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Coal Dissolution Kinetics and its Potentials in the Aqueous Phase Abatement of Antibiotics from Binary Solution

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Abstract
Adsorption and dissolution kinetics were carried out to assess the performance of Okobo coal for the sorptive treatment of the solution of Ampiclox as well as the ability of the adsorbent to withstand dissolution using analytical techniques. The Okobo coal adsorbent was activated by impregnating it with 1M H_3PO_4. Batch adsorption method was adapted for the adsorption kinetics while gravimetric method was used for the dissolution kinetics of the coal in Acid and Base. The Attrition of the adsorbent was (5.4 %), conductivity (26 μS/cm**)**, pH (6.11), Bulk density (1.78±0.03 g/cm^3), specific surface area (189.4 m^2/g**)** and Iodine number (1235.79 mg/g). All these values were similar to other activated carbon adsorbents worked with in literatures. The FTIR shows clear peaks after adsorption indicating the presence of new bonds which were coming from the adsorbate. For the kinetic models plotted only the Second order kinetic model describe best the adsorption of the Ampiclox onto Okobo coal. The Second order model's R^2 value for the adsorption of Ampiclox (AMP) was 0.9910 while (CLO) was 0.9810. The dissolution model were also applied for the dissolution kinetic study of the Okobo coal and all showed a poor data fitting of dissolution of the adsorbent except for the Second order model which showed some levels of applicability with R^2 values above 0.6. The statistical analyses obtained indicated that there was no statistical difference between the adsorption of Ampiclox by Okobo coal adsorbent and CAC while for the dissolution studies clear difference exist between the dissolution of adsorbent in 0.1 M HCl and H_2O, 0.1 M NaOH and H_2O but not 0.1 M HCl and 0.1 M NaOH. Therefore, it can be concluded that the adsorbent prepared is a potential adsorbent for antibiotic remover or detoxification.
Keywords: Antibiotics, Adsorption, Ampiclox, Okobo, Dissolution kinetics, Binary Solution, Coal

Introduction

Antibiotics are unique among medicines in that they act selectively on bacteria, among them the pathogens, while leaving human cells and tissues unaffected [1]. There are over 250 different antibiotic entities registered for use in human and veterinary medicine. Most of these substances have a microbial origin, but they can also be semi-synthetic or totally synthetic. Antibiotics are the potent medicines that have been used for several decades in both human and animals, for therapeutic treatment of infections related diseases and for protecting their health [2]. Particular concerns are that antibiotic residues in the environment can induce antibiotic resistant genes (ARGs) from extended exposure at relatively low concentrations [3]. The past and ongoing usage of antibiotics produces significant residues which are directly or indirectly introduced into the aquatic and terrestrial environments [4], and report has it that residues of human and veterinary antibiotics have been detected in many different matrices [2]. Antibiotics have different half-lives in the environment, some are highly persistent and therefore their contamination levels in the environment have been increasing. A study by [5] showed significant impacts that exposure to antibiotics (μg/L - mg/L) may cause on aquatic organisms their survival, growth and body weight. The release of antibiotics into the natural water bodies mainly comes from the effluents of municipal sewage treatment plants (STPs) and pharmaceutical manufacturing plants. As reviewed by [6] urban wastewater treatment plants are likely to be hotspots for the release of antibiotics and ARGs in the natural environment [7]. Thus pharmaceutical chemicals especially antibiotics are gaining the recognition of emerging environmental contaminants as being classified as recalcitrant bio-accumulative compounds [8], hence antibiotics are regarded as toxic and hazardous chemicals [2]. Before discharging wastewater into the environment it is highly important for antibiotic residues such as Ampiclox (ampicillin and cloxacillin) as used in this research (figure 1) to be removed but it usually involves high cost [9].

Adsorption is the most convenient and effective technique to remove organic compounds (antibiotics inclusive) [10]. Coal is a complex porous medium and natural adsorbent. After adsorption, the coal may be used in its original purpose and its value not reduced [11].

Since coal is advantageous in the removal of antibiotics in the sense that it can be reused after regeneration. 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 its intense usage.

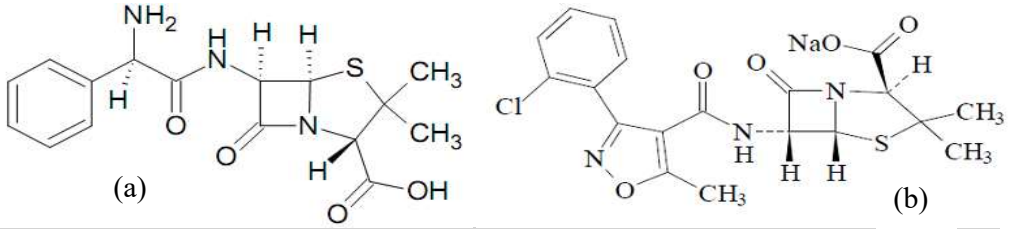

Figure 1: (a) and (b) Shows Structural Formula of Ampicillin and Cloxacillin Sodium Respectively [12].

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

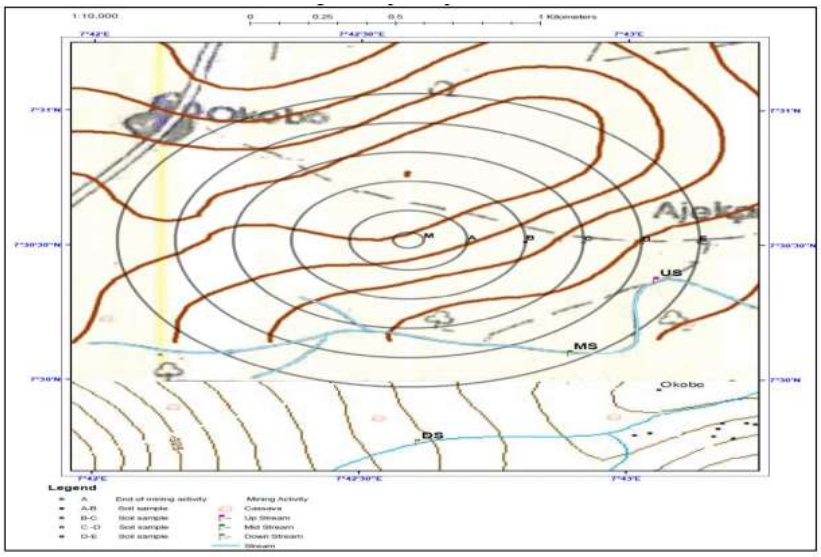

Figure 2: Map of Study Area and Sample Location [13]

Methods

Sample collection and treatment

A method of coal collection by [14] was carefully followed with slight changes. 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 [15,16].

