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Adsorptive Removal of Ampiclox from Aqueous Solution using Treated Okobo Coal

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ABSTRACT
This research work assessed the performance of Okobo coal for sorptive treatment of binary solution containing Ampicillin (AMP) and Cloxacillin (CLO) in a brand name called Ampiclox using analytical techniques. The Okobo coal adsorbent was activated by impregnating it with 1M H_3PO_4. Batch adsorption method was adopted for the adsorption studies. The adsorbent prepared was subjected to classical and instrumental techniques. The classical techniques were Attrition, conductivity, pH, bulk density and specific surface area while the instrumental techniques were limited to FTIR, SEM and TGA. The Attrition of the adsorbent was (5.4 %), conductivity (26 µS/cm**)**, pH (6.11), Bulk density (1.78±0.03 g/cm^3) and specific surface area (189.4 m^2/g**)**. All these values were similar to other activated carbon adsorbents used in the literatures. The FTIR shows clear peaks after adsorption indicating the presence of new bonds which were coming from the adsorbate. Four adsorption isotherms (Henry, Langmuir, Freundlich and Temkin) were used to fit the data to describe the adsorption and all fitted the data with Langmuir been the best model for the experiment with R^2 values of 0.991 and 0.994 for AMP and CLO respectively. For the transport models plotted (Film diffusion and intraparticle diffusion model) the diffusion of the antibiotics onto the adsorbent was multi-mechanistic since the plots of the transport models deviate from origin. The statistical result of the analyses obtained indicated that there was no statistical difference between the adsorption of Ampiclox by Okobo coal adsorbent and CAC (commercial activated carbon). Therefore, it can be concluded that the adsorbent prepared was good for carrying out adsorption studies given the results presented herein for the adsorption of Ampiclox.

Keywords: Adsorption, Ampiclox, Antibiotics, Binary Solution, Coal, Pollution, Simultaneous

INTRODUCTION
Antibiotics have been used for several decades in both human and animals for treatment of microbial infections and also as feed additives for promotion of growth of livestock animals. The surged in antibiotics global production eventually enter into the environment after usage and as residuals in sewage (Bingquan *et al.*, 2016). At the moment, pollution of water resources by pharmaceutical wastes is one of the greatest and serious environmental challenges facing communities, especially in places where there is reliance on these sources for drinking purposes (Oh *et al.*, 2017). Excessive pharmaceutical products in environmental matrices such as Ampiclox (Ampicillin and Cloxacillin) as in Figure 1 are classified as hazardous materials that can affect adversary the natural ecosystem by changing the status of the equilibrium (Kalhori *et al.*, 2018; Ji *et al.*, 2014). These chemicals can enter the aquatic bodies including surface and ground water through various anthropogenic activities, which includes; waste streams from hospitals, pharmaceutical and veterinary industries from their manufacture to disposal (Mohammed *et al.*, 2019). Antibiotics are part of pharmaceutical compounds that are consumed in great quantities as they are highly effective in treating a wide spectrum of bacterial diseases in humans, livestock, poultry and fish (Soori *et al.*, 2016; Huang *et al.*, 2017). Among the various types of antibiotics; Ampiclox and a host of others are widely used in the world as effective therapeutic agents in the treatment of a variety of bacterial diseases (Al-Musawi *et al.*, 2019; Samarghandi *et al.*, 2015). The discharge of pharmaceutical wastewater loaded with antibiotics can cause lethal health risks to non target humans and biota related to their chronic or acute exposure, as they contain toxic and carcinogenic elements. More also, they may cause fetal abnormalities (Shi *et al.*, 2019; Bondarczuk and Piotrowska-Seget, 2019). Various studies have reported that the disinfection of by-product chemicals, which are considered as carcinogenetic agents, were detected in the final treating stages due to the chlorination of wastewater containing antibiotics. Therefore, it is urgent to reduce the antibiotic compounds to the permissible limits prior to being discharged into

water bodies (Mohammed *et al*., 2019). Unarguably, antibiotics are characterized by their stability in the environment and their long standing degradation time. One of the most interesting treatment methods is the adsorption process (Zou *et al*., 2019). The adsorption treatment method is simple efficient and universal advanced treatment technology. This treatment method employs using natural or synthesized material (known as adsorbent) for the adsorption of pollutant molecules (known as adsorbates) from contaminated solutions (Zou *et al*., 2019; Mohammed *et al*., 2019). For the adsorption process to be integrated in terms of removal efficiency and economic feasibility, the adsorbent should be chosen with great care (Gisi *et al*., 2016; Ghorai *et al*., 2014). In this context, the adsorbent should be tested for the adsorption performance toward numerous contaminants before being applied.

Since coal is advantageous in the adsorption process as a result of its ability to be stable after usage Li *et al.* (2015), there is need to ascertain its effectiveness in removal of Ampiclox which is one of the most commonly used antibiotics and one of the suspected pollutants of the day due to intense usage.

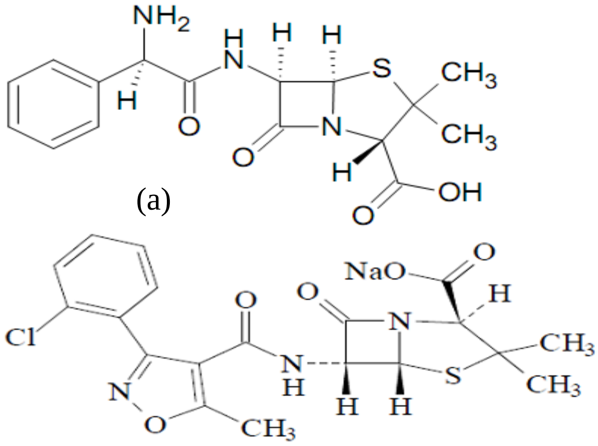

Figure 1: (a) and (b) Shows Structural Formula of Ampicillin and Cloxacillin Sodium Respectively (Garba, 2015)

MATERIALS AND METHODS

Materials

The reagents used include; Laboratory Reagents (H_3PO_4= 85 %, 1.685 g/mL, NaOH = 97.0 %, 2.13 g/cm^3 and HCl = 37%, 1.2 g/mL), Ampiclox capsules, distilled water, deionized water and Okobo Coal.

UV spectrophotometer (Jenway 7415 Single beam), muffle furnace, orbital shaker, magnetic stirrer, water bath shaker, FTIR (Agilent Technologies – Cary 630), SEM (Phenomenon Prix, MVE016477830) and TGA (PerkinElmer-8000).

Study Area and Sample Location

Okobo settlement, is a small town in Enjema district of Ankpa Local Government Area (7°22′14″N 7°37′31″E) in Kogi state with a high reserves estimate of up to 380 million tonnes of coal. A GPS mapping of the study area and sample location is given in Figure 2.

