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Adsorption Mechanism of Paracetamol, Salbutamol, Chlorpheniramine Maleate onto Locally Produced Nigeria bamboo Activated Carbon

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ABSTRACT

The use of activated carbon in removal of Pharmaceutical active compound (PhACs) is an emerging aspect of environmental research with sparse information. This study investigates the adsorption mechanism of carbonized activated carbon from *Oxythenantera abyssinica* (COA KCl) and (CBV H_3PO_4) in removal of PhACs from Pharmaceutical wastewater. Produced activated carbon COA KCl and CBV H_3PO_4 were characterized using Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). The adsorbent were then used in remediating of PhACs from Pharmaceutical wastewater in terms of contact time ranging from 30-1440min and carbon dosages of 1-5g in batch adsorption processes. Visible-ultra violet spectrophotometry was used in determination of influent and effluent parameters. Data generated were then fitted into pseudo-first and second order kinetic models, and Langmuir and Freundlich adsorption isotherms. The FTIR analysis showed sharp adsorption peaks at 3432 and 1632cm^{-1} indicating O-H stretch and N-H stretch. The SEM analysis shows both close and open pore with good porosity when read with java interactive software program, image J. The optimal contact time for adsorption of PhACs is 30 min for all adsorption tested, while the optimal carbon dosage is 2g.The value of the correlation coefficients R^2 for second-order is 1.00 for all adsorbent employed, while first-order lies between 0.02-0.4. The Langmuir isotherm gave R^2 values of 1while values for Freundlich isotherm ranges from 0.6 to 0.74. K_L values for PhACs fell between 0.3 and 0.9 while the n values ranging from 1.37-6.68 shows that adsorption process where physical. Pseudo-second order model was seen to best describe the sorption dynamics of PhACs with R^2 value giving a better fit to the adsorption process then the first order model. Both the Langmuir and Freundlich show a good fit for COA KCL and CBV H_3PO_4 adsorption of PhACs.

Key words: Activated Carbon, Pharmaceutical Actives Contaminants, Adsorption Isotherms, Wastewater

1. INTRODUCTION

Pharmaceutical industry activities have resulted in Environmental problems due to lack of appropriate waste treatment system. The potential of pharmaceutical product as pollutant is high as thousands of different active ingredients are released from human and veterinarian yearly (Chanti and Durga Prasadu, 2015).

Pharmaceutical active compounds (PhACs) are seen as micro-pollutants which are endocrine-disrupting compounds (EDCs), (EPA 505, 2008). Paracetamol, Salbutamol and Chlorphenamine are medical use for pain, fever and asthma and the likes of it, but when it is abused they are refereed as pharmaceutical waste which can cause feminization of male fish, reduced appetite and make their activities to be sluggish. Trace amount of less than 1μg^{-1} in potable water or surface water for a long time leads to adverse effects of human health (WHO, 2020). One way of reducing pharmaceutical pollution is the installation of conventional wastewater Treatment Plants (WWTPs). However, these are not always effective in the removal of huge class of pollutants such as PhACs hence, further treatment are necessary. Pharmaceutical waste can be removed when treated through physical processes, such as sorption or volatilization, biological degradation or chemical reactions (Jones et al., 2005) came up with the use of Granular activated carbon (GAC) as a potential for the removal of pharmaceutical organic pollutant from wastewater streams and noted that though it is expensive, more attention should be directed to optimal usage of GAC in treatment of emerging pollutant or PhACs found in environmental matrices.

Activated Charcoal also call activated carbon or activated coal, is a form of carbon that has been processed under heat for it to be extremely porous and thus have a very large surface area available for adsorption or chemical reactions (Caron, 2008). It is also seen as a caonaceous material with large internal specific surface area and highly developed porous structure that had been employed successfully as a pollutant adsorbent. The use of difference forms of activated carbon (Powder, Granular and Brittle) has been investigated over the years in the treatment of environmental pollutant. Considering the strength of activated (AC) on adsorption and the cost of getting commercial AC for treatment, Engineers and Scientists further made a spirited effort in generating activated carbon from available raw materials like agricultural residues or by-product. These materials are lignocellulogic biomasses that are mostly abundant and bio-renewable feed stock which has great potential for sustainability and its production can replace commercial activated carbon (Chowdhury et al., 2013; Wang et al., 2013). Among the biomass that can be used for production of activated carbon are coal, wood, coconuts, bagasse, palms, shells, maize cob, rice husk and bamboos.

To reduce the pollutant potential of pharmaceutical waste discharged into surface waters, it is essential to develop a technology with GAC this being envisaged as the next step in improvement of pharmaceutical wastewater treatment.

This study assesses the effectiveness of locally produced activated carbon from bamboo as adsorbent of organic compound in pharmaceutical wastewater. An attempt is also made to compared sorption dynamics and the level of fit of Freundlich and Langmuir isotherms.

2. MATERIALS & METHODS

Two species of fresh bamboo culms were cut at about 20cm above the ground level. They were reduced to 20cm and external materials were removed. They were dried at room temperature and further reduced to 5cm. weighted mass of bamboo species were wrapped in double layers of aluminum foil before carbonization to ensure completely deoxygenated condition.

Carbonization temperature of 350^{O}C was used for 2hrs in an electric muffle furnace. Species were cooled and oven dried at 105^{O}C for 360min. The char samples were granulated and sieved to 1.18m size and stored. Activation was done with Phosphoric acid (H_3PO_4) and Potassium chloride (KCl) as dehydrating agent. About 26.25w/w of activator was used in activation of the carbon samples. Characterization was chemically done using Fourier Transform Infrared Spectroscopy (FTIR), to determine the surface functional groups. The Scanning Electron Microscopy (SEM) was used to view the surface structural of the samples at magnification of 100, 300, 500, 2000 and 5000 times the original size in order to view the pore space development and reveal other information such as texture (external morphology) and structural orientation.

