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Studies on the adsorption efficiency of activated carbon for pesticide vapour

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Chlorpyrifos pesticides are endocrine disruptors, inhibitors of acetyl cholinesterase, used to control pests and prime contributors to indoor pollution in retail stores. Seven selected locally sourced adsorbents; Bone charcoal (BCA), corncobs, cotton seed, kokoli, sawdust, coconut shell (CSA) and Muruchi were evaluated. Only BCA and CSA shows peaks and were further examined at adsorptive temperatures of 283, 293, 303, and 313K. Adsorbents physical properties that is, micro pore surface area, total pore volume; micro pore volume, particle density and true density were measured and compared. Results from gas chromatography and surface characterization revealed that the adsorptive capacities of carbon (CSA) at various temperatures were higher than that of carbon (BCA). The plots of Langmuir and Freundlich Isotherms were well fitted by the measured adsorption data. The parameters of adsorption equation for both Langmuir and Freundlich were determined for the two adsorbents, which indicates increased values of adsorptive capacity at low temperature and decreases at high temperature. This study shows that activated carbon made from coconut shell has high surface area, micro porous structure, high degree of surface reactivity and higher heterogeneous properties that suggest it to be a better adsorbent sufficient for the adsorption of chlorpyrifos vapour in an indoor environment.

Key words: Chlorpyrifos pesticide, activated carbon, adsorption isotherms.

INTRODUCTION

People usually think of air pollution as being outdoors, but air in your house or office could also be polluted. Source of indoor pollution include biological contaminants like mold and pollen, tobacco smoke, household products and pesticide gases. Indoor air pollution is caused by high levels of contaminants that become trapped indoors because of poor ventilation.

Pesticides are classed as semi-volatile organic compounds and include a variety of chemicals in various forms; exposure to it has been a concern to public health because of their persistence, toxicity and carcinogenicity (Febre et al., 2005). Research has documented the presence of biologic markers of pesticide exposure in adults and children (Arcury et al., 2006, 2007; Perara et al., 2006; Rauth et al., 2006; USEPA, 2006; Lu et al., 2008). Detectable level of pesticide have been reported in home dust, floors, children toys primarily in families residing in agricultural areas (Quadt et al., 2005).

Scientific field investigations have indicated that the air in homes and other building are more seriously polluted than the outdoor pollution. Study suggested that 80% of most people exposure to pesticide occurs indoors and the measurable level of up to a dozen pesticides have been found in the air inside home. The health effect of exposure includes irritation to eye, nose and throat, damage to central nervous system and kidney, headache, dizziness, muscular weakness and nausea. Chronic exposure to some pesticide can result to damage in the liver, endocrine, nervous systems and death. Both the active and inert ingredients in pesticide can be organic compound, therefore, both could add to the level of airborne organic in an indoor environment. A study of the effects of chlorpyrifos on human exposed over time showed that people on high levels have autoimmune antibodies that are common in people with autoimmune disorders. There is a strong correlation to chronic association with autoimmune disorder after exposure to

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chlorpyrifos (Thrasher et al., 2002). Chloropyrifos pesticide belongs to the class of organophosphorus pesticide that is widely used and sold by agrochemical retailers in north -eastern Nigeria. Chlorpyrifos is a neurotoxin and suspected endocrine disruptor, and it has been associated with asthma, reproductive and developmental toxicity.

However, it is impossible to eliminate these chemical substances completely within an indoor retail outlet as long as the volatility of the pesticide, high temperature and humidity are in place. Nevertheless, it is necessary to limit the pesticide vapour to a considerable level. According to the US Environmental protection agency toxic release inventory (TRI) under title III of the CAAA, the organic vapours are to be regulated. The regulation requiring their emission sources to install maximum achievable control technology (MACTS). Current MACTS for organic vapors are condensation, incineration, carbon adsorption and liquid absorption. Of these technologies, carbon adsorption is a very common one because it offers some advantage over the others (Ruddy and Carroll, 1989; Spivey, 1988).