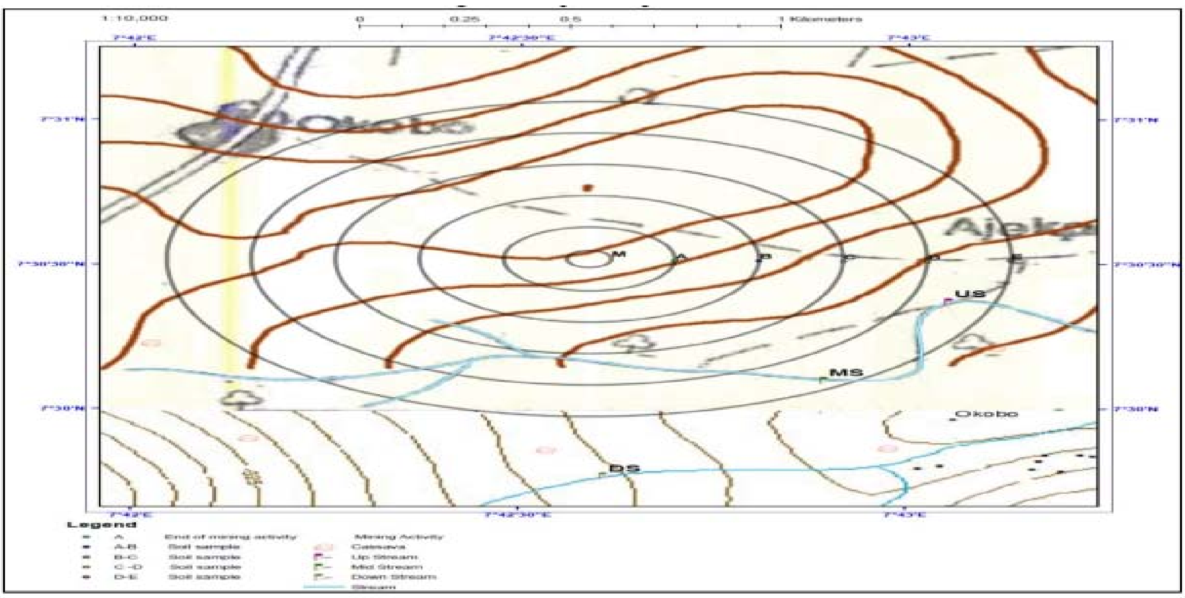

Figure 2: Map of Study Area and Sample Location (Itodo *et al*., 2020a)

Methods

The method of coal collection by Itodo *et al*. (2020b) was carefully followed with slight changes. A sample grid was established in which ten samples of mass 20 g of coal was obtained from a split which was taken each 50 m away from the grid and then harmonized as one sample by means of a hand trowel and a hammer at the coal site. A gross sample of 200 g was obtained after homogenisation of the ten samples.

The sample was thoroughly washed, to remove extraneous materials such as dirt, sand and other impurities and subsequently dried and milled to fine particle sizes. The grounded coal was dried in an oven at 90 ^{0}C for 24 hours and later sieved with mesh of 350 μm particle size (Aneke and Echegi, 2015; Ezeokonkwo *et al*., 2018).

The stock solution of ampiclox 1000ppm was obtained by dissolving 1 g of ampiclox in a 50 mL beaker with distilled water and transferred into a 1000 mL standard flask and the volume made up to the mark. The solution was then diluted using serial dilution method to desired working concentrations with distilled water and stored at room temperature.

The standard solutions were prepared using equations 1 and 2.

$$V_{stock}\,(mL) = \frac{M.wt \times C \times V}{10 \times \%p \times d} \quad (1)$$

$$Wt\,(g) = \frac{M.wt \times C \times V}{10 \times \%p} \quad (2)$$

Where V_{stock} is volume (mL) of solution to be measured, M.wt is the molecular mass of the compound, C and V is the concentration and volume to be prepared, d is the density, %p is the percentage purity and wt is the weight of the compound to be measured (Chia, 2023).

Activation of Coal Sample

To activate, 3 g sample was weighed into a crucible and impregnated with 3 cm^3 of 1 M H_3PO_4 and allowed to stand for some time, then the furnace was set up to 800 ^{0}C after the sample was introduced for 2 hours being a predetermined activation time under inert condition using Nitrogen gas. The sample was washed with water, then with 0.1 M NaOH solution to remove surface ash, followed by warm and cold water rinsing to remove residual acid. The sample was oven dried after which the weight was measured (Itodo *et al*., 2014b; Ezeokonkwo *et al*., 2018).

Characterization of Adsorbent (Coal)

Bulk density

A 10 cm^3 cylinder was filled to 8 cm^3 with the activated carbon. The weight in gram (g) of the sample was recorded from weighing balance. The bulk density calculated as in equation 3 (Itodo *et al*., 2014b).

$$Bulk\ Density\ (g/cm^3) = \frac{Mass\ (g)}{Volume\ \ cm^3} \quad (3)$$

pH

For the pH 1 g of activated carbon was weighed and dissolved in 20 cm^3 of deionized water, then warmed and allowed to cool. The pH electrode was dipped into the solution and the value read from the meter until a desirable pH reached between 6-8 (Aziza, 2008; Itodo *et al*., 2014a).

Conductivity

For conductivity test 1 g of activated carbon was weighed and dissolved in 20 cm^3 of deionized water, it was warmed and the conductivity electrode dipped into the mixture and the readings were taken from the meter (Aziza, 2008; Itodo *et al*., 2014a).

Attrition or Hardness

The method by Louarrat *et al* (2019) was adopted. To determine attrition factor, 1.0 g of the adsorbent was placed in 50 mL of distilled water and stirred with a magnetic stirrer for 24 hours. The solution was filtered and the residue was dried and weighed. Percentage of attrition was calculated using equation 4;

$$Attrition\,\% = \frac{W_i\,(g) - W_f\,(g)}{W_i\,(g)} \times 100 \quad (4)$$

Porosity/ specific surface area

Saers' method was used for the determination of the surface area. A sample of the activated carbon 0.5 g was acidified with 0.1M HCl to pH 3-3.5; the volume was made up to 50 cm^3 with de-ionized water after addition of 10.0 g of NaCl. The titration was carried out with standard 0.1M NaOH in a thermostatic bath at 298±0.5 K to pH 4.0, and then to pH 9.0. The volume V required to raise the pH from 4.0 to 9.0 was noted and the surface area was computed using equation 5 (Dada *et al*., 2012).

$$S(m^2/g) = 32V - 25 \quad (5)$$

Instrumental characterization

The IR spectra were recorded with FTIR Spectrophotometer in the wave number range of 4000–400 cm^{-1} (Parimalam *et al*., 2011; Szychowski *et al*., 2012). The morphology of the prepared adsorbent was studied by using scanning electron microscope (SEM) (Ezeokonkwo *et al*., 2018).

Thermogravimetric Analyzer (TGA) was used to analyze the moisture content, volatile matter, fixed carbon and ash contents in adsorbent from coal sample (Olugbenga *et al*., 2015).

