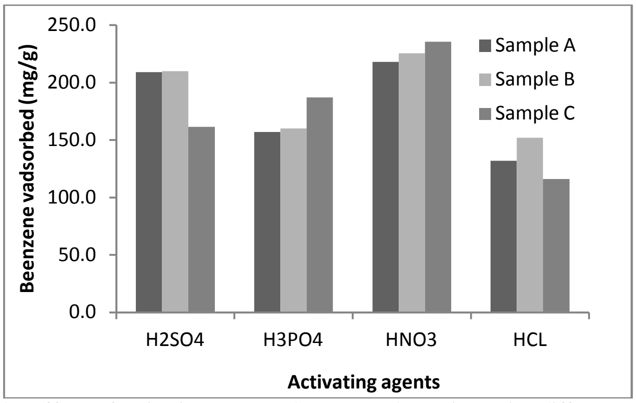

Fig 7: Shows the effect of activating agent on benzene adsorption using different Nigerian bamboos

Table 4.1: Physical geometry of bamboo used

Sample	A (mm)	B (mm)	C (mm)
Average nodal distance	403	315.67	351.67
Inner diameter	6.20	5.33	2.93
Outer diameter	7.75	8.3	4.5
Thickness	0.65	1.43	0.9

*Effectiveness of activated carbon from Nigerian Bamboo to adsorb BTX compared with Commercial Activated Carbon:*Fig. 8 – 10 shows the adsorption of BTX using activated carbon from Nigerian bamboo and a commercial activated carbon. Activated carbon from Nigerian bamboo (Sample A) exhibited high adsorption capacity for BTX more the commercial type. The adsorption rate also increased with time consistently for Benzene, toluene and xylene than the commercial type.

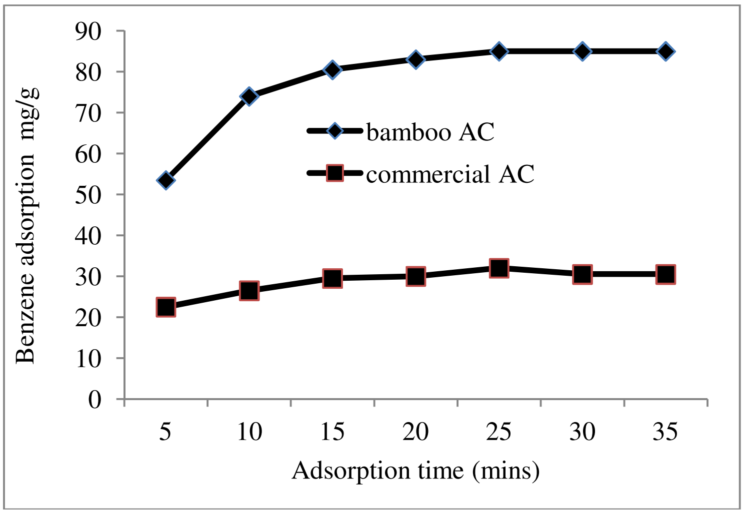

Fig. 8: Rate of Adsorptiion of benzene vapour by commercial and bamboo activated carbon

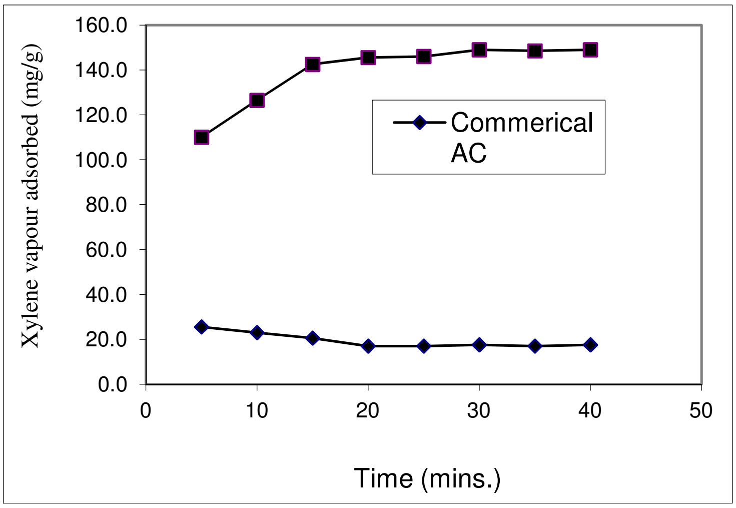

Fig. 9 Rate of Adsorptiion of Xylene vapour by commercial and bamboo activated carbon

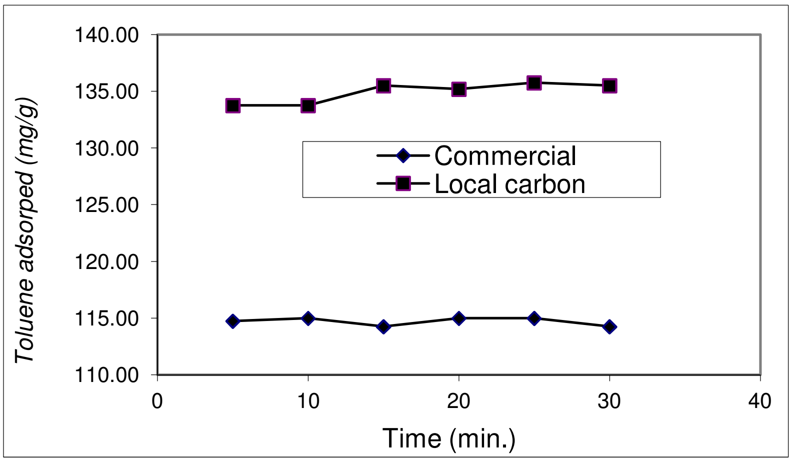

Fig. 10 Comparison of Adsorption rate of Toluene vapour using bamboo and Commercial activated carbon

Conclusions: Effect of activating agents on the adsorption of BTX vapour and aqueous BTX was investigated. Benzene adsorption was found to increase at low concentrations (0.1–

0.143M) for bamboo activated with hydrochloric acid, trioxonitrate (v) acid, and tetraoxosulphate (vi) acid while increasing phosphoric acid concentration during activation was found to increase benzene vapour adsorption. The best activating agent for adsorption of BTX vapour was 0.143M trioxonitrate (v) acid, while the best activating agent for activating bamboo for adsorption of BTX in aqueous solution was hydrochloric (0/1M) and trioxonitrate (v) acid (0.1 – 0.143M). Adorption of BTX which was found to be more of chemisorptions than ordinary physical adsorption. The differences in the adsorption of the three bamboo type was not affected by the physical geometry of the bamboo but by the chemical composition of the bamboo and type of activating agent used. The activated carbon from bamboo with the best concentration was also found to adsorb BTX favourably and better than a commercial activated carbon with same particle size.

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