Adsorption behavior of PhACs in pharmaceutical effluents onto bamboo activated carbon was studied in batch process. Experiments were carried out in ambient temperature and adsorption capacity of activated carbon from bamboo was tested on the basis of contact time and carbon dosage. Half liter of pharmaceutical effluent was put into conical flasks of 600ml capacity. Two grammes of each selected bamboo activated carbons were weighed into conical flasks to from an adsorbent/solute solution. Solutions were agitated at stirring speed of 160rpm to ensure intimate contact of the adsorbent and solute in solution. Each solution was observed for 6 hours contact time at which it attains dynamic equilibrium. Thereafter, solutions were filtered with filter paper 0.45µm size. The filtrate of 300ml was poured into sampling bottles with tie cap sealed with aluminum foils and kept at temperature of 4^{0}C for further analysis of extraction, clean up and Vis-UV. To obtain accuracy, all experimental analysis was duplicated. The amount of PhACs (q_e) adsorbed by bamboo activated carbons can be expressed mathematically as:

$$q_{e\ =\frac{C_O-C_e}{M}}\ \times v \qquad 1$$

The percentage removal is evaluated using

$$\%\ Removal\ = \frac{C_o-C_e}{C_o} \times 100 \qquad 2$$

Where
V is the volume of PAHs in solution (L)
Co is initial concentrations of PAHs (mg/l)
Ce is equilibrium concentrations of PAHs (mg/l)
M is the mass of the adsorbent.

Visible Ultra-violet spectrophotometry Analysis

Pure standards of all active ingredients observed with minimum of 98.5-99% purity were used for this study. Derivative form of Solid Phase Extraction SPE extraction procedure was used for extracting PhACs from sampled solutions.1cm of moderate packed cotton wool was placed at the bottom of each 10mm ID.250mm Loup chromatographic column used. 2g of activated silica gel 10ml of 1:1 acetonitrile and methanol was prepared and placed into the chromatographic column. To the top of the column was added 0.8cm of anhydrous sodium sulphate.

The column was rinsed with additional 3ml of acetonitrile followed by 3ml of methanol and 3ml acidify ultra-pure milli-Q water to pre-elute the column. Elute was allowed to flow though the column at the rate of about 1ml/min until the liquid in the column was just above the sulphate layer and immediately 300ml untreated or treated sampled effluents were transferred into each prepared column. The sample bottles were rinsed with 1ml methanol eluent and added to the column as well. The eluent were collected into sampling bottles, after which acidified methanol pH 2 was immediately used to extract compounds adsorbed to the silica sorbent at a flow rate of 0.1ml/sec. Samples were collected in a graduated cylinder each and allowed to concentrate to 10ml under air vacuum after which sample was increased to 20ml by adding 10ml of methanol and kept at 4^{O}C temperature before Vis-UV analysis. Visible Ultra-violet spectrophotometry, UV-Vis spectrophotometer S/N 18-1901-01-0243 made by PG instrument limited with UV win-Spectrum coupled with T90+UV/vis spectrometer scanner was further used to analysis the pharmaceutical effluents in order to ascertain concentration of PhACs of interest in the simulated pharmaceutical effluents. The software used in interpreting concentration of pollutant or chromatogram was UV win5 spectrophotometer version 5.2.0. Extracted concentrated

analytes were further diluted with methanol and scanned with visible-UV to determine the wavelength of each PhACs in the samples.

The wavelength of Paracetamol, Salbutamol and Chlorpheniramine was set at 257, 278 and 262nm respectively. The concentrated analytes were transferred into 10ml cuvette to read each concentration of PhACs with UV win5 spectrophotometer version 5.2.0 at different determined wavelength. Prior to each UV reading, the instrument was blanked with methanol in order to set a new baseline.

Quantification of PhACs was by an external standard method, which relies on the reproducibility of the standard preparation. The linearity of external calibration was done by preparing different concentration of Paracetamol, Salbutamol and Chlorpheniramine standards at different dilution rate of between 0.2 to 3.5.

3 RESULTS & DISCUSSION

FTIR spectra of CBV and COA in Figs. 1-4 show a large number of functional groups which constitute each modified bamboo species. The spectra of modified CBV and COA show that the surface functional groups of all tested samples do not exhibit significant difference irrespective of the activating agent used. Differences were slightly noticed on the intensity of the bands and spectrum shapes, with some functional groups shifted to different frequency levels.

All peaks assigned on the spectra were interpreted according to Coates [Coates, 2000]. For all activated carbon analyzed the spectra shows a broad absorption peak at 372 - 597cm^{-1} which was assigned to C-X alkyl; chloride with C-OH stretching out of plane, and 1042.53cm^{-1} was assigned to S=O stretch strong band. The absorption of 1247.66cm^{-1} was assigned to C-N amines stretch with aliphatic amines, while 1345.90cm^{-1} was assigned to CH_3 bending methyl group and bending S=O asymmetric stretch or sulfonyl chlorides. Adsorption of 1509.84cm^{-1} was assigned to N=O bands with strong aromatic-nitro compound conjugated, while 1632cm^{-1} was assigned to N-H bending (medium-strong, amines). The 2931.42cm^{-1} was assigned to C-H stretching bands to alkane or C-H bond to OH. The 3424cm^{-1} wave length was associated to OH hydrogen bonded phenol, alcohol hydroxyl group with H bonded to OH stretch. The results for all carbon tested show similar functional groups but different structural shapes. This can be linked to the different activating salt and change in temperature.