Adsorption Studies

Batch adsorption method was adopted in this research to investigate the effect of different parameters such as concentration, temperature, contact time, pH and dosage. Batch experiments were carried out to determine the adsorption isotherms of Ampiclox onto the adsorbent in 250 mL glass flask. The flasks were shaken at a constant rate of 200 rpm, allowing sufficient time for adsorption equilibrium. It was assumed that the applied shaking speed allows all the surface area to come in contact with Ampiclox over the course of the experiments. The mixture was then filtered using whatman (No 1) filter paper and the filtrate was analysed using UV-Vis spectrophotometer. The solution volume (V) was kept constant. The amount of Ampiclox adsorbed per unit mass according to Desta, (2013) was calculated from equation 7.

$$q_e = \frac{(C_o - C_e)}{m} \times V \qquad (7)$$

Where q_e is the amount adsorbate adsorbed at equilibrium (mg/g) C_o and C_e is the initial and equilibrium concentration (mg/L), m is the mass of the adsorbent (g) and V is the volume of the solution (L). Percent removal efficiency (% RE) was calculated using equation 8.

$$RE\ \% = \frac{(C_o - C_e)}{C_o} \times 100 \qquad (8)$$

Where C_o and C_e is the initial and equilibrium concentration (mg/L) respectively (Desta, 2013).

Effect of parametric factors

The effect of solution pH was monitored by changing the initial pH of the solutions to 2, 4, 6, 7, 8, 10 and 12. The pH was adjusted by using 0.1 M hydrochloric acid or 0.1 M sodium hydroxide and was measured using a pH meter. The initial adsorbate concentration was fixed at 50 ppm with adsorbent dosage of 1.0 g in 20 mL and solution temperature of 30 °C (Zaira, 2013; Parimalam *et al*., 2011). In order to study the effects of initial concentration on the adsorption uptake, 20 mL of adsorbate solutions with known initial concentrations (10, 20, 30, 40, 50 and 60 ppm) was prepared in a series of 50 mL Erlenmeyer flasks. 1.0 g of adsorbent was placed inside the flask. The flasks were then placed in an isothermal water bath shaker at constant temperature of 30 °C, with agitation speed of 150 rpm (Zaira, 2013). The effect of adsorbent dosage on the adsorption of Ampiclox was studied using a series of adsorption experiments with different adsorption dosages varying from 1.0 to 5.0g (Nsami and Mbadcam, 2013). Contact time was varied between 30 to 180 minutes under neutral conditions with constant amount of sorbent of 1 g, initial concentration of 50 ppm, and shaking speed set at 150 rpm (Yang *et al*., 2009). The effect of solution temperature on the adsorption process was studied by varying the temperature at an interval from 30 to 55 °C by using the temperature control system of the water bath shaker, while other process parameters such as adsorbent dosage, agitation speed, pH and volume of the solution remained constant (Zaira, 2013, Fozia *et al*., 2018).

Adsorption Kinetics

The batch test was conducted in 250 cm^3 conical flasks. 1 g of activated carbon was mixed with 20 mL of 50 ppm concentration of the Ampiclox solution in 6 different flasks for each experimental set. These solutions were shaken in a mechanical shaker for equilibration using an orbital shaker at 200 rpm and allowed to stand for 30, 60, 90, 120, 150 and 180 minutes contact time. Mixtures were filtered using Wattman No. 2 filter paper (Abdulrahaman *et al*., 2009; Itodo *et al*., 2014b). Equilibrium phase Ampiclox concentrations (mg/L) were measured using the UV-VIS Spectrophotometer (Yusuff *et al*., 2017).

Comparative Studies

The comparative studies were done using commercial activated carbon (CAC) as a control experiment for the adsorption studies. Statistical test of significance between the adsorption of Ampiclox onto Okobo coal and CAC adsorbent for different adsorbent dosage was tested using ANOVA (Hussain *et al*., 2013).

Simultaneous determination of concentration in binary mixture

Concentrations of individual antibiotics in Ampiclox (AMP and CLO) were obtained using the simultaneous equation method (equations 9 and 10).

$$C_{AMP} = \frac{(A_2 a_{CLO\,1} - A_1 a_{CLO\,2})}{(a_{AMP\,2} a_{CLO\,1} - a_{AMP\,1} a_{CLO\,2})} \qquad (9)$$

$$C_{CLO} = \frac{(A_1 a_{AMP\,2} - A_2 a_{AMP\,1})}{(a_{AMP\,2} a_{CLO\,1} - a_{AMP\,1} a_{CLO\,2})} \qquad (10)$$

Where A_1 is absorbance of the Ampiclox (AMP) at λ_1 (200 nm), A_2 is absorbance of the Ampiclox (CLO) at λ_2 (205 nm), a_{AMP1} is molar absorptivity of AMP at λ_1 (200 nm), a_{AMP2} is molar absorptivity of AMP at λ_2 (205 nm), a_{CLO1} is molar absorptivity of CLO at λ_1 (200 nm) and a_{CLO2} is molar absorptivity of CLO at λ_2 (205 nm) (Kamal *et al*., 2016).

RESULTS AND DISCUSION

Physico-chemical Parameters of the Activated Okobo Coal

The quality of any given adsorbent is dependent on its physicochemical parameters. A few of the parameters were carried out and the detailed results of the quality of the activated Okobo coal as an adsorbent were obtained. Parameters determined include the following: bulk density (g/cm^3), pH, conductivity (μS/cm), attrition (%) and specific surface area (m^2/g) as presented in Table 1.

Table 1: Physico-chemical Parameters of Activated Okobo Coal Adsorbent

Parameters	Values
Bulk density (g/cm^3)	1.78±0.03
Ph	6.11
Conductivity (µS/cm)	26.80
Attrition (%)	5.44
Specific surface area (m^2/g)	189.40

FTIR Characterization of Okobo Coal

The investigated of Okobo coal adsorbent before (unspent) and after (spent) adsorptions were carried out for the active sites that is, functional groups using FTIR spectrophotometer. The spectral of the analyses are presented in Figure 3a and b. Table 2 shows the comprehensive comparison between observed frequencies obtained before and after adsorption.