The stock solutions of ampiclox (ampicilin trihydrate/cloxacillin sodium) was obtained by dissolving 1 g of ampiclox in distilled water in a 1000 mL standard flask and made up to mark. The solution was then diluted to desired working concentrations with distilled water and stored at room temperature. The standard solutions were prepared by using these equations.

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

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

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 [17].

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 ^0C 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 [16,18].

Pyhsico-chemical parameters

The method used previously by researchers was followed for each parameter. The bulk density [18], pH [19,20], conductivity [19,20], attrition or hardness [21] and porocity/surface area [22]

Instrumental characterization of Okobo coal adsorbent

The adsorbent prepared was monitored using FTIR Spectrophotometer in the wave number range of 4000–400 cm^{-1} [23,24]. The morphology of the prepared adsorbent was studied by using scanning electron microscope (SEM) [16]. Thermogravimetric Analyzer (TGA) was used to analyze the moisture content, volatile matter, fixed carbon and ash contents in adsorbent from coal sample [25].

Dissolution studies (gravimetry)

A 1 g amount of coal modified adsorbent was added to the 5 reactor vessel containing 100 mL 0.1 M acid and 0.1 M base separately. Other factors were kept constant at stirring speed of 200 rpm for 1, 2, 3, 4 and 5 hours. This was done using a temperature controlled magnetic stirrer. The sample was removed, filtered and dried in the oven and weighed till constant weight was obtained [26].

Adsorption studies

Batch experiments were carried out to determine the adsorption kinetics 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. The mixture was then filtered using whatman 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 was calculated as

$$q_e = \frac{(C_o - C_e)}{m} \times V \quad (3)$$

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 the equation

$$RE\ \% = \frac{(C_o - C_e)}{C_o} \times 100 \quad (4)$$

Where C_o and C_e is the initial and equilibrium concentration (mg/L) respectively [27]

Effect of parametric factors

The effect of solution pH was monitored by changing the initial pH of the solution to 2, 4, 6, 7, 8, 10 and 12. See method by [28] and [23]. The effects of initial concentration on the adsorption uptake, was carried out with known initial concentrations (10 to 60 ppm) following method by [28]. The effect of adsorbent dosage was studied as well using a series of adsorption experiments with different adsorption dosages varying from 1.0 to 5.0 g [29]. Contact time was varied from 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 [30]. The effect of solution temperature on the adsorption process was studied by varying the adsorption temperature between 30 to 55 °C. See method by [28] and [31].

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 filter paper [18]. Equilibrium phase Ampiclox concentrations (mg/L) were measured using the UV-VIS Spectrophotometer [32]

Statistical test of significance

Statistically, the relation between the adsorption of Ampiclox onto Okobo coal and CAC adsorbent for different adsorbent dosage was tested. The dissolution of Okobo coal adsorbent in Acid and water, Base and water as well as Acid and Base was compared to see if there was significant difference between one medium to the other using **SPSS** at 95% confidence interval [33].

Results and Discussion

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

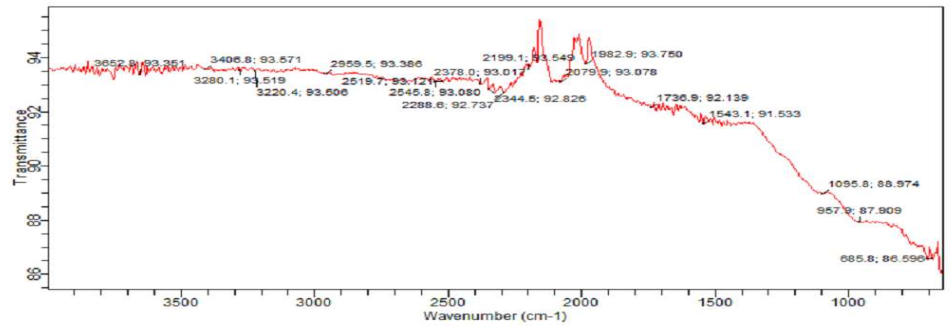

Figure 3: FTIR Spectrum of the Adsorbent before Adsorption of Ampiclo [34]

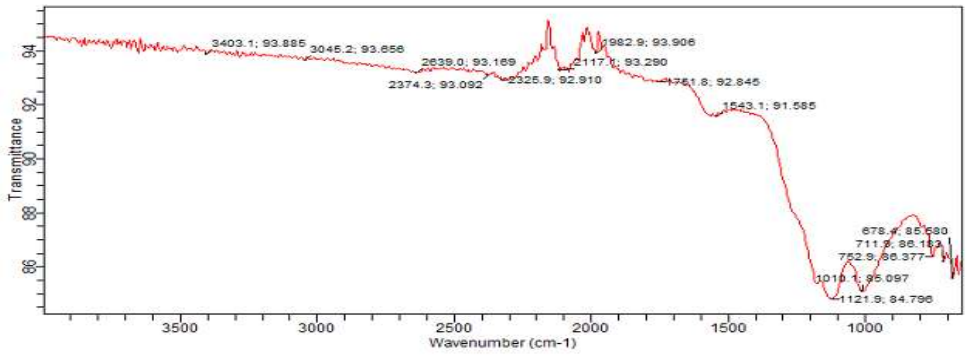

Figure 4: FTIR Spectrum of the Adsorbent after Adsorption of Ampiclox [34]