According to a recent survey in Northeastern Nigeria, 90% of agrochemical retailers were occupationally exposure to and carries a body burden of multiple pesticides in their system due to the sales, storage and handling of pesticides in retail stores (Hotton et al., 2010). To this end, this research work was geared toward developing an adsorbent that has the potential to adsorb pesticide vapour within an indoor retail environment. We examined and evaluated the adsorptive efficiency of seven selected locally sourced adsorbents; Bone charcoal (BCA), corncobs, cotton seed, kokoli, sawdust, coconut shell (CSA) and muruchi.

MATERIALS AND METHODS

Selected grades of cattle bones and coconut shell were locally sourced in Jalingo abattoir and market. They were washed in hot water and boiled for 10 min to remove fat and oil. The carbonized processes of the shell and bones include drying and heating in order to remove undesirable by-products such as ash and other hydrocarbon. The carbonization process is completed by heating the material at 400 to 600°C. The carbonized particle s were made "active" by exposing them to steam at high temperature for an hour. The steam burns off the decomposition products from the carbonization phase to develop a porous activate pore size. The carbonized charcoal were separately grated and sieved to fine particle size on a U.S standard mesh size No. 40 sieve (0.42 mm). Corncob, cotton seed, kokoali seed, murichi fibre, and sawdust were dried, grated and sieved.

Procedure for adsorption

Commercial pesticides (Chlorpyrifos) were obtained from Zee agrochemical Ltd Jalingo with an emulsion concentration of 25% EC. Different percentages of concentrations were prepared with distilled water, that is, 0.4, 0.6, 0.8 and 4%. 20 ml of the already

prepared concentration of each pesticide were measured separately and placed at the centre of an enclosed heating glass bowl. 2 g each of the selected adsorbents were measured and placed within 20 cm^2 radius of the measured 20 ml pesticide in the heating bowl. The vaporization of the pesticide occurred at a given temperature. The adsorption temperature was performed at 283, 293, 303 and 313K which were regulated and maintained in a hot water bath, the process was allowed to stay for 2 h. The entire experiment was repeated for the pesticide and adsorbents at various concentrations and temperature. The respective adsorbents were collected after the exposure duration of 2 h and placed in a sealed glass vial label properly and stored at 4°C u ntil analysis. Pesticide reference standards of organophosphorus pesticides were obtained from Niger- Sigma chemicals Ltd.

Surface characterization measurements

The surface characterizations of carbon were carried out only on the adsorbent of CSA and BCA for they were the only adsorbents that yielded peaks result by the gas chromatography (Gc) in this study. The particle size distribution was determined by Shimadzu Laser Diffraction particle size analyzer. The particle density was measured by a mercury displacement method using a mercury porosimeter (Autopore II 9200; Micromeritics, Inc GA, USA). The true density was determined by a helium displacement method using a pycnometer (Accupyc 1330; micromeritics, Inc, GA USA). The specific surface areas, total pore volume were determined from BET method and the adsorption volume of 0.95 relative pressure (adsorption /desorption apparatus ASAP 200 (Micromeritics Inc GA USA) using a continuous flow method.

Sample extraction, clean up and analysis

The adsorbent samples were analysed for organophosphorus compound using USEPA method 8141A by Gas chromatography-capillary column technique. Extraction was based on the method followed by Agarwal et al. (1976) with some modification using hexane: acetone (1.1) 20 ml (thrice) as solvent for extraction. Clean up was done by USEPA method 3620B by column chromatogram-phy. The extract were transferred to the column and eluted with hexane (10 ml), 6% diethyl ether in hexane (10 ml), 50% diethyl ether in hexane (10 ml) and finally with diethyl ether (10 ml). Eluent were collected and evaporated to dryness. Final samples were prepared in 2 ml hexane (HPLC grade). Quantification of organophosphorus pesticide adsorbed by the adsorbent was done by Shimadzu – 17A series GAS chromatography equipped with 63 NI selective electron capture detector. Quantitative analysis of OP residues in each sample was done by comparing the peak area with those obtained from a chromatogram of a mixed OP standard of known concentration. The average recoveries of fortified samples were exceeding 95%. An aliquot of reagent water was treated exactly as a sample including exposure to all glass ware, equipments, solvents and reagent used with the sample matrix. No analyte peak was detected in laboratory regents blank.