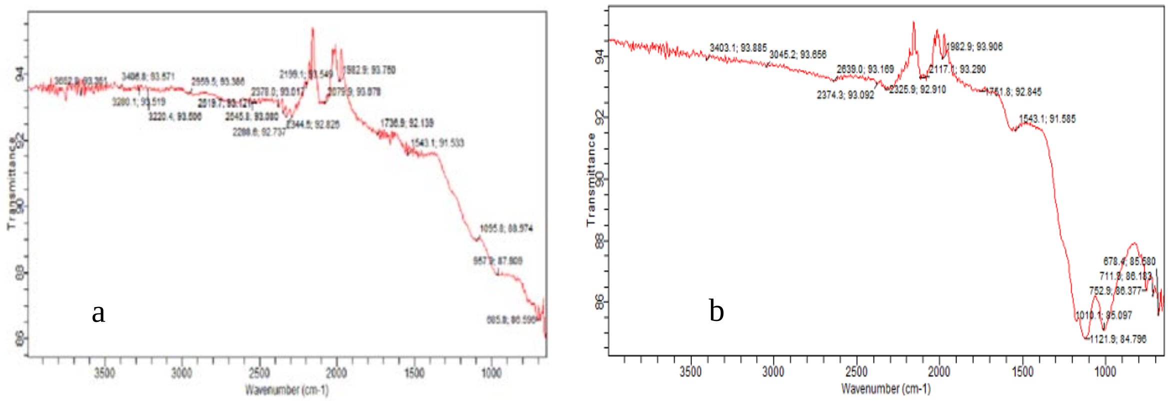

Figure 3: FTIR of the Adsorbent before (a) and after (b) Adsorption of Ampiclox

Table 2: FTIR of the Adsorbent before and after Adsorption of Ampiclox

Vibrational frequency(cm^{-1})	Class of Organic Compound	Observed frequency (cm^{-1})		Functional group
		Before adsorption	After adsorption	
3800 – 3080	Alcohol,		3045.2	O-H
	Amines	3652.8	-	N-H
		3406.8	3403.1	
		3280.1	-	
		3220.4	-	
2950 – 2500	Alkanes	2959.5	2639.0	C-H
		2545.8		
2450 – 2010	Alkynes	2378.0	2374.3	C≡C stretch
		2344.5	2325.9	
		2288.6	2117.1	
		2199.1	-	
		2079.9	-	
2000 – 1680	Alkenes	1982.9	1982.9	=C-H
		1736.9		
1770 – 1750	Acids	-	1751.8	C=O
1660 – 1400	Amides,	1543.1		N-H
	Amines		1543.1	
1390 – 1010		-	1121.9	C-O
			1010.1	
1000 – 680	Alkenes	1095.8	-	=C-H
		957.9	-	
		685.8	-	
< 600 – 840	Aromatics,	-	752.9	C-H
		-	711.9	C-H
	aryl helides	-	678.4	C-Cl stretch

SEM Characterization of Okobo Coal

The morphology of the prepared Okobo coal adsorbent was studied using scanning electron microscope (SEM). Figure 4a and b shows the SEM image of the adsorbent before and after adsorption of Ampiclox as presented.

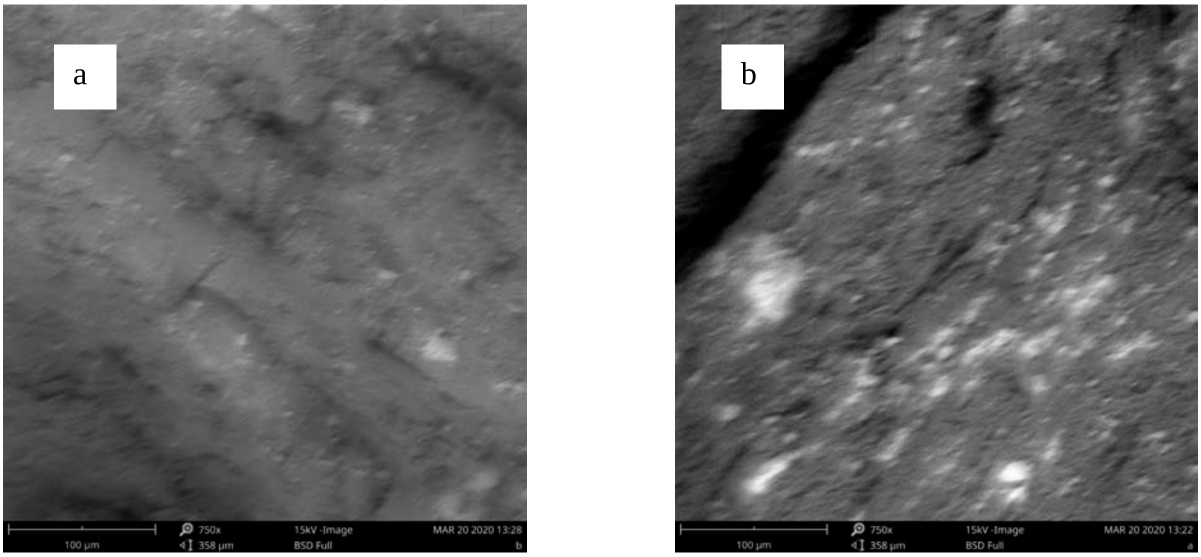

Figure 4: SEM Images of the Adsorbent before (a) and after (b) Adsorption

TGA Analysis of Okobo Coal

The Okobo coal adsorbent was subjected to physical decomposition using thermogravimetric analyzer. Figure 5 present the thermograph of weight % against temperature and the thermograhy of derivative weight % against temperature. The summary of the information obtained from the various decomposition stages is spelled out in Table 3.

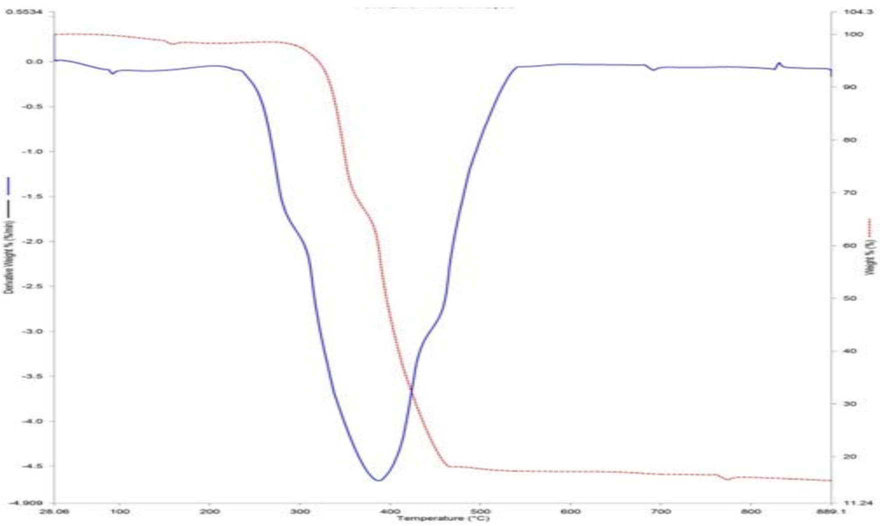

Figure 5: TGA/DTA Thermograph of Okobo Coal

Table 3: The Result of TGA Analysis of Okobo Coal Adsorbent

Temperature (^{0}C)			Total Weight loss (%)
Onset	Midpoint	Endset	
28.07	379.99	886.15	84.54

Batch Adsorption Studies

The effect of parametric factors such as concentration, temperature, contact time, pH and dosage often checked in adsorption studies were considered for the uptake of Ampiclox onto Okobo coal. Commercially activated carbon (CAC) was used as a control experiment. Figures 6 to 11 show the % RE of the Ampiclox under the factors mentioned in that order.