Table 2: FTIR Data of the Adsorbent before and after Adsorption of Ampiclox [34]

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

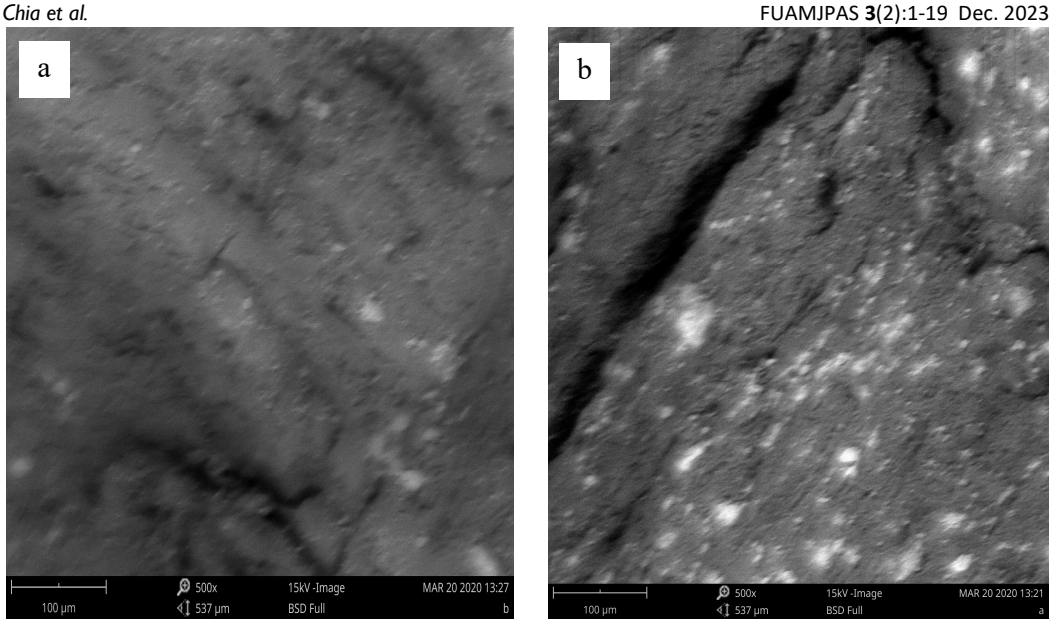

Fig 5: SEM Images of the Adsorbent before (a) and after (b) Adsorption

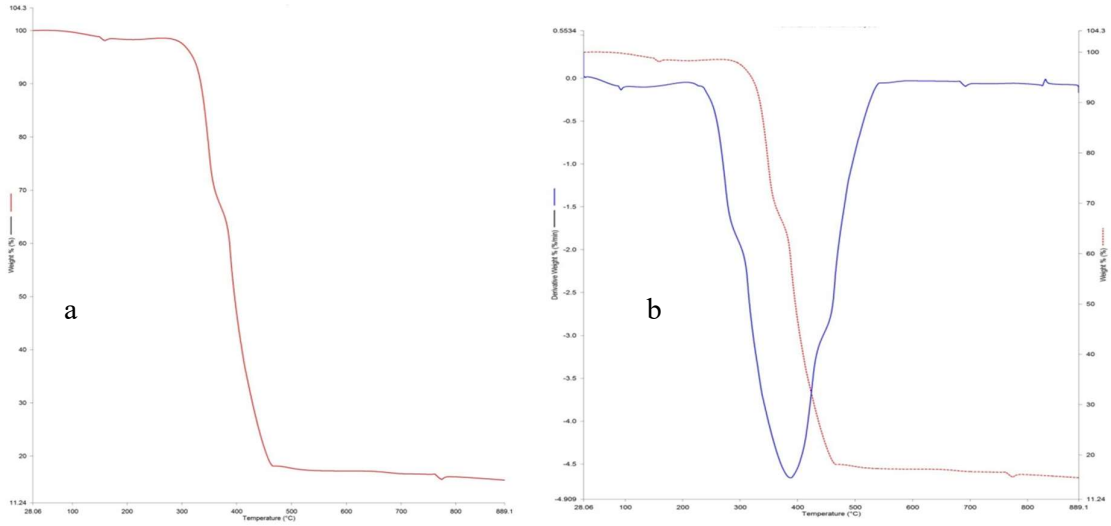

Figure 6: (a) TGA and (b) Thermographs of Okobo Coal

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

Temperature (°C)			Total Weight loss (%)
Onset	Midpoint	Endset	
28.07	379.99	886.15	84.54

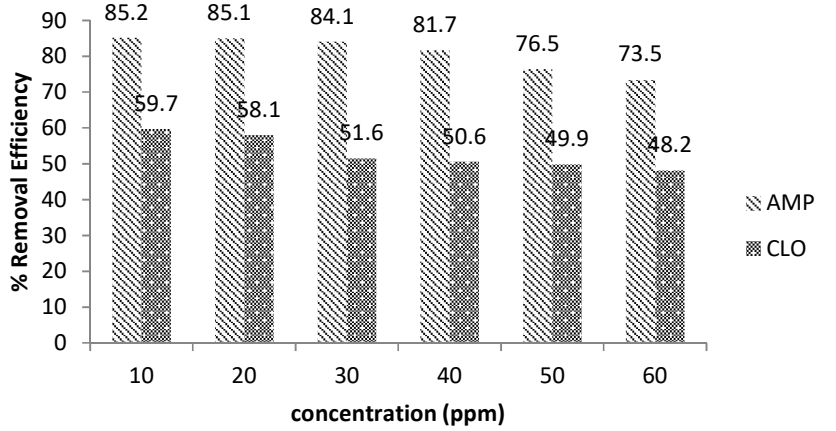

Figure 7: Effect of Concentrations on Removal Efficiency of Ampiclox (AMP and CLO)