RESULTS

Table 1 shows the general trends of the adsorption capacity of the seven adsorbents that is, CSA, BCA, corncob, cotton seed, kokoali seed, murichi fibre, and sawdust conducted at different temperatures and concentrations.

At a constant temperature of 283 K and at varying

Table 1. Adsorptive capacity of the adsorbents used.

Temp (K)	Conc. (%)	CSA (mg/g)	BCA (mg/g)	Corn cob	Kokoli	Saw dust	Murichi fiber	Cotton seed
283	0.4	0.420	0.350	N.D	N. D	N.D	N. D	N.D
	0.6	0.63	0.450	N.D	N. D	N.D	N. D	N.D
	0.8	0.830	0.600	N.D	N. D	N.D	N. D	N.D
	4.0	2.500	1.800	N.D	N. D	N.D	N. D	N.D
293	0.4	0.290	0.172	N.D	N. D	N.D	N. D	N.D
	0.6	0.420	0.220	N.D	N. D	N.D	N .D	N.D
	0.8	0.560	0.250	N.D	N. D	N.D	N. D	N.D
	4.0	1.670	1.100	N.D	N. D	N.D	N. D	N.D
303	0.4	0.250	0.180	N.D	N .D	N.D	N. D	N.D
	0.6	0.360	0.250	N.D	N .D	N.D	N. D	N.D
	0.8	0.450	0.350	N.D	N .D	N.D	N .D	N.D
	4.0	1.250	1.200	N.D	N. D	N.D	N. D	N.D
313	0.4	0.190	0.150	N.D	N. D	N.D	N. D	N.D
	0.6	0.280	0.190	N.D	N. D	N.D	N .D	N.D
	0.8	0.360	0.250	N.D	N .D	N.D	N. D	N.D
	4.0	1.000	0.750	N.D	N. D	N.D	N .D	N.D

N.D = Not detected.

Table 2. Surface characterization of activated carbon CSA and BCA used.

Physical properties	Activated carbons CSA	Activated carbons BCA
Total surface area (N_2 BET Method) (M^2g^{-1})	1001	985
Micropore surface area (M^2g^{-1})	762	525
Total pore volume (Cm^3g^{-1})	0.4271	0.5525
Micropore volume (Cm^3g^{-1})	0.305	0.201
Particle density (gcm^3)	0.7672	0.6982
True density (gcm^3)	1.9250	1.6947

CSA = Coconut shell 'activated carbon, BCA = borne charcoal activated carbon.

concentrations, the adsorptive amount for CSA were 0.420, 0.630, 0.830 and 2.500 mg/g, respectively and 0.350, 0.450, 0.600 and 1.800 mg/g for BCA. While the remaining adsorbents that is, corn cob, cotton seed, kokoali seed, murichi fibre, and sawdust whose values were below the detection limit recorded as N.D in Table 1.

Table 2 shows the general trends of the adsorption capacity of the two adsorbent CSA and BCA at various concentrations and temperatures.

DISCUSSION

The results obtained from this study in Table 1 revealed the adsorptive values of CSA and BCA adsorbed at all levels of the varying temperatures and concentrations while the remaining five adsorbents displayed no results,