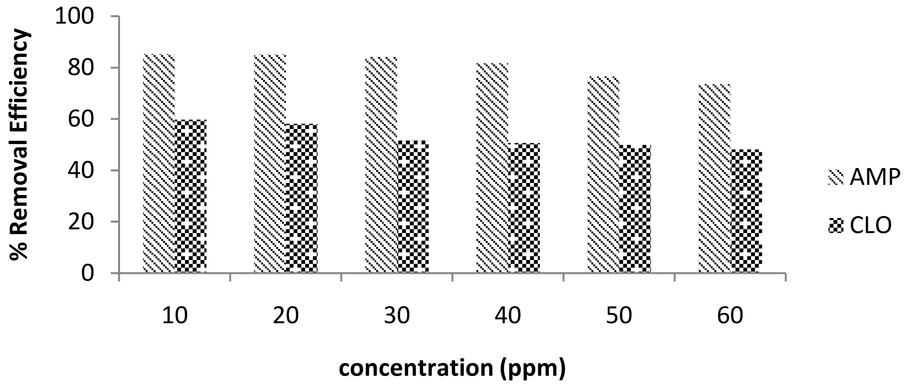

Figure 6: Effect of Concentrations on Removal Efficiency of Ampiclox (AMP and CLO)

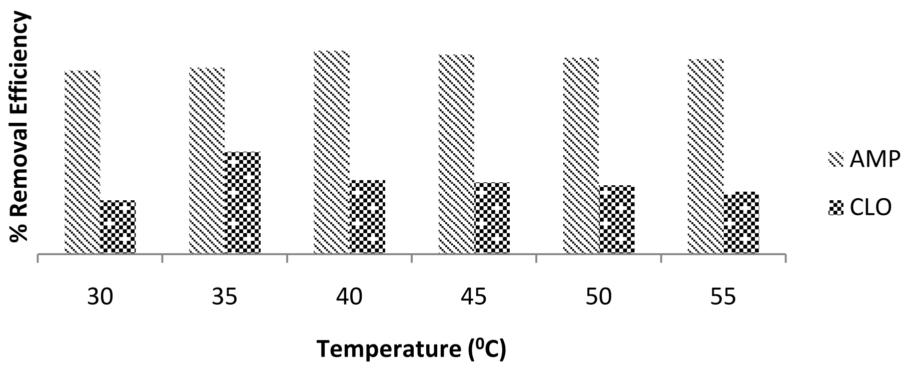

Figure 7: Effect of Temperature on Removal Efficiency of Ampiclox (AMP and CLO)

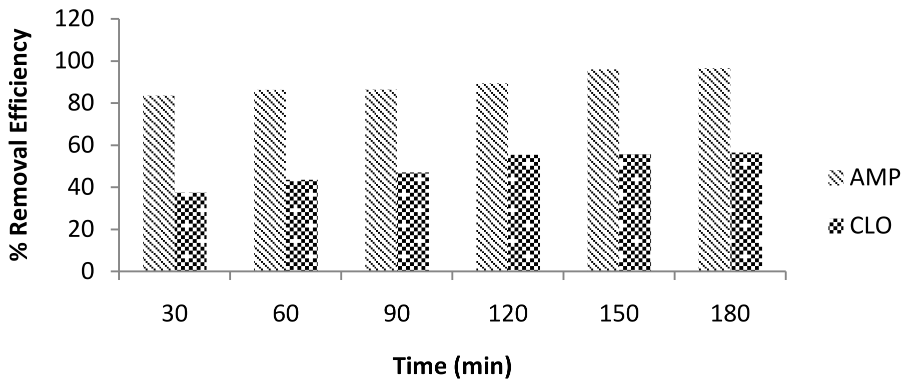

Figure 8: Effect of Time on Removal Efficiency of Ampiclox (AMP) and (CLO)

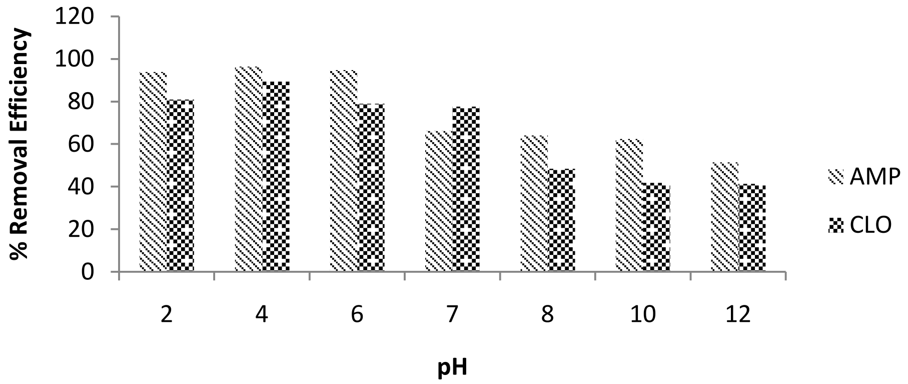

Figure 9: Effect of pH on Removal Efficiency of Ampiclox (AMP) and (CLO)

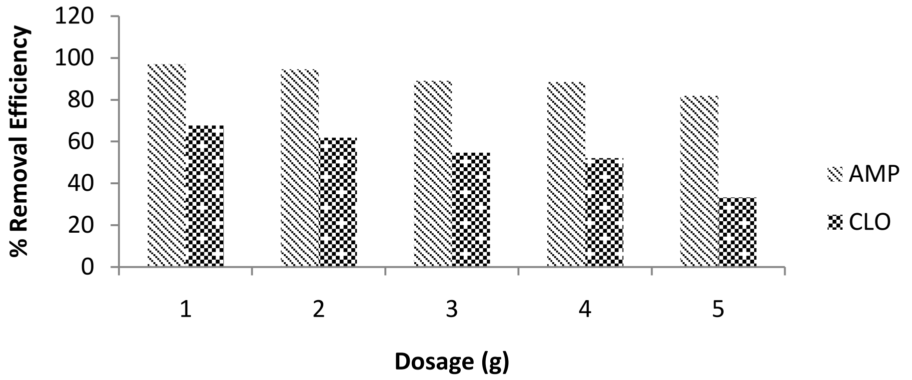

Figure 10: Effect of Dosage on Removal Efficiency of Ampiclox (AMP and CLO) using Okobo Coal

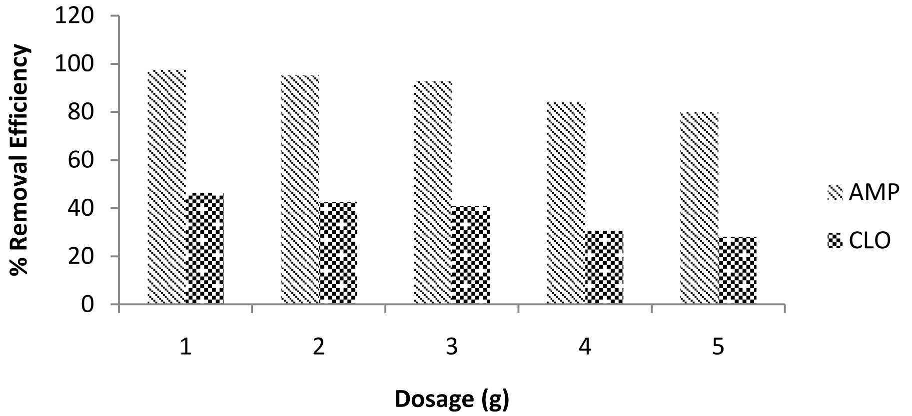

Figure 11: Effect of Dosage on Removal Efficiency of Ampiclox (AMP and CLO) using Commercial Activated Carbon

Isotherm Models

Adsorption is usually described through isotherms, that is, the amount of adsorbate on the adsorbent as a function of its pressure or concentration at constant temperature. The investigated Isotherms were Henry, Langmuir, Freundlich and Temkin as presented in Figure 12 to 15 while the constants and parameters describing the adsorption of the Ampiclox are shown in Table 4.