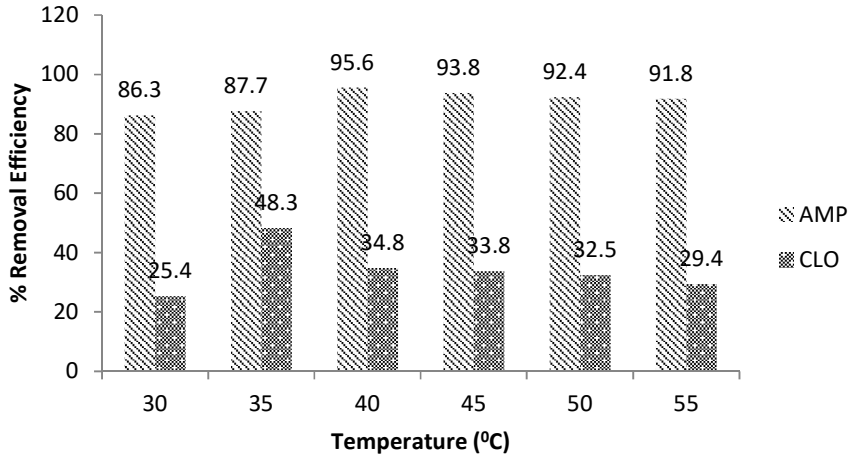

Figure 8: Effect of Temperature on Removal Efficiency of Ampiclox (AMP and CLO)

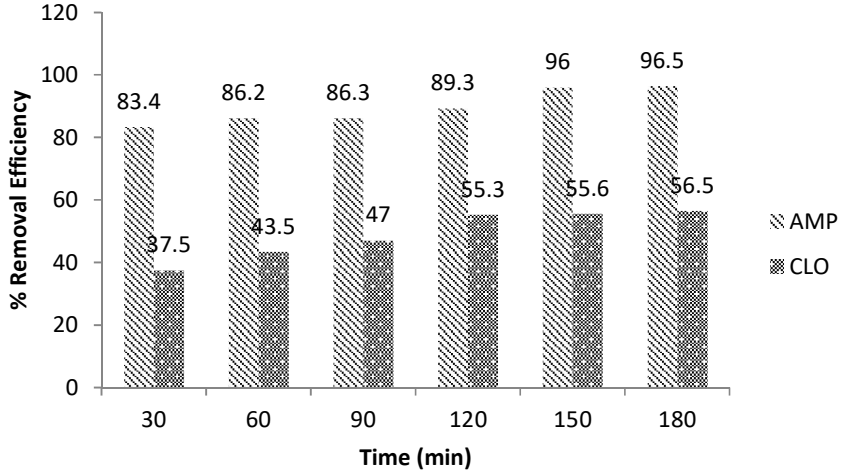

Figure 9: Effect of Time on Removal Efficiency of Ampiclox (AMP) and (CLO)

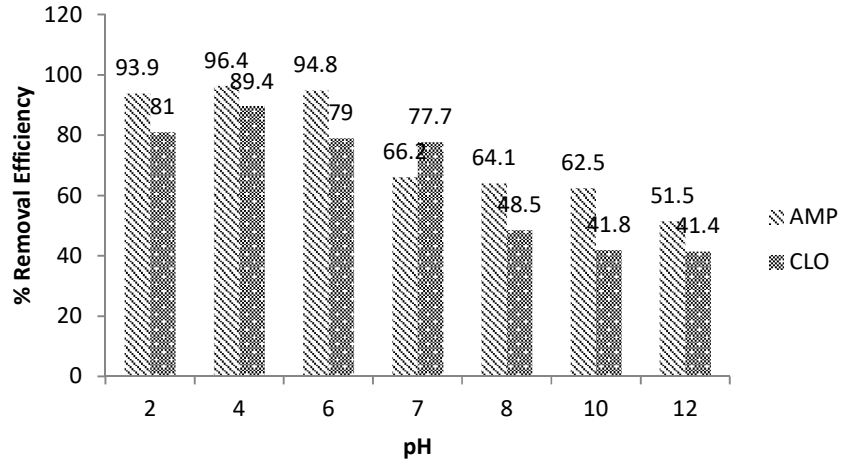

Figure 10: Effect of pH on Removal Efficiency of Ampiclox (AMP) and (CLO)

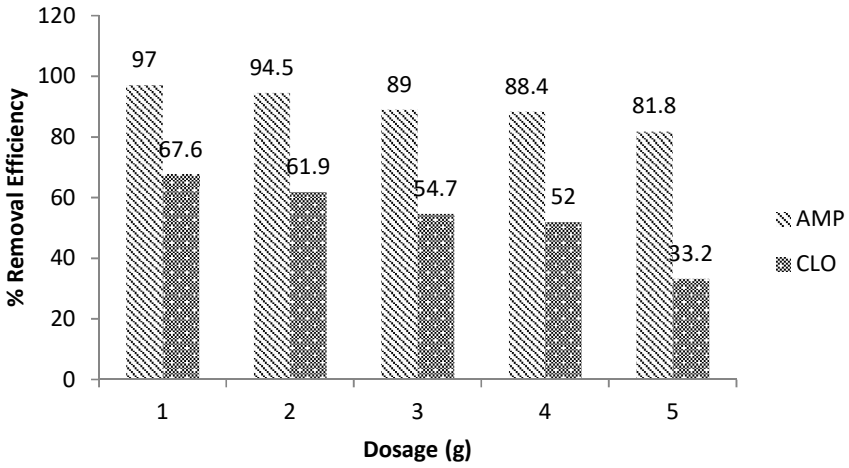

Figure 11: Effect of Dosage on Removal Efficiency of Ampiclox (AMP and CLO) using Okobo Coal