as such they were not discussed further. The physical properties of the two adsorbents based on their surface characterization, shows that CSA has a large surface area property of 1001 M^2g^{-1} over the BCA with 985 M^2g^{-1}. Under an electron microscope in Figure 1, the high surface area structures of CSA are revealed. Individual particles are intensely convoluted and display various kinds of porosity; there may be many areas where flat surfaces of graphite-like materials run parallel to each other. The lager surface area is a measure of how much exposed area the adsorbent CSA has, expressed in square units. The finer the particle sizes of the activated carbon, the better the access to the surface area and the faster the rate of adsorption kinetics. The most fundamental property of the surface area is its additives. In vapour phase systems this needs to be considered against pressure drop, which will affect energy cost. Careful consideration of particle size distribution can
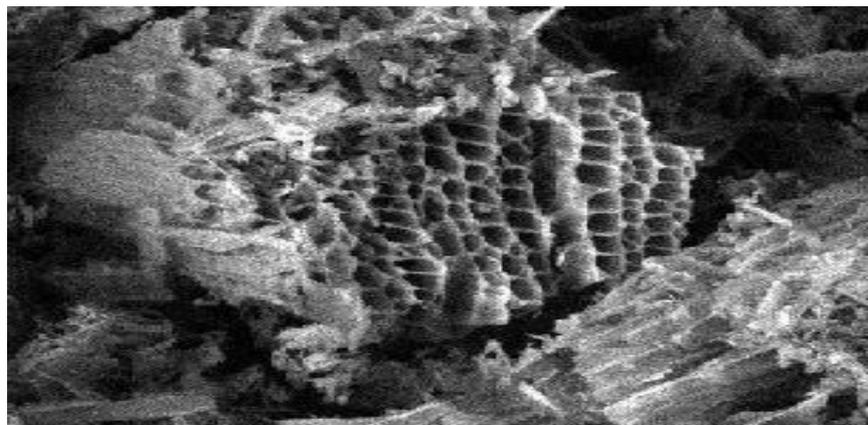
Figure 1. Activated carbon of CSA as viewed by an electron microscope.
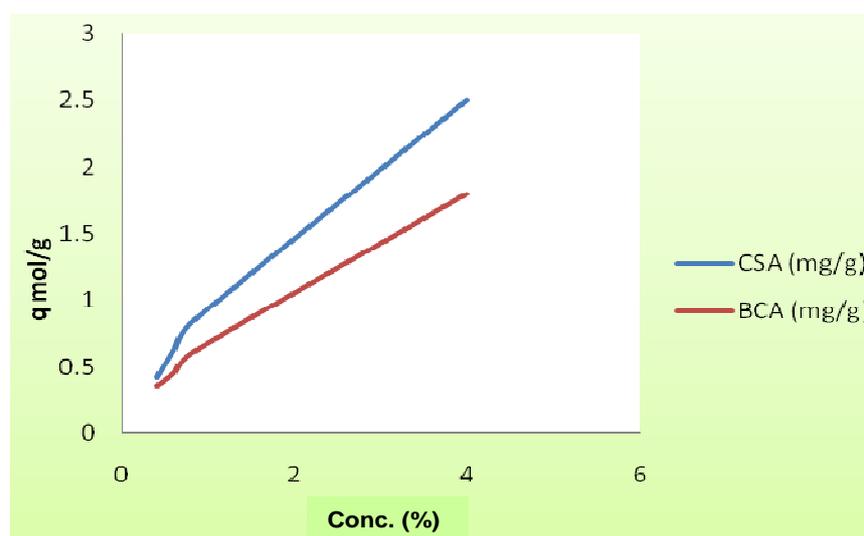
Figure 2. Plots of adsorbed amount against concentration at 283K for CSA and BCA.

provide significant operating benefits. The reaction rate or speed of reaction for a reactant or product in a particular reaction is intuitively a function of how fast or slow a reaction takes place. The rate of reaction increases as the surface area does. That is because more particles of the solid are exposed and can be hit by reactant molecules. This means that the more finely divided a solid or liquid reactant, the greater its surface area per unit volume, and the more contact it makes with the other reactant, thus the faster the reaction. The two adsorbents in this study displayed large surfaces but CSA appears to adsorb better than BCA, this may be attributed to the large proportion of surface area.

The micro pore surface area of CSA shell was found to be 762 m^2g^{-1} larger than carbon from BCA (525 m^2g^{-1}). The micro pore volume of carbon (CSA) appeared also to be higher with 0.305 cm^3g^{-1}, while the micro pore volume

of BCA yielded a lower value of 0.201 cm^3g. These micro pores provide superb conditions for adsorption to occur, since adsorbing material can interact with many surfaces simultaneously. However, the results indicate that the values of the micropore surface area of CSA were higher than BCA which is a pointer that increasing the surface area of a substance generally increases the rate of a reaction. The particle density yielded 0.7672 gcm^3 CSA higher than the result obtained for BCA (0.6982 gcm^3). The result also shows that the true density of the two adsorbents in the study were 1.9250 for CSA and 1.6947 for BCA. Higher density provides greater volume activity and normally indicates better quality of the activated carbon.