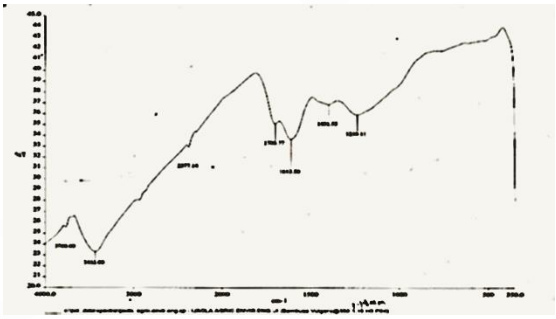


Fig 1 Fourier Transform Infrared Spectrometer of CBV at 350^{O}C H_3PO_4

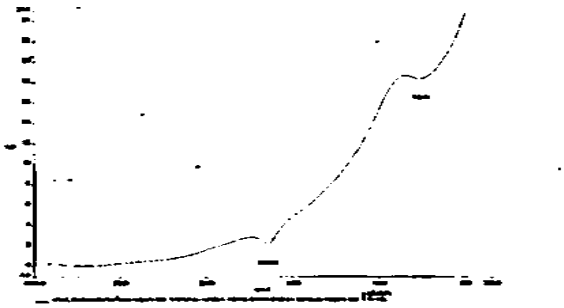


Fig 2 Fourier Transform Infrared Spectrometer of CBV at 350^{O}C KCl

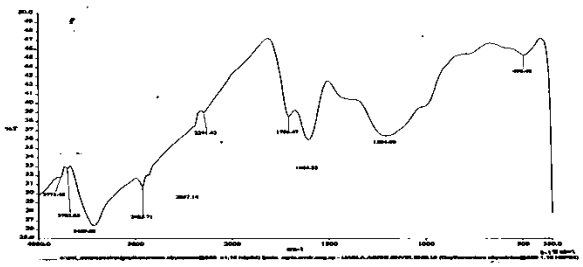


Fig 3 Fourier Transform Infrared Spectrometer of COA at 350^{O}C H_3PO_4

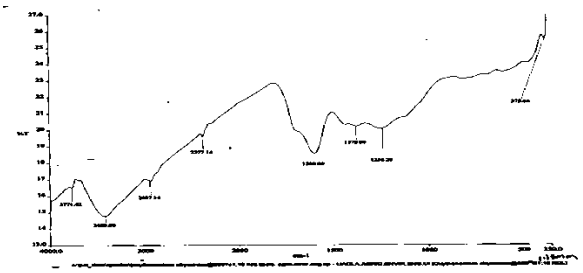
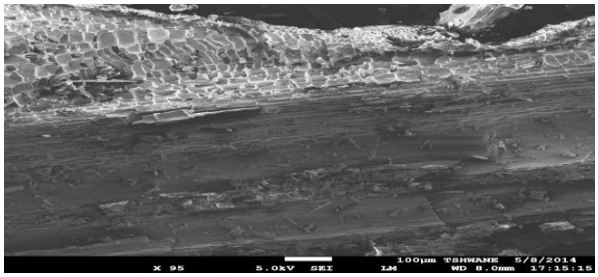


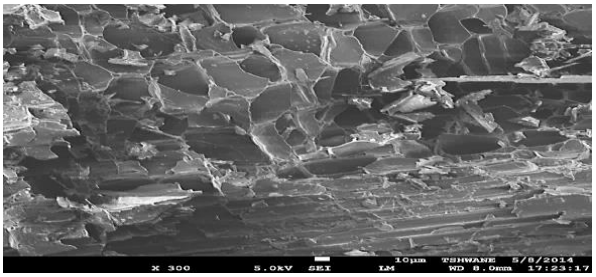
Fig 4 Fourier Transform Infrared Spectrometer of COA at 350^{O}C KCl

Plates 1-4 show the SEM micrographs for modified *Bambusa vulgaris* and *Oxytenanthera abyssinaca* at different magnification levels of 100-5000 times the original size. The SEM micrographs also reveal the surface structure i.e textures and morphology characteristics of the activated carbons. Images in Plates 1-4 reveal the porous structure of the samples, the amount of pores within each species for sorption and the agglomeration of particles within the structures in distinctive irregular shapes. Both species show layers of micro pore material clustered and woven together with a semi-permeable bio-membrane indicating that bamboo can undergo both filtration and adsorption processes progressively. The SEM image of Bambusa *vulgaris* seem to have more open pores when compared with Oxytenanthera *abyssinaca* which has a close pore with a thread-like surface. This indicates that Bambusa *vulgaris* may be better in adsorption or sorption processes when compared with Oxytenanthera *abyssinaca*. Pore diameters of each SEM images of the bamboo *sp*. ranges between 1-100µm with an average pore of 10µm.

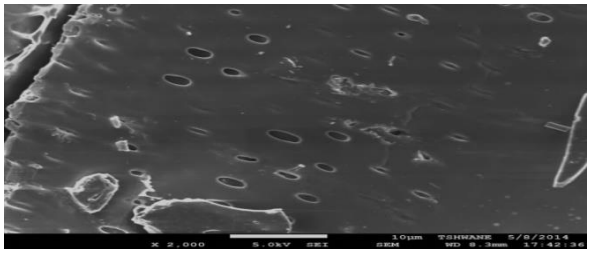
(a)



(b)



(c)



(d)

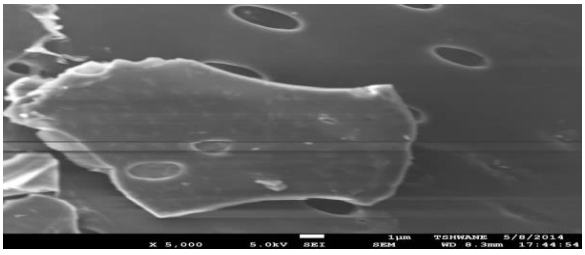
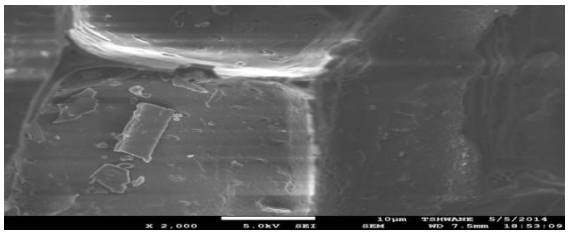
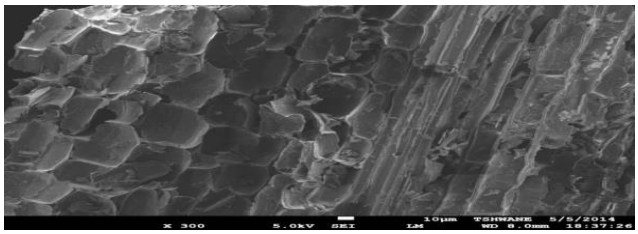