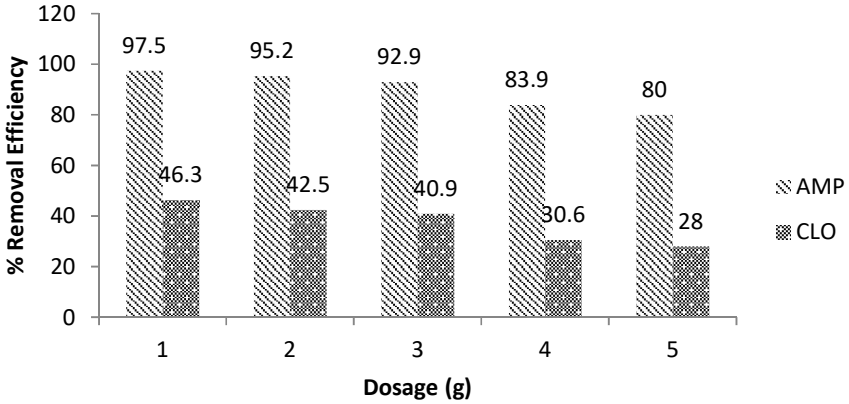

Figure 12: Effect of Dosage on Removal Efficiency of Ampiclox (AMP and CLO) using Commercial Activated Carbon

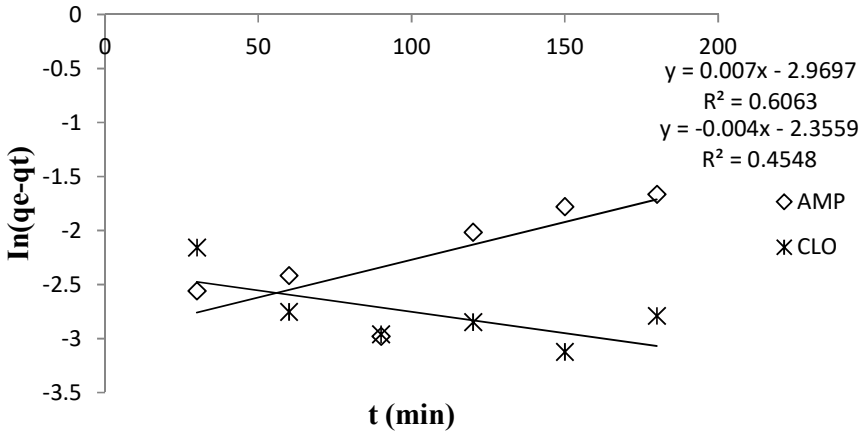

Figure 13: A Plot of Pseudo-first Order Kinetics Model for Ampiclox (AMP and CLO) Adsorption onto Okobo Coal

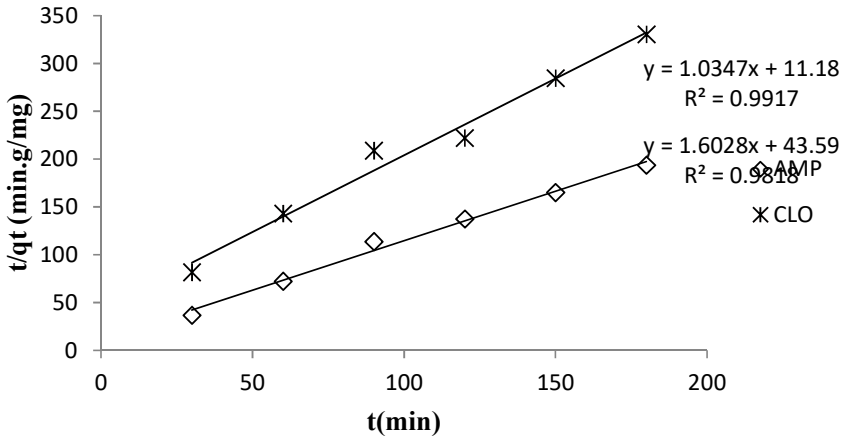

Figure 14: A Plot of Pseudo-second Order Kinetics Model for Ampiclox (AMP and CLO) Adsorption onto Okobo Coal.

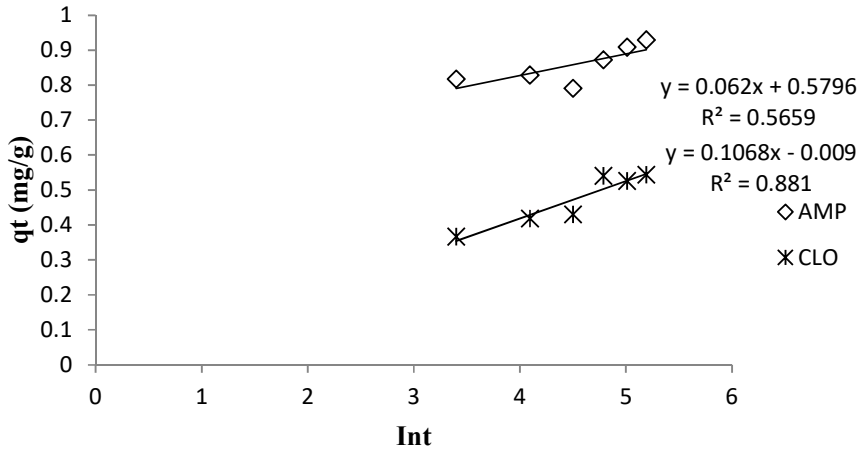

Figure 15: A Plot of Elovich Kinetics Model for Ampiclox (AMP and CLO) Adsorption onto Okobo Coal.