However, the plot of the amount adsorbed for both adsorbents against concentrations as showed in Figures 2 to 4 shows the adsorbent CSA with a high adsorption
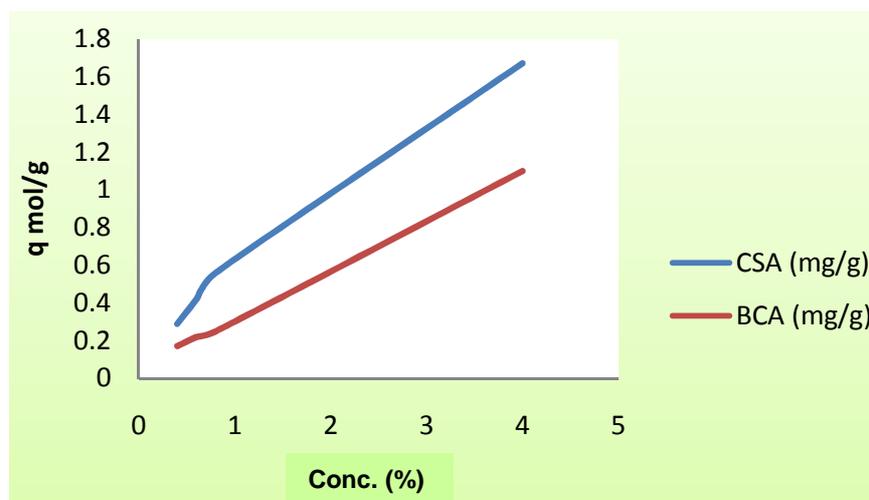
Figure 3. Plots of adsorbed amount against concentration at 293K for CSA and BCA.
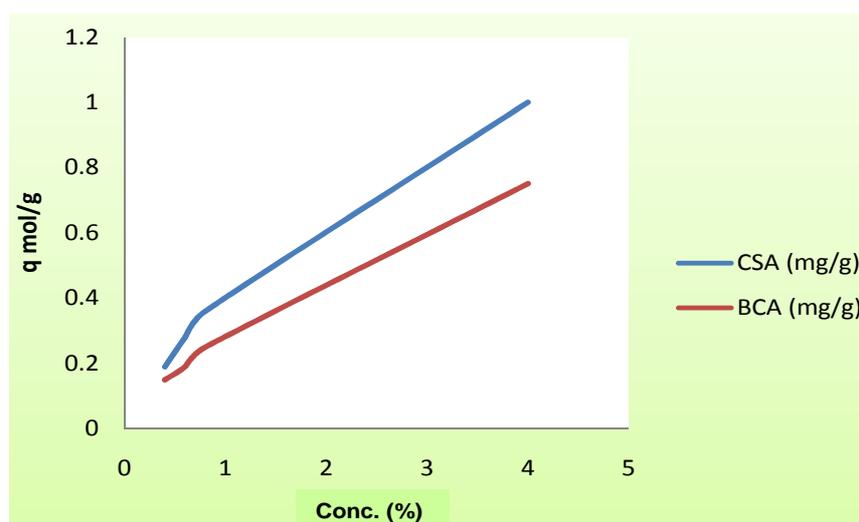
Figure 4. Plots of adsorbed amount against concentration at 313K for CSA and BCA.

rate than BCA. From the adsorption amount of BCA and CSA in Table 1, it can be deduced that the adsorption potential of CSA is of higher affinity than the BCA values. It was revealed also that the value of the adsorption capacity increases as the concentration increases at constant temperature for both adsorbent.

However, the overall trend at various temperatures and concentration shows that the Adsorbed amount decreases as the temperature increases. Generally, results indicate that the values of the surface areas, micro pore surface area, micro pore volume, particle density and true density support the fact that CSA in this studies exhibited a better heterogeneous distribution of surface energy for the adsorption of the adsorptive and that the micro pores are responsible for a large proportion of the surface area.

Adsorption isotherms

Since physical adsorption is non-specific every gas will adsorbed on the surface of active solid. How much gas adsorbed depends on the nature of the adsorptive, the surface area and temperature.