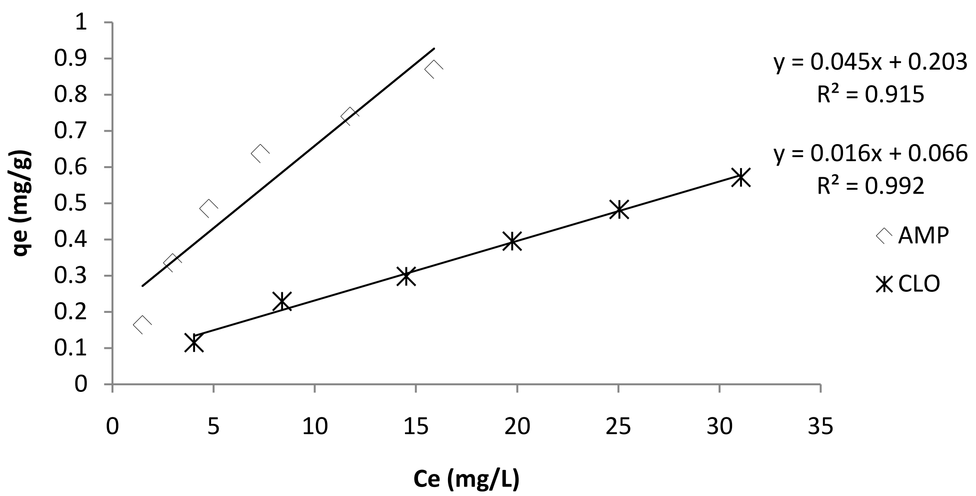

Figure 12: A Plot of Henry Isotherm for Ampiclox (AMP and CLO) Adsorption onto Okobo Coal

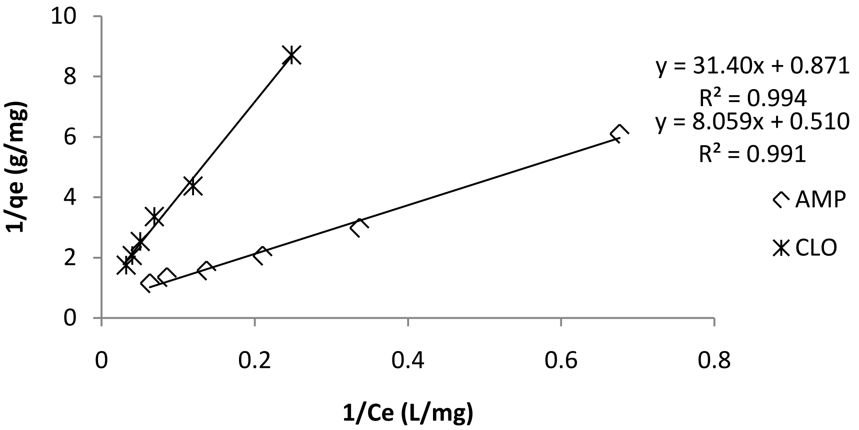

Figure 13: A Plot of Langmuir Isotherm for Ampiclox (AMP and CLO) Adsorption onto Okobo Coal

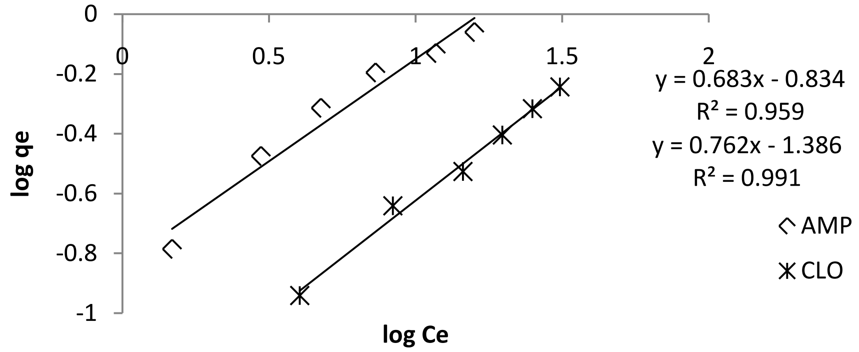

Figure 14: A Plot of Freundlich Isotherm for Ampiclox (AMP and CLO) Adsorption onto Okobo Coal

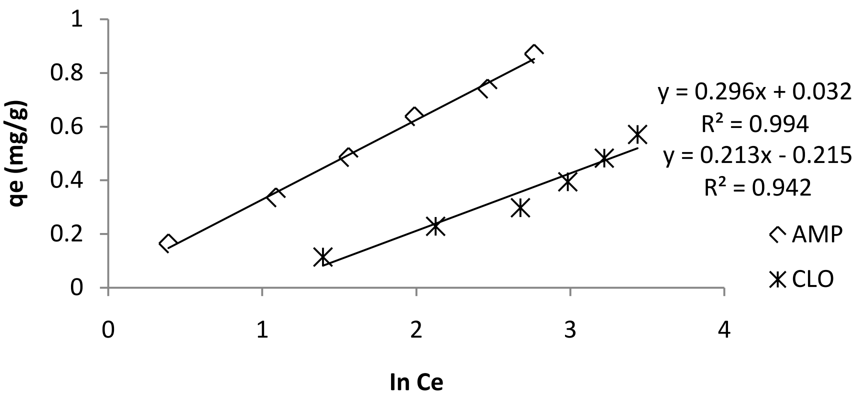

Figure 15: A Plot of Temkin Isotherm for Ampiclox (AMP and CLO) Adsorption onto Okobo Coal

Table 4: Isotherm Experimental Constants and Parameters for the Adsorption of Ampiclox (AMP and CLO) onto Okobo Coal

Isortherm	Constants/Parameters	AMP	CLO
Henry	R^2	0.9150	0.9920
	K_{HE} (L/g)	0.0450	0.0160
Langmuir	R^2	0.9910	0.9940
	Q_o (mg/g)	1.9608	1.1481
	K_L (L/mg)	0.0633	0.0277
Freundlich	R^2	0.9590	0.9910
	1/n	0.6830	0.7620
	K_f (L/mg)	0.1466	0.0411
Temkin	R^2	0.9940	0.9420
	b_T (KJ/mol)	8.3702	11.6318
	A_T (L/g)	1.1142	0.3644

Transport Models

To investigate the mechanism of sorption and potential controlling steps such as mass transport, Intra-particle diffusion transport models are presented on Figure 16 and 17. Meanwhile, the transport models experimental constants are presented in Table 5.