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

Isortherm	Constants/ Parameters	Values	
		AMP	**CLO**
Pseudo-first order	R^2	0.6060	0.4540
	K_1 (g/mg.min)	-0.0070	0.0040
	q_e exp (mg/g)	0.8293	0.4189
	q_e cal (mg/g)	0.0011	0.0044
	% SES	0.3381	0.1692
Pseudo-second order	R^2	0.9910	0.9810
	K_2 (mg/g.min)	0.0956	0.0589
	q_e exp (mg/g)	0.8293	0.4189
	q_e cal (mg/g)	0.9665	0.6239
	% SES	0.0560	0.0837
Elovich	R^2	0.5650	0.8810
	β (g.min/mg)	16.1290	9.4340
	α (gmin2/mg)	28.7461	0.9629

Key: AMP=ampicillin and CLO=cloxacillin (Ampiclox)

Table 5: The Dissolution of Coal Adsorbent in Different Media; Acid and Base using Water as a Control

Medium	Weight of adsorbent at different times														
	60 s			120 s			180 s			240 s			300 s		
	W_i	W_f	W_d	W_i	W_f	W_d	W_i	W_f	W_d	W_i	W_f	W_d	W_i	W_f	W_d
Acid	**1.0026**	0.9477	0.0549	**1.0086**	0.9527	0.0557	**1.0043**	0.9483	0.0561	**1.0045**	0.9433	0.0612	**1.0050**	0.9473	0.0577
Base	**1.0033**	0.9460	0.0573	**1.0050**	0.9601	0.0449	**1.0100**	0.9275	0.0822	**1.0110**	0.9201	0.0909	**1.0035**	0.9377	0.0658
Distil Water	**1.0059**	1.0039	0.0020	**1.0040**	0.9951	0.0089	**1.0059**	1.0010	0.0049	**1.0036**	0.9971	0.0065	**1.0034**	0.9985	0.0049

Key: W_i = initial weight of coal, W_f = final weight of coal and W_d = difference in weight of coal

Table 6: Percentage Dissolution of Adsorbent in Different Media; Acid and Base using Water as a Control

Medium	% Dissolution values at different Time				
	60s	120s	180s	240s	300s
Acid	5.4758	5.5225	5.586	6.0926	5.7413
Base	5.7112	4.4677	8.1386	8.9911	6.5571
Distil water	0.1988	0.8865	0.4871	0.6477	0.4883

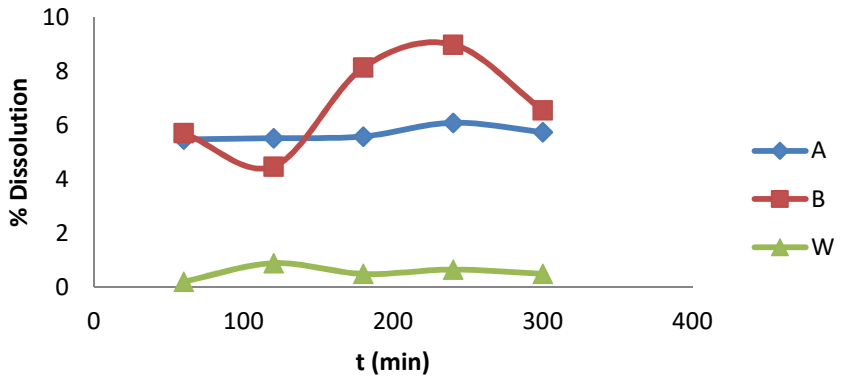

Figure 16: Dissolution Profile of Okobo Coal in HCl (A) and NaOH (B) using H_2O (W) as Control

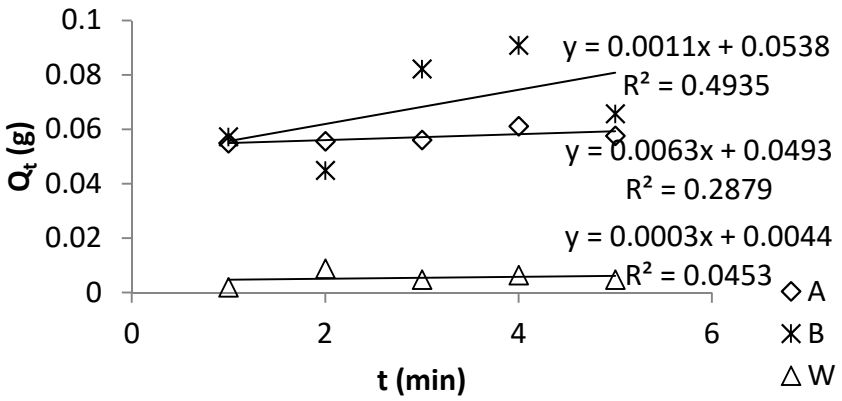

Figure 17: A Plot of Zero Order Dissolution Model for Adsorbent in Acid (A), Base (B) and Water (W).

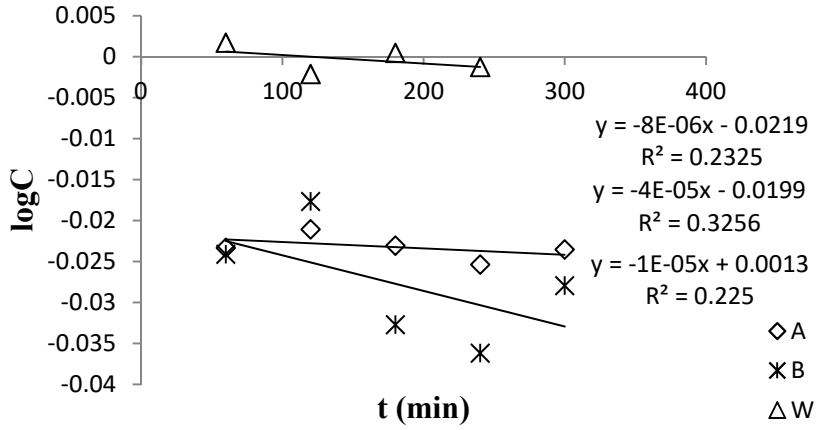

Figure 18: A Plot of First Order Dissolution Model for Adsorbent in Acid (A), Base (B) and Water (W).