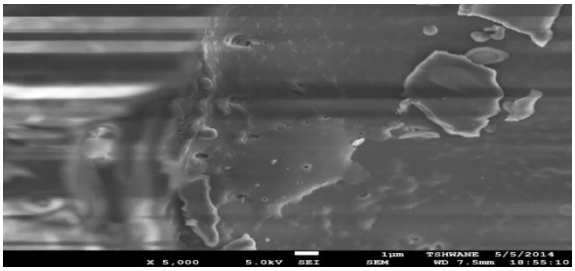
Plate 1 SEM image of Bambusa *vulgaris*(CBV 350^{O}CH_3PO_4)at different magnification levels (a) Mx,95, porosity 100µm (b) Mx 300, porosity 10µm (c) Mx 2,000, porosity10µm (d)Mx 5000, porosity 1µm

(a) (b)





(c) (d)



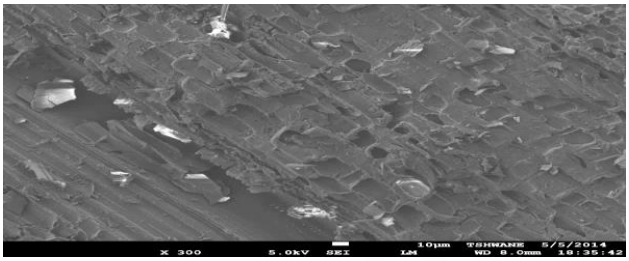
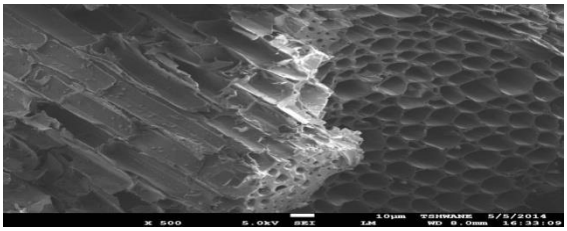
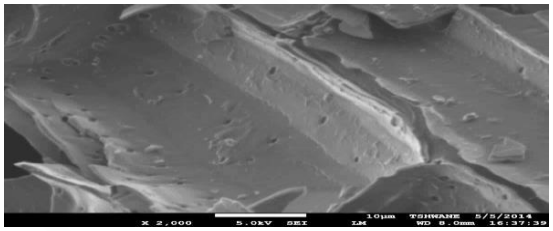


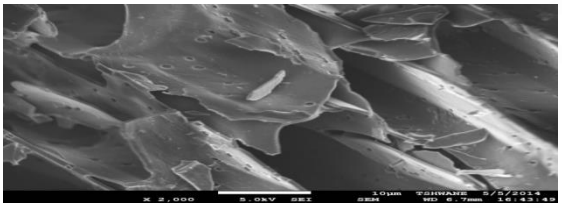
Plate 2 SEM image of Bambusa *vulgaris* (CBV 350^{O}C KCl)at different magnification level (a) Mx, 300, porosity 100µm (b) Mx 2000, porosity 10µm (c) Mx 5,000, porosity1µm (d) Mx 300, porosity 10µm

(a) (b)





(c) (d)



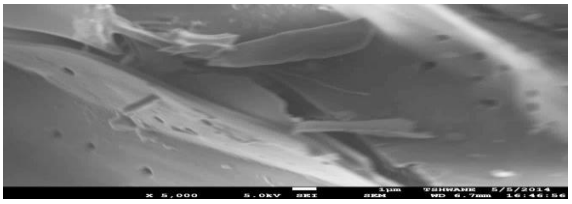
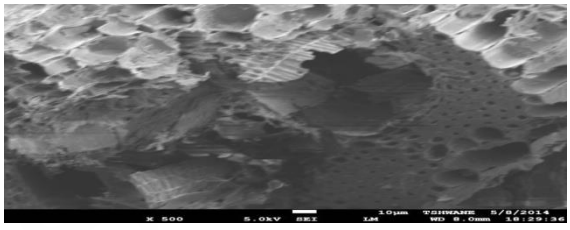
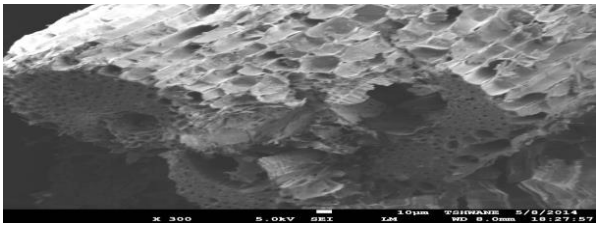


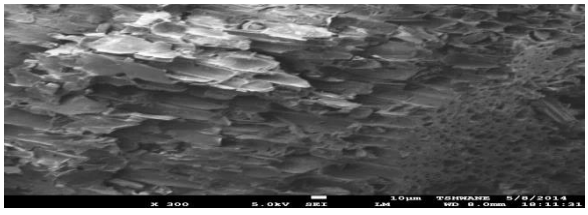
Plate 3 SEM image of Oxytenanthera *abyssinaca* (350^{O}C KCl)at different magnification level (a) Mx, 500, porosity 10µm (b) Mx 2000, porosity 10µm (c) Mx 2000, porosity10µm (d) Mx 5000, porosity1µm

(a) (b)





(c) (d)



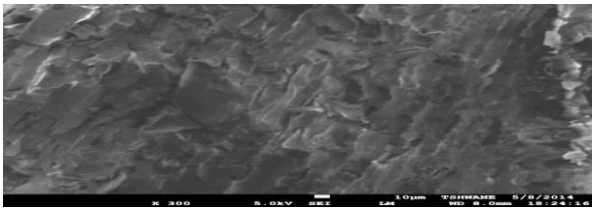


Plate 4 SEM image of Oxytenanthera *abyssinaca* (350^{O}C H_3PO_4)at different magnification levels (a) Mx, 500, porosity 10µm (b) Mx 300, porosity 10µm (c) Mx 300, porosity10µm (d) Mx 300, porosity10µm

On this basis of pore space, porosity and surface area which was read with java interactive software programme called image J. CBV (350^{O}C H_3PO_4) and COA (350^{O}C KCl) were selected for adsorption experiment.