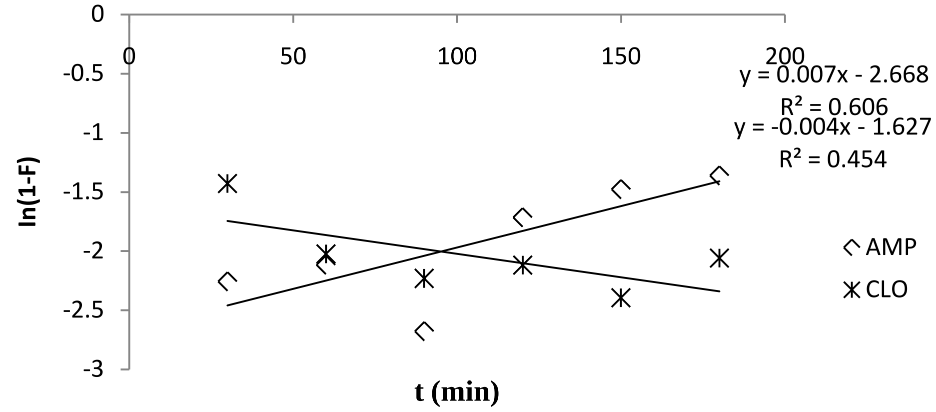

Figure 16: A Plot of Film Diffusion Model for Ampiclox (AMP and CLO) Adsorption onto Okobo Coal

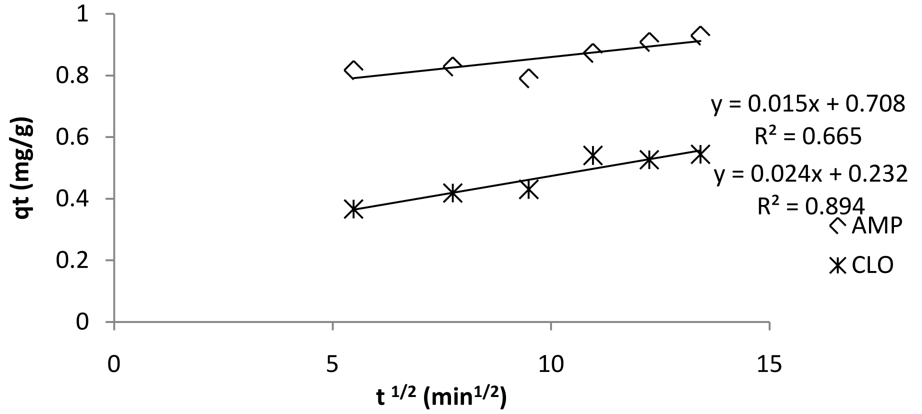

Figure 17: A Plot of Intraparticle Diffusion Model for Ampiclox (AMP and CLO) Adsorption onto Okobo Coal

Table 5: Transport Models Experimental Constants and Parameters for the Adsorption of Ampiclox (AMP and CLO) onto Okobo Coal

Model	Constants/Parameters	Values	
		AMP	CLO
Intra-particle diffusion	R^2	0.6650	0.8940
	K_{ip} (mg/g $min^{0.5}$)	0.0150	0.0240
Film diffusion	R^2	0.6060	0.4540
	K_{fd} ($min^{0.5}$)	-0.0070	0.0040

Table 6: Statistical Comparison between Okobo and CAC for Ampiclox (AMP and CLO) Adsorption at 95 % Confidence Interval

Parameter used	P- Values	
	Ampiclox (AMP)	Ampiclox (CLO)
Dosage	0.2890 (not sig.)	0.0822 (not sig.)

Key: not sig.= not significant

DISCUSSION

Physico-chemical Parameters

The bulk density of the adsorbent was determined to be 1.78±0.03 g/cm^3 as stated in Table 1 above. The bulk density obtained for the Okobo coal is of great potential for adsorption studies since the density is higher than 0.25 g/cm^3 which is minimum requirement for commercial adsorbents. This result is similar to the one obtained in literature for coconut and palm kernel shells (Boadu *et al*., 2018). The pH of the adsorbent was measured to be 6.11 within the range of values that many literatures have reported adsorbent with good adsorption performances. Dada *et al* (2012) reported a range of pH values from 6.30 – 6.50. The value obtained as conductivity for adsorbent was 26.8 µScm^{-1} as presented in Table 1. A low conductivity value (< 28.74 µScm-1) is an indication that there are little ions attached to the adsorbent. The conductivity value for the adsorbent is similar to those obtained by Itodo *et al* (2010b) ranging from 13.9 – 34.05 µScm^{-1}. Another parameter that is important for assessing the suitability of the activated carbon is resistance to attrition. Attrition is the measure of wear or grinding of a substance to smaller particles. The value of the attrition was measured in percent for the adsorbent to be 5.44 % and this shows that the material is good for the adsorption since the wearing tendency is low just as it will not colour the solution during the adsorption process (Louarrat *et al*., 2019). The result of the adsorbent for specific surface area was 189.4 m^{2}g^{-1} as presented in Table 1. This is in line with the results in the literature which range from 143.84 – 671.68 m^2 (Jibril *et al*., 2019).

Instrumental Characterization

FTIR analysis were carried out on the adsorbent before and after adsorption study as shown in Figure 3 and 4. From the result obtained, peaks for the FTIR before adsorption appears to be extended in height as can be seen on the FTIR after adsorption. The appearance of 1751.8 (C=O), 1121.9, 1010.1 (C-O), 678.4 (C-Cl stretch) groups prominent on the adsorbate which were not there before adsorption were seen after adsorption. These changes can only be as a result of a possible adsorption of the ampiclox. The details of the FTIR spectra are shown in Table 2 which also gives an insight on possibility of the adsorbent to take up adsorbate (Ezeokonkwo *et al*., 2018). The morphology and surface structure of the adsorbent before and after the adsorption as shown on Figure 4a and b respectively revealed that there was an adsorption on the adsorbent surface as the morphology before adsorption changed after adsorption experiment. That shows the adsorbate occupied some spaces in the adsorbent hence, the change in morphology. These images taking at the same magnification of 750x, show clearly the difference in morphology which is in agreement with the work by Ezeokonkwo *et al.* (2018). The coal adsorbent prepared was subjected to TGA/DTA analyses as presented in Figure 5. These analyses were carried out to study the extent of the stability of the adsorbent with respect to temperature. The TGA curve shows three degradation steps, having initial weight loss of 2.992 % from 28.07 ^{0}C to 306.07 ^{0}C. This is due to loss of moisture. The decomposition occurred between 306.07 ^{0}C to 484.01 ^{0}C and the burnout temperature was observed between 484.01 ^{0}C to 889.15 ^{0}C for the organic carbon matter. The DTA shows the prominent endothermic peak at 397.99 ^{0}C which implies decomposition of the adsorbent. The Okobo coal adsorbent prepared was thermally stable up to 397.99 ^{0}C (Wuana *et al*., 2019).