Adsorption of chlorpyrifos vapour on CSA and BCA at various concentrations and temperatures plots showed linear relationship that fits both the theories of Freudlich adsorption isotherm and the langmuir equation (Ching-Yuan, 1994; Ruthven, 1984; Susaki, 1991). The Langmuir adsorption isotherm equation can be
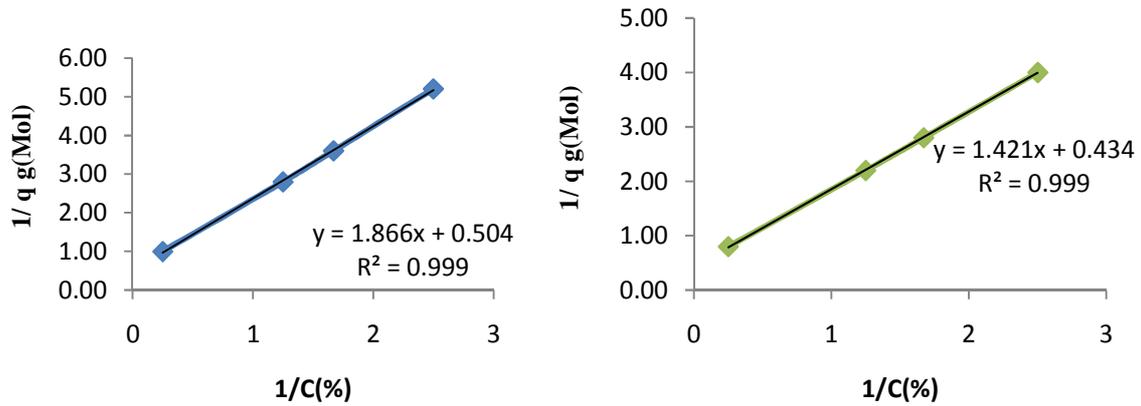
Figure 5. Langmuir plots on carbon CSA at 283 and 293K.
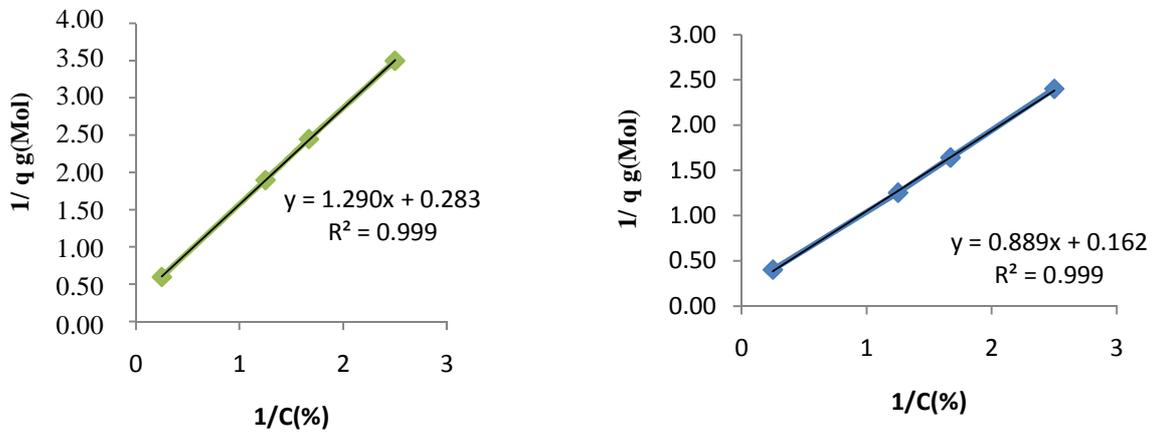
Figure 6. Langmuir plots on carbon CSA at 303 and 313K.

represented by:

$$1/q = (1/q_m) + (1/q_m KC)$$

Where q = the adsorbed amount (Unit mass of adsorbent), q_m = adsorption capacity at monolayer saturation, C = equilibrium concentration of adsorbate (pesticide concentration in solution), K = adsorption equilibrium constant

A plot of (1/q) versus (1/c) for Langmuir isotherm for both CAC and BCA yielded:

Slope = (1/q) k with $1/q_m$ = intercept

The plot of the Langmuir Isotherm shows a positive linear graph with the regression co-efficient justifying the fitness of the plotted experimental data which also agrees with the theory of adsorption as presented in Figures 5 and 6 for CSA. In order to find and calculate the values of the Langmuir isotherm parameters the least square method

was adopted using the slope and the intercept to compute the values of q_m and K for both CSA and BCA.