3.1 Adsorption Mechanism of PhACs

3.1.1 Effect of Contact Time

Figs 5 a-c shows the adsorption rate and removal efficiency of PhACs by COA KCl and CBV H_3PO_4 at varying contact time of 30, 180, 360, 720 and 1440 mins. The trend of adsorption in Figs. 5a-c revealed a slight reduction of adsorption rate before an increase after which equilibrium was observed for COA KCl adsorbent. Adsorption trend of CBV H_3PO_4 revealed a sharp reduction to a level and there after an increase was observed before equilibrium point was reached. These observations are consistent with (vergilli and Barlas, 2009; Meenakshisundaram et al., 2011 and Lateefa et al., 2014) findings. It can be explained that absorption of PhACs with COA KCl and CBV H_3PO_4 occurred in two different stages. The first stage occurred during the first 30-360mins contact time, with high number of active binding sites on the adsorbents surfaces. Adsorption rate is rapid in this stage and points to adsorption being controlled by diffusion processes of Paracetamol, Salbutamol and Chlorpheniramine molecule from the bulk phase to the adsorbent surface. The second stage of adsorption is an attachment-controlled processes due to decrease in the number of active site available for Paracetamol, Salbutamol and Chlorpheniramine molecule onto the adsorbents surfaces. Slow uptake of adsorbate and establishments of equilibrium over a longer period indicate strong chemical binding of adsorbate with adsorbent.

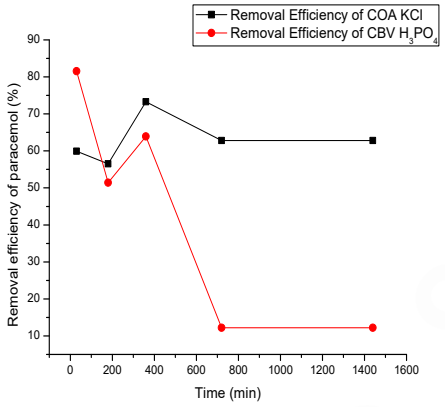


Fig 5a

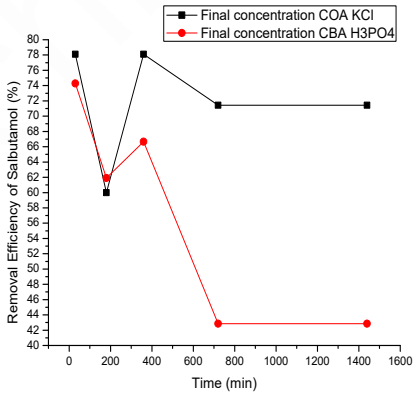


Fig 5b

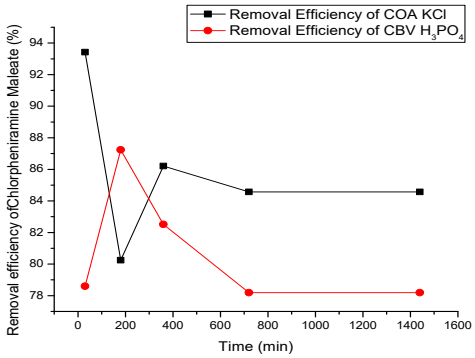


Fig 5c

Fig 5a-c Adsorption comparsion of PhACs with selected adsorbent **(a)** Paracetamol **(b)** Salbutamol **(c)** Chlorpheniramine

3.1.2 Effect of Carbon Dosage

Figs 6a-c show the results of adsorption of PhACs by COA KCl and CBV H_3PO_4 when adsorption process is conditioned under varying amount of carbons dosage (1-5g). These were done to investigate the effect of adsorbent masses on adsorption of PhACs. The adsorption pattern of COA KCl and CBV H_3PO_4 revealed an increase adsorption rate with increase in carbon dosage. There was increase in adsorption rate with increase in carbon dosage, for dosages between 1-2g after which reductions were observed in removal efficiency of tested pharmaceutical actives, until equilibrium was noticed at an addition of 5g. The increase in adsorption rate with increase in carbon dosage may be attributed to increase in the number of adsorption sites or increase in surface areas resulting from the conglomeration of the adsorbents (Meenakshisundaram et al., 2011). The reduction and equilibrium phenomenon may be due to constant movement between the ions bound to the adsorbent and the amount of free ions in the solution in which an additional carbon dosage will further have no effect.

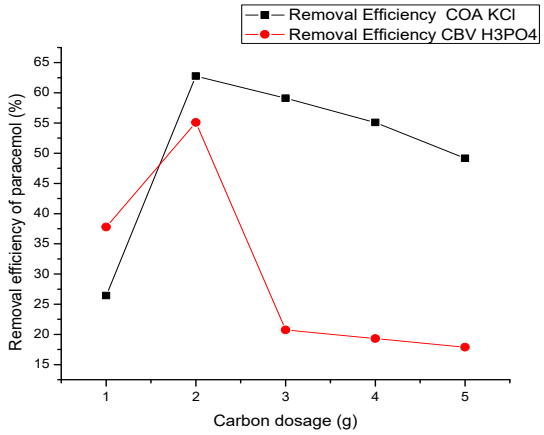


Fig. 6a

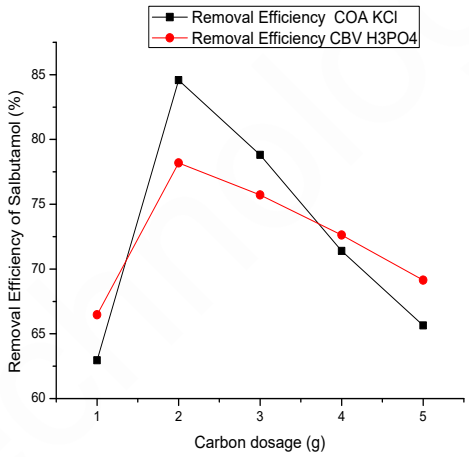


Fig. 6b

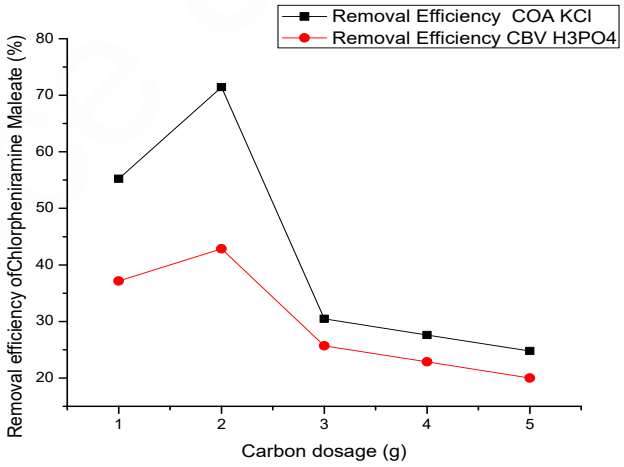


Fig. 6c

Fig 6a-c Adsorption comparison of PhACs with selected adsorbent in term of carbon dosage **(a)** Paracetamol **(b)** Salbutamol **(c)** Chlorphenamine