Effect of Parametric Factors on Adsorption Studies

The result shows a general increase in the percentage removal efficiency as the concentration of the ampiclox increases from (10 -.60 ppm). At low initial concentrations, the ratio of initial number of Ampiclox molecules to the accessible active sites of adsorbent is low; therefore, the removal efficiency of Ampiclox is higher and at higher concentrations, further residual Ampiclox molecules remain in the aqueous solution. Gorzin and Abadi (2018) reported a similar result for the Adsorption of Cr(VI). Temperature affects equilibrium, rate, spontaneity and randomness of the adsorption processes. An increase in temperature can affect the adsorption process (Zhang *et al*., 2011). In Figure 7 the adsorption of the ampiclox shows highest adsorption of 95.6% and 48.3 % for ampicillin and cloxacillin constituents of the drug and decline steadily. According to the adsorption theory, adsorption decreases with increase in temperature and molecules adsorbed earlier on a surface tend to desorb from the surface at elevated temperatures. The result of this experiment is in line with the above statement right and is in agreement with the work by Chen *et al*. (2011). The effect of time was observed to have increased steadily as the time increases showing more adsorption of Ampiclox (AMP) as compared to (CLO) component of the anti-biotic. According to Wu *et al*. (2015) at initial stages of contact time, adsorption takes place rapidly due to higher adsorbate concentrations leading to existence of stronger mass transfer driving forces. In addition, more uncovered active sites are available. As time passes, adsorption rate decreases gradually. The pH is regarded as an important factor affecting adsorption behavior. The pH of a solution affects the structure of antibiotics. At pH between 2.9 and 7.2 the components of ampiclox (AMP and CLO) shows a zwitterionic structure while at pH above 7.2 an anionic structure emerges as predominant species. This means that ampiclox adsorption is likely to be affected by the increase or decrease in the pH of the solution (Xin *et al.*, 2020). In this experiment, the effect of pH on the removal of ampiclox was determined over a pH range of 2.0 – 12.0. The results of the effect on the percentage removal of the ampiclox were presented in Figure 9. From the results, it was observed that the adsorption appears to be higher at lower pH However it was noted that the adsorption was maximum at pH 4 and lowest at pH 12 in line with the proposed behavior of the adsorbate. This indicated that the adsorption capacity of the activated carbon was pH dependent (Nsami and Mbadcam, 2013). Adsorbent dose had a very profound effect on the ampiclox removal. Adsorption was carried out at varying adsorbent dosage (1.0 - 5.0 g). The results of the effect of dosage are shown in Figure (10 and 11) for the prepared Okobo coal and commercial activated carbon adsorbent respectively. The removal of ampiclox decreases as the dosage of the adsorbent increases and more effective at the wavelength of Ampicillin than Cloxacillin. The result is in agreement with the research by Chen *et al*. (2015) and Uduakobong and Augustine, (2020) which reported that the trend of adsorption capacity with an increase in adsorbent dose was shown to be as follows: initially increasing, reaching a maximum value and finally decreasing. The initial increase in adsorption capacity can be due to the fact that increasing adsorbent dose resulted in availability of more active sites. Meanwhile the descending trend of adsorption capacity at a higher range of adsorbent dose was attributed to active sites overlapping and adsorbent partial aggregation.

Adsorption Isotherm Studies

The result of Henry isotherm is presented in Figure 12 and Table 4. The plot shows R^2 value for the adsorption of Ampiclox (AMP) 0.915 and (CLO) 0.992. These values indicate good applicability since R^2 values are > 0.9. The parameter K_H estimated as 0.045, 0.016 for AMP, CLO respectively is the Henry's adsorption binding constant of the adsorbate on the adsorbent surface. The constant indicates the adsorbate affinity toward a solid surface. The data fits the model and agrees favourable with research by Deocaris and de Osio, (2020).

Langmuir isotherm has a wide application in lots of pollutants sorption process. In the Table 4, R^2 for Ampiclox (AMP and CLO) adsorption is 0.991 and 0.994 which shows a good applicability of the model. This indicates a homogenous surface condition of the adsorbent, having affinity to adsorbate molecule (Vinodhini and Das, 2010). The essential features of Langmiur adsorption isotherm can be expressed in terms of a dimensionless constant called separation factor on equlibrium parameter (K_L) (Agarwal *et al*., 2016). The diagnostic criterion about the shape of the isotherm is as follows: K_L >1, unfavourable isotherm, K_L = 1, linear isotherm, 0< K_L <1, favourable isotherm and K_L = 0, irreversible isotherm. Table 4 for Adsorption of Ampiclox onto Okobo Coal shows that the value of K_L for AMP is = 0.0633 and that of CLO is = 0.0277. In the present investigation, adsorption of Ampiclox (AMP and CLO) on adsorbent is favourable (0< K_L <1, favourable isotherm).

The Freundlich Isotherm assumes a multilayer adsorption occurring on heterogeneous surface of adsorbents with sites that have different energies of sorption (Mulu, 2013). The results as presented in Table 4 shows Freundlich Isotherm parameters calculated from the analysis. The R^2 value of Ampiclox (AMP = 0.9590 while CLO = 0.9910). The R^2 values above 0.9 indicate that the isotherm data followed Freundlich Isotherm. The values of 1/n for Ampiclox (AMP = 0.6830 while CLO = 0.7620). The 1/n indicates favourable sorption when 0.1<1/n<1 (Mulu, 2013). The 1/n values imply that the adsorption was favourable and the data fits the model.

The results as presented in Table 4 showed Temkin Isotherm constants calculated from the analysis. The R^2 value of Ampiclox (AMP = 0.9940 while CLO = 0.9420). The R^2 > 0.9 and above shows there was a good correlation which implies good applicability of Temkin Isotherm.

The b_T is a constant related to heat of adsorption, where a high value indicate strong interaction between adsorbate and the adsorbent. From the result, the constant b_T was observed to be significant for Ampiclox (AMP = 8.3702 KJ/mol while CLO = 11.6318 KJ/mol). The result shows that the adsorption process was purely endothermic reaction (hence the positive values of b_T) (Ghogomu *et al*., 2013). The high energy involve in the process indicates suitability of the isotherm at the set conditions.

Transport models

The liquid film diffusion model plotted for Ampiclox (AMP and CLO) as presented in Figure 16 has (R^2) values for Ampiclox (AMP = 0.606 and CLO = 0.454). This is low suggesting that the film diffusion is not the rate determining factor in the adsorption process. This model describes the movement of adsorbate across the external liquid film to external surface sites on the adsorbent particles. Table 5 shows R^2 values of Ampiclox (AMP and CLO) as 0.665 and 0.894 for intraparticle diffusion model. This could indicate that film and intraparticle diffusion model is not the only rate determining step since the straight line did not pass through the origin and the intercept is greater than zero (Balarak *et al* 2017; Itodo *et al*., 2010a).

Statistical Analysis at 95 % Confidence Interval

From the analyses performed, Table 6 compared Okobo coal and CAC adsorption of Ampiclox (AMP and CLO) to see if the adsorption was statistically different or not. The P-values of the antibiotics indicate that there is no significant difference between Okobo coal and CAC for the adsorption of Ampiclox (AMP and CLO) given that all the p- values for the comparison were above p- value (0.05).

CONCLUSION

This study applied the simultaneous equation method for the adsorptive treatment of Ampiclox (Ampicillin and Cloxacillin) using Okobo coal. The adsorbent prepared was subjected to both classical and instrumental techniques; the results indicate that the adsorbent was good for adsorption process. In addition, the parameters of the adsorption process were optimized with the variation in values of concentration, temperature, contact time, pH and dosage. From the optimized data of the effect study, the isotherm, kinetic and transport studies were carried out using the appropriate models. The studies were successfully carried out and the results obtained as discussed earlier are not different to other adsorbents reported in literatures giving that Okobo coal compared favourably with the commercial activated carbon (CAC) for the adsorption of Ampiclox as can be seen for their application for the effect of dosage and T-Test analyses.

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