Higher density and surface area provides greater volume activity and normally indicates better quality activated carbon. Physically, activated carbon binds materials by van der Waals force or London dispersion force. Micro pores of CSA provide superb conditions for adsorption to occur, since adsorbing material can interact with many surfaces simultaneously.

The evaluation of the values of Langmuir adsorption isotherm parameter computed from the plot, results shows that the adsorptive amount of CSA based on the isotherm parameter buttressed the fact that the carbon of CSA adsorbed higher than the carbon of BCA in Table 1. This also is in agreement with values obtained in Table 2 that shows adsorption potential of CSA over BCA. The results from this study shows that the values of K decreases with increase temperature and K increases with decrease in temperature which confirms that the adsorbents displayed a higher adsorption affinity at lower temperatures. Table 3 shows the evaluation of the values

Table 3. Langmuir parameters for adsorption of chlorpyrifos on activated carbon at various temperatures.

Adsorbent	Adsorption temperature (T)	Langmuir parameter		
		q_m (molg^{-1})	K	R^2
BCA	313	11.85	3.10	0.999
	303	13.62	3.40	0.998
	293	18.45	3.60	0.992
	283	20.6	3.80	0.996
CSA	313	19.8	3.27	0.999
	303	23	3.70	0.999
	293	35	4.55	0.999
	283	61.7	5.48	0.999

Table 4. Freundlich parameters for adsorption of chlorpyrifos on activated carbons at various temperatures.

Adsorbent	Adsorption temperature (T)	Freundlich parameter		
		K	n	R^2
BCA	313	3.5	3.35	0.999
	303	4.31	3.89	0.998
	293	2.7	4.57	0.996
	283	6.8	4.75	0.998
CSA	313	4.2	3.5	0.999
	303	5.9	2.9	0.999
	293	6.0	3.9	0.999
	283	8.5	3.6	0.999

of Langmuir adsorption isotherm parameter computed from the plot in Figures 5 and 6.

The Freundlich adsorption isotherm was also used whose equation was transformed into linear by taking the logarithm on both sides.

$$Inq = Ink + (1/n) Inc$$

Hence, using the values of q and C in Table 1 a plot of In q versus In C yielded a straight line graph as shown in Figures 7 and 8. This implies that the adsorption process conforms to Freundlich adsorption isotherm.

The values of the parameter K and n obtained as shown in Table 4 reveals that the values of the parameter n decreases with increasing temperature. A higher value of K increases the adsorptive amount of the adsorbent. The value of K also agrees that carbon CSA values were higher than carbon BCA at the same temperature. The results confirmed and agreed also with our findings using the Langmuir adsorption isotherms, the Freundlich isotherm and the adsorptive amount.

The overall results reveals that both adsorbent adsorbed better at low temperature of 283 K yielding high values of 61.7 mol/g at a monolayer saturation of CSA

and 20.6 mol/g monolayer saturation for BCA as shown in Table 3, relating the values of the monolayer saturation to the values obtained for the BET total surface area of CSA (1001) as shown in Table 2, it can be deduced that the surface area of CSA has the potential to adsorb the pesticide vapour at an amount of 61,700 mol/g.

In conclusion, our findings shows that it is achievable to control and limits chloropyrifos vapour to some considerable level in an indoor environment using coconut shell activated carbon adsorption technology. This study reveals that the adsorption capacity of carbon CSA is higher than that of carbon BCA because of its sufficient porosities and surface area which values agrees with the measured physical properties. The adsorption was more favorable at low temperature and shows that the adsorption is of physical reaction which can be reversible. The plots of Langmuir and Freundlich Isotherms were well fitted by the measured adsorption data.

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