3.2 Adsorption Dynamics

The adsorption kinetics theory depends on the interactions between the adsorbate, adsorbent and the system conditions. Kinetic study provides valuable information about the mechanism of adsorption and subsequently investigation of the controlling mechanism of the bio-sorption process as either mass transfer or chemical reaction in order to obtain the optimum operating

conditions for industrial-scale batch processes. In this study, PhACs adsorption onto adsorbent (COA KCl and CBV H_3PO_4) in simulated wastewater were investigated using a simple mathematical expression containing the pseudo-first and second order model (Lagergen, 1898; Ho et al., 2000)

The Pseudo-first order rate of equation derived by (Lagergen, 1898) can be expressed mathematically as:

$$\frac{d_{qt}}{dt} = K(q_e - q_t)^2 \quad 3$$

Where
q_e and q_t (mgl-1) are the adsorption capacities at equilibrium and at time t respectively.
K (min-1) is the rate constant of pseudo-first order adsorption.

Thus, applying first-order model of adsorption, the plot of log (q_e-q_t) against (t) gave a linear relationship from which values of qe and k were determined from the slopes and intercepts of the plots.

The rate of sorption as second order mechanism was described by (Ho *et al.*, 2000). The second order model is a chemisorptions kinetic rate equation and is derived from first order equation that was expressed as:

$$\frac{d_{qt}}{dt} = K(q_e - q_t)^2 \quad 4$$

Where
qe and q_t are the sorption capacity at equilibrium and at time t, respectively in mg/l
k is the rate constant of pseudo-second order of sorption (g/mg/min).
If equation 2 is integrated and rearranged with h_o (mg/g/min) as the initial adsorption rate, when $q_t/t \rightarrow 0$ equation 2 becomes:

$$\frac{t}{q_t} = \frac{1}{h_o} + \frac{1}{q_e\, t} \quad 5$$

Since $h_o = kq_e^2$ 6

Hence, applying second-order model of adsorption, the plot of t/q_t against t gave a linear relationship from which values of q_e and k are determined from the slopes and intercepts of the plots.

Table 1: Kinetic Parameters of COA KCL and CBV H_3PO_4 in the adsorption of PhACs

PhACs	Adsorbent	Pseudo-First Order			Pseudo-Second Order			
		q_e mg/l	K_l	R^2	q_e mg/l	K^2	h_o	R^2
Paracetamol	COA KCl	8.90	5.13	0.41	59.4	0.65	1	0.829
	CBV H_3PO_4	1.26	0.07	0.02	11.56	17.24	1	0.723
Salbutamol	COA KCl	13.66	5.18	0.10	20.12	25.30	1	0.838
	CBV H_3PO_4	9.12	5.08	0.07	12.45	36.27	1	0.796
Chlorpheniramine	COA KCl	7.45	6.45	0.16	64.60	0.65	1	0.843
	CBV H_3PO_4	2.60	0.06	0.09	57.70	17.23	1	0.835

q_{el} (mg/l): adsorption capacity, K_1: rate constant of pseudo-first order adsorption (g/mg/min), K_2: rate constant of pseudo-second order adsorption (g/mg/min), h_o: (mg/g/min) initial adsorption rate, R^2: correlation coefficients. Kinetic model was done under experimental condition of pH 7, adsorbent mass of 1g, solution volume of 200ml and temperature: room temperature at varying contact time.