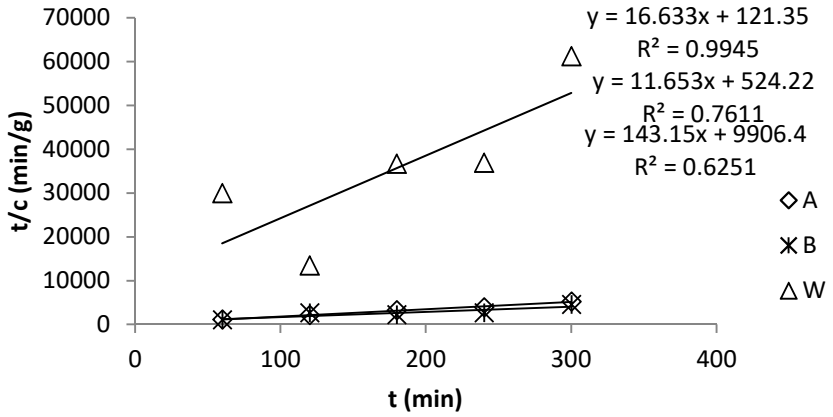

Figure 19: A Plot of Second Order Model Dissolution for Okobo Coal in Acid (A) and Base (B) using Water (W) as Control

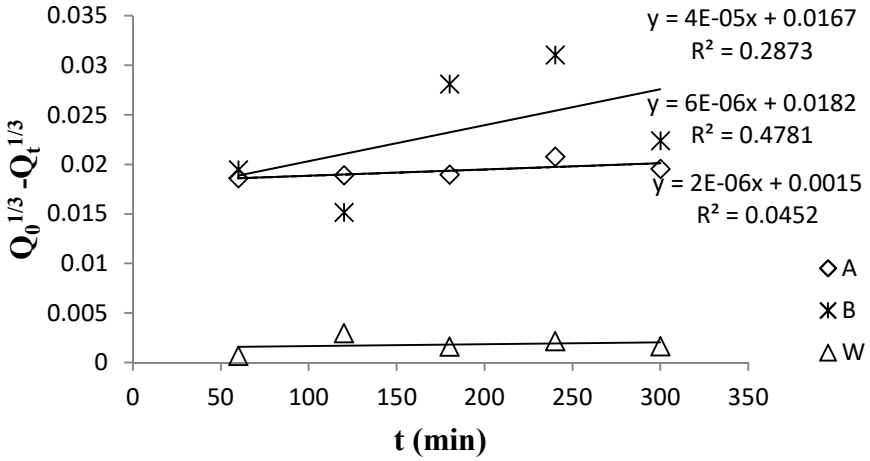

Figure 20: A Plot of Hixson-Crowell Cube Root Law for Adsorbent in Acid (A), Base (B) and Water (W).

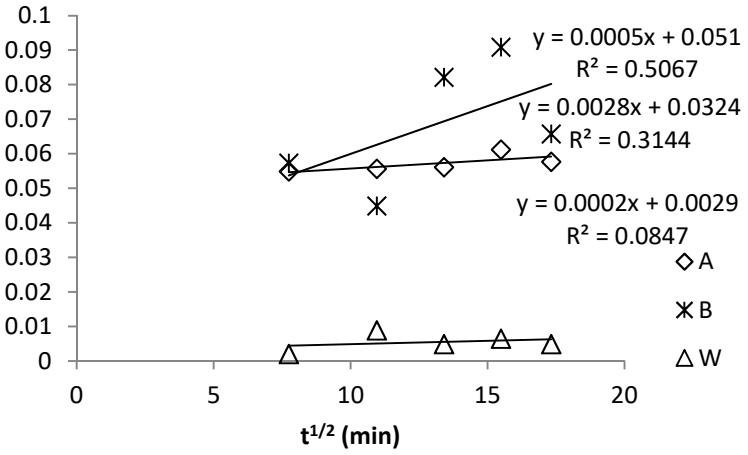

Figure21: A Plot of Higuchi Model for Adsorbent in Acid (A), Base (B) and Water (W)

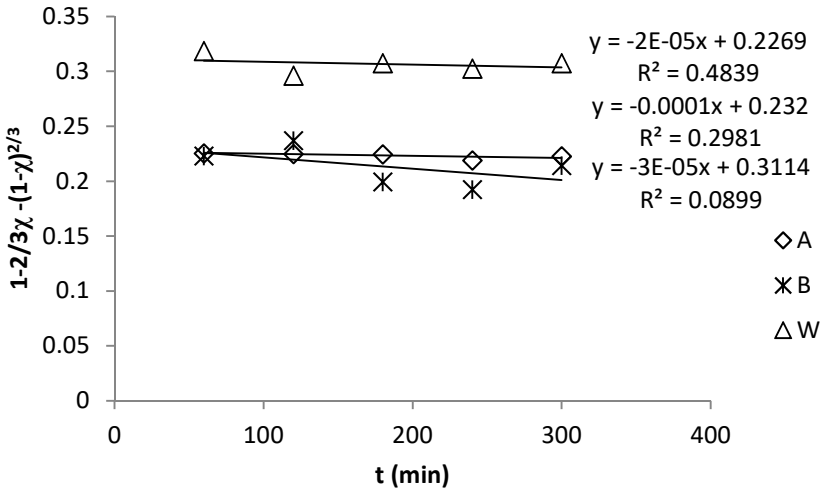

Figure 22: A Plot of Shrinking Core Model Dissolution for Okobo Coal in Acid (A) and Base (B) using Water (W) as Control

Table 7: Experimental Constants and Parameters for the dissolution of Okobo Coal

Dissolution models	Constants	Values		
		Acid	**Base**	**Water**
Zero order	R^2	0.4935	0.2879	0.0453
	k_o	2E-05	0.0001	6E-06
First order	R^2	0.2325	0.3256	0.2250
	k_1	2E-05	9E-05	2E-05
Second order	R^2	0.9940	0.7610	0.6250
	k_2	2.2799	0.2589	2.0672
	C_s (L/g)	0.0601	0.0858	0.0070
Hixson-crowell	R^2	0.4781	0.2873	0.0452
	K_{HC}	6E-06	4E-05	2E-06
Higuchi	R^2	0.5067	0.3144	0.0847
	K_H	0.0005	0.0028	0.0002
Shrinking Core	R^2	0.4830	0.2980	0.0890
	k_{SC}	-2E-05	-0.0000	-3E-05
	D	-4.0679E-04	-0.0000	-8.6542E-03

Key: A=Acid, B=Base and W=Wate

Table 8: 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

Table 9: Statistical Comparison between Acid and Water, Base and Water, Acid and Base for the Dissolution of Okobo Coal

Experiment	P- Values		
	Acid – Water	Base – Water	Acid – Base
Dissolution	3.0867E-06 (sig.)	0.0017 (sig.)	0.2126 (not sig.)