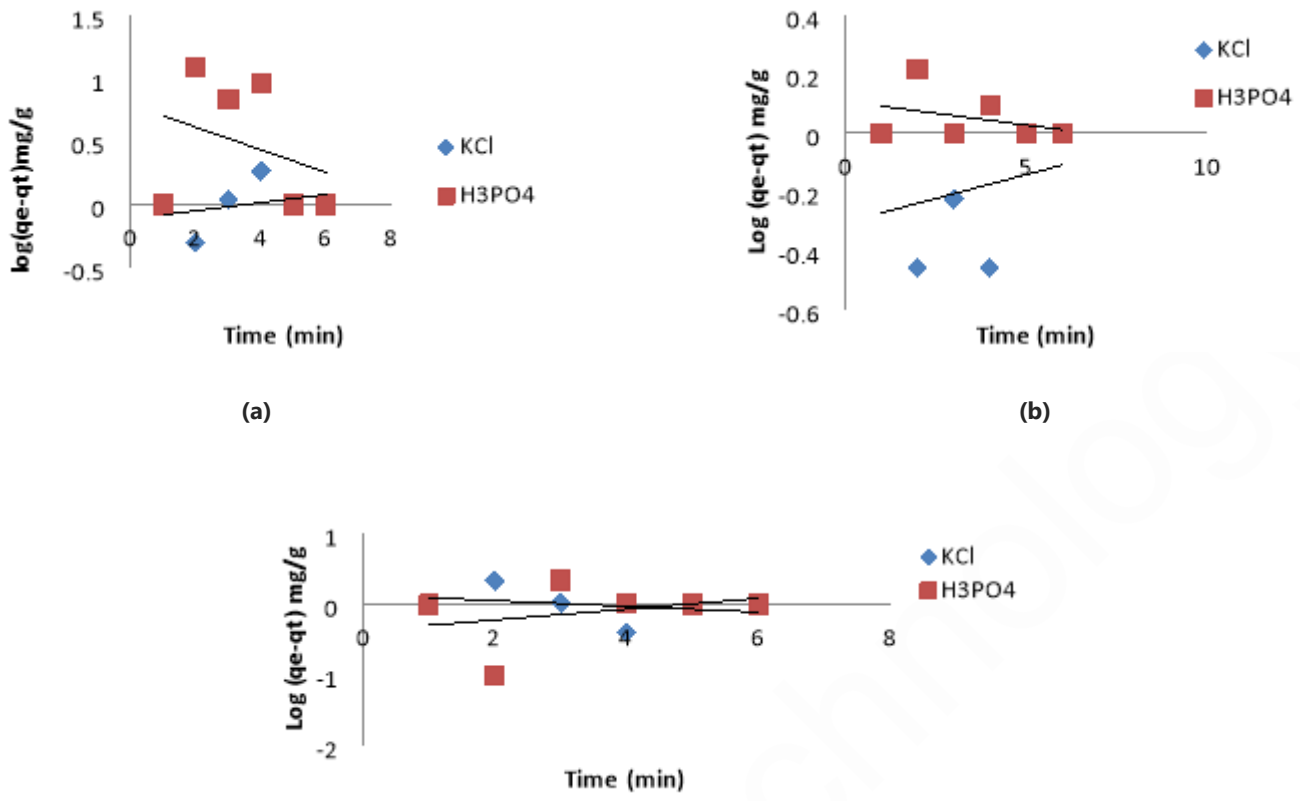
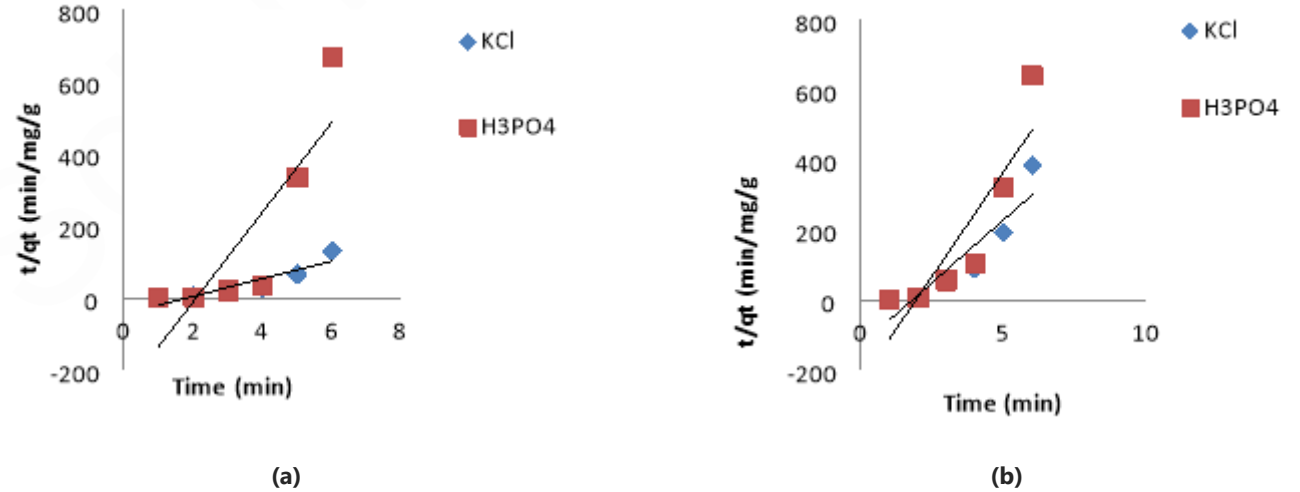
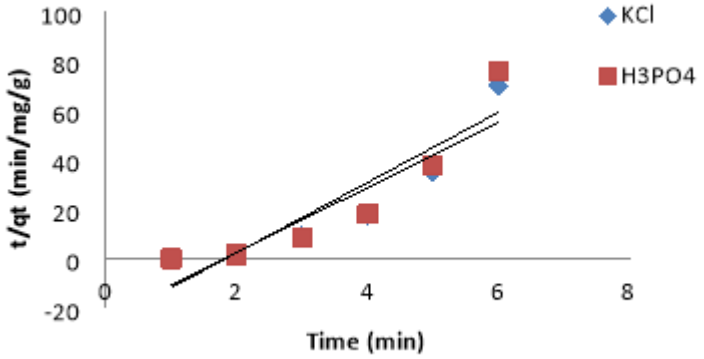


Fig 7 First order adsorption kinetics for **(a)** Paracetamol **(b)** Salbutamol and **(c)** Chlorpheniramine

Applying first-order model of adsorption, the plot of log (q_e-q_t) against (t) on fig 7 gave a linear relationship from which the values of q_e and k were determined from the slopes and intercepts of the plots. Similarly, applying second-order model of adsorption, the plot of (t/q_t) against (t) in fig 8 gave a linear relationship from which values of q_e and k was determined from the slope and intercept of the plots. PhACs adsorption with COA KCl and CBV H_3PO_4 adsorption gave a good straight line as indicated in figs 7&8. The correlation coefficients R^2 in table 1 gave a least value of 0.41 for COA KCl in the adsorption of tested PhACs and 0.09 for CBV H_3PO_4. The K_1 value as shown in Table 1 was very low meaning that pseudo-first order model may not be applicable in describing the adsorption of PhACs onto COA KCl and CBV H_3PO_4.





(C)

Fig 8 Second order adsorption kinetics for (**a**) Paracetamol **(b)** Salbutamol **(c)** Chlorpheniramine

The pseudo second-order parameters in Table 1 shows the values of q_e, K_2, h_o and R^2. The value of R^2 in the table shows that the pseudo-second order model gave a better fit to the adsorption process than the first order. Higher values of K_2 and h_o indicate that the adsorbent had more pore space that could aid adsorption. Table 1 revealed that for every high value of K_2 there were low values of q_e and vis-versa indicating that if the value of K_2 is higher, adsorption rate will be greater while q_e will be lower at greater adsorption. It then means that the higher the value of q_e the lesser the adsorption rate. This is similar to Igwe and Abia, (2007) observation on adsorption of metal ions to local adsorbent.

3.3 Adsorption Isotherms

The study made use of most common adsorption isotherms used in describing the adsorption of wastewater contaminant. The Langmuir and Freundlich isotherms reflect the capacity of activated carbon in adsorbing waste (Addagalla et al., 2009).

The mathematical expression of Langmuir and Freundlich can be stated as:

$$\frac{Ce}{qe} = \frac{1}{Q_m K_L} + \frac{Ce}{Q_m} \quad (7)$$

$$q_e = \frac{q_m K_l C_e}{1 + K_l C_e} \quad (8)$$

And

$$q_e = K_f C_e^{1/n} \quad (9)$$

Linearizing the above equation we have:

$$\log q_e = logK_f + \frac{1}{n}(logC_e) \quad (10)$$

Where

q_e is the PAHs and PhACs concentration on the adsorbent at equilibrium (mg/g)

C_e is the equilibrium PAHs and PhACs concentration in the solution (mg/l)

Q_m is the monolayer adsorption capacity of the adsorbent (mg/g) and

K_L is the Langmuir adsorption constant (l/mg).

For the Freundlich equation,

q_e is the equilibrium PAHs and PhACs concentration on the adsorbent (mg/g dry weight)

C_e is the equilibrium PAHs and PhACs concentration in the solution (mg/L),

K_f is a constant that describes the adsorption capacity of the adsorbent and n is an empirical parameter which indicates the intensity of the adsorption.

Table 2: Isotherm Constant for Adsorption of PhACs in simulated wastewater onto COA KCl and CBV H_3PO_4

Parameters	Adsorbent used in Remediation	Langmuir				Freundlich		
		Ka	Q_m	K_L	R^2	K_f	N	R^2
Paracetamol	COA KCl	0.1426	34.2466	0.6657	1	1.7161	2.5826	0.7685
	CBV H_3PO_4	0.6129	1.3848	0.8594	1	3.9968	1.7349	0.6178
Salbutamol	COA KCl	4.4596	0.8121	0.1759	1	3.1427	4.0128	0.1565
	CBV H_3PO_4	2.0344	0.3635	0.8802	1	8.2712	6.6979	0.2557
Chlorpheniramine	COA KCl	0.0056	16.7504	0.9731	1	1.6966	1.3650	0.5458
	CBV H_3PO_4	0.3776	20.3527	0.3527	1	3.0367	3.0581	0.6668

Q_m : is the monolayer adsorption capacity of the adsorbent (mg/g), K_L: is the Langmuir adsorption constant (l/mg), K_F: is a constant that describes the adsorption capacity of the adsorbent , n:is an empirical parameter which dictates the intensity of the adsorption, R^2: correlation coefficients Isotherm model. The experiments were carried out under the condition of pH 7, adsorbent mass of 2g, solution volume of 500ml and temperature: room temperature at varying contact time.

The constants Q_m and K_L in Table 2 indicate Langmuir monolayer saturation capacity and Langmuir isotherm constant for PhACs, and these were obtained from the intercepts and slopes of the linear plots.

The value of the correlation coefficients R^2 for PhACs is 1 for all adsorbent employed. Indicating that the adsorbents are satisfactory in the removal of PhACs. It also indicates that perfect order of adsorption may have been reached. The Langmuir adsorption constant, Q_m, could be used as an indicator of the extent of affinity between the adsorbate and the adsorbent; that is, the higher Q_m value represents greater affinity of the adsorbent (Bulut and Aydin , 2006; Srivastava et al., 2009) . Table 2 shows that the Q_m values are not consistent, as there is no clear trend. The higher values show that the adsorbent had greater affinity for the adsorbate. A dimensionless constant called separation factor or equilibrium parameter K_L, according to (Hall *et al*., 1966) and (Malik, 2004), is often used to predict the affinity between an adsorbent and adsorbate:

The expression K_L is

$$K_L = \frac{1}{1+K_a C_o} \qquad 10$$

Where
K_a is the Langmuir constant
C_o is the initial concentration.

The value of K_L indicated the type of Langmuir isotherm. If K_L= 0 it means irreversible, linear when K_L=1, unfavorable when K_L>1, or favorable at 0<K_L<1) (Reed and Matsumoto, 1993). K_L values for PhACs in Table 2 fell between 0.3 and 0.9 indicating favorable adsorption. The results for Langmuir adsorption isotherm show a good fit for the removal of PhACs when COA KCl and CBV H_3PO_4 are used.

In Freundlich adsorption Isotherm model, the constants K_f and n correspond to adsorption capacity and adsorption intensity, respectively. The constants were determined from plot of log q_e versus log C_e. Considering linear relationship for Freundlich equation, the n value indicates the degree of nonlinearity between solution concentration and adsorption as follows: if n=1, then adsorption is linear; if n<1, then adsorption is a chemical process; if n>1, then adsorption is a physical process. The n values for PhACs in Table 2, shows that adsorption process was physical, with n values ranging from 1.37- 6.68. According Reed and Matsumoto [20] the most common situation is n>1 which may be due to a distribution of surface sites or any factor that causes a decrease in adsorbent-adsorbate interaction with increasing surface density. When n values are within 1-10 it indicates that adsorption is good (Özer, and Pirinççi, 2006). The results obtained shows that adsorption process of PhACs is favorable with Freundlich model since n values were between good adsorption ranges.

4. CONCLUSION

The use of COA KCl and CBV H_3PO_4 as adsorbent of PhACs and with FTIR and SEM analysis shows a clear trend of large pore space and porosity. The trend of adsorption in term of contact time revealed two stages of sorption mechanism with COA KCl having better sorption trends when compared to CBV H_3PO_4. The dosage of carbon that best removed pollutant in all stage of adsorption for both COA KCl and CBV H_3PO_4 is 2g. The Pseudo-second order model best describe the sorption dynamics of PhACs. Both the Langmuir and Freundlich model gave a good fit for COA KCl and CBV H_3PO_4 adsorption of PhACs.

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Conflicts of Interest

The authors declare no conflict of interest

Data and materials availability

All data associated with this study are present in the paper.

Peer-review

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