Key: sig.= significant, not sig.= not significant

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. 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 [35]. 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. [22] 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 [36] 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 [21]. The result of the adsorbent for specific surface area was 189.4 m^2g^{-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 [37].

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 [16]. The morphology and surface structure of the adsorbent before and after the adsorption as shown on Figure 5a 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 [16]. The coal adsorbent prepared was subjected to TGA and TGA/DTA analyses as presented in Figure 6a and b. 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 [38].

Effect of parametric factors

The result on Figure 7 shows a general increase in the percentage removal efficiency as the concentration of the ampiclox increases from (10 -.60 ppm). The highest percentage removal was 85.2 % for the Ampiclox (AMP) component while for (CLO) it was 59.7 %. 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. [39] 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 [40]. The result for the effect of temperature is presented in Figure 8. According to the adsorption theory, adsorption decreases with increase in temperature and molecules adsorbed earlier on a surface tend to desorbed from the surface at elevated temperatures. The result of this experiment is in agreement with the work by [41]. 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. Figure 9 presented the data on a bar chat. According to [42] 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 ampiclox 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 [43]. 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 10. 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 [29]. Adsorption was carried out at varying adsorbent dosage (1.0 - 5.0 g). The results of the effect of dosage are shown in Figure (11 and 12) 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 [44] and [45] reported that increase in adsorbent dose initially increase adsorption capacity, 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 kinetics

Adsorption via mass transfer from liquid phase to the adsorbent surface is physiochemical process [46]. The study of adsorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. [47] inferred that a kinetic model helps in the study of adsorption rate and predict information about adsorbent to adsorbate interaction (physiosorption or chemisorptions). Pseudo first-order kinetics, pseudo second-order kinetics and Elovich were employed for adsorption kinetic behavior of the adsorbates on the adsorbent. The accepted kinetic model for a given adsorption is based on three fundamental validity test; A good and high correlation coefficient (R^2) indicating the applicability and reliability of a given model, a

close agreement between the calculated and experimental q_e values and the accepted model must have the least values for the sum of error squares (%SES), determined using equation below [48].

$$\%SES = \sqrt{\sum \frac{(q_e exp - q_e cal)^2}{N}} \quad (5)$$

Going by the three points highlighted as validity test for a kinetic model to be accepted, the coefficient of regression for the pseudo-second order model suggested the applicability of the kinetic model to describe the adsorption processe of Ampiclox (AMP and CLO) uptake on the adsorbent. Table 4 clearly shows that the kinetics of the adsorption is pseudo-second order kinetics as R^2 for Ampiclox (AMP and CLO) is 0.9910 and 0.9810 respectively [49]. Further consideration to the qe_{exp} for Ampiclox (AMP and CLO) is 0.8293 and 0.4189 while qe_{cal} is 0.9665 and 0.6239 in the same order as in the former. The qe exp and qe cal values are much more closer which implies that the adsorption follows the pseudo second order.

Dissolution profile

The dissolution profile plots for % dissolution against t presented in Figure 16 shows a rather slow and steady release of coal sample in Acid as well as control medium (water). In Basic medium though low dissolution characterized the experiment also however, the dissolution of the coal in base was a bit higher than acid and control experiment [50]. This gave the coal a good quality as adsorbent to adsorbed antibiotics under the experimental conditions and in the two media which were 0.1 M Acid and Base solution.

Dissolution models

The results of the analysis for the fitting of Zero-order, first order, second order, Hixson- Crowell cube root law, Huguchi and Shrinking core model, as presented in Figure 17 to 22 and the parameters in Table 9 all fitted poorly with the low values of R^2 which is an indication that the dissolution of the Okobo coal was not effective except for the second order dissolution model. The correlation coefficients of the second order model for Acid, Base and Water are 0.9940, 0.7610 and 0.6720 meanwhile, k_2 = 2.2799, 0.2589 and 2.0672 in the same order and the C_s values (0.0601, 0.0858 and 0.0070). The R^2 values clearly show that the dissolution of the Okobo coal fitted better the experimental data [51].

Statistical Analysis at 95 % Confidence Interval

From the analyses performed, Table 8 compared Okobo coal and CAC adsorption of Ampiclox (AMP and CLO). 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). On a separate consideration, the comparison for the dissolution of Okobo coal in Acid and Water, Base and Water as well as Acid and Base was performed. The result shows that there is significant difference in the dissolution of adsorbent between (Acid and Water) and (Base and Water). This is because the p-values in Table 9 for the said analyses were less than p- value (0.05) while the dissolution of the coal in Acid and Base was not significantly different since the p-value calculated was greater than p- value (0.05).

Conclusion

This present study considered the performance of Okobo coal as adsorbent to remove Ampiclox (AMP and CLO) from aqueous medium by batch adsorption as well as investigation of its dissolution kinetics. Characterization of the adsorbent prepared was carried out using both classical and instrumental techniques to study (Attrition, conductivity, pH, Bulk density, specific surface area and Iodine number) and (FTIR, SEM and TGA) respectively. The data gotten from the experiment was found to fit best Langmuir isotherm and followed Pseudo second order kinetics with higher R^2 values. On the other hand, the dissolution of Okobo Coal was slightly in 0.1 M solution of both Acid and Base as shown by the dissolution models used. This is further, supported by the low percentage value of attrition of 5.4 %. The studies were successfully carried out as discussed earlier and the results obtained are not in deviance 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.

Declaration of conflicting interests

The authors declared no potential conflict of interest

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