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Removal of doxycycline from aqueous solution using silica extracted from corn cob ash and natural kaolin: characterization, kinetics, equilibrium and thermodynamics

*Ajayi O.A., Okoronkwo A.E., Adebayo M.A, and Dimas J.J.

Department of Chemistry, Federal University of Technology, Akure, Ondo State, Nigeria

*Corresponding Author: shinab2006@yahoo.com; ajayiolabisi@futa.edu.ng

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ABSTRACT

The resistance to antibiotics use against bacteria has become a thing of concern in recent times. This is because of the presence of antibiotic residue which are continuously detected worldwide in wastewater effluents. In this study, the effectiveness of silica extracted from corn cob ash via sol-gel method in comparison with naturally occurring silica (kaolin) to adsorb doxycycline from aqueous solution was investigated. The silica and kaolin were characterized using FTIR, XRD, BET and TEM to reveal the functional groups, type of materials, surface area and morphology of the adsorbents, respectively. The effect of pH, contact time, initial concentration, adsorbent dosage and temperature were studied using batch technique. The study showed that adsorption of doxycycline was pH dependent, while equilibrium was reached at 180 and 240 min for silica and doxycycline respectively. Increase in temperature led to low removal of the antibiotics. Three kinetics models were employed, namely; pseudo first order, pseudo second order and Elovich. The aadsorption process fitted into non-linear pseudo second order kinetics. Adsorption equilibrium data were subjected to Langmuir, Freundlich, Dubinin-Raduskevich and Liu isotherms. The experimental data fitted more into Liu isotherm. The negative values of ΔG^o revealed feasible and spontaneous process and the negative enthalpy (ΔH^o) values confirmed exothermic nature of the process. Add concluding statement.

Keywords: Corn cobs, Silica, kaolin, Doxycycline, adsorption isotherm, kinetics

INTRODUCTION

Antibiotics are largely used in human, agriculture, and veterinary pharmaceuticals to attack diseases caused by bacteria. However, the way and manner by which it is administered is of great concern. This is because doses are not consumed completely as it has been reported that 30-90% of antibiotics found their ways into the environment in their active forms due to effluents runoff. Excessive use and improper disposal of these antibiotics had caused bacterial to develop

resistance that prevents the drugs to effectively cure bacterial diseases. As a result of this, the World Health Organization (WHO) has classified antibiotic-resistant bacteria as one of serious threat to public health, economic growth or development and food security [1]. Another important factor about antibiotics is their persistent nature in the ecosystem. These residual antibiotics are detected continually in effluents of wastewater around the world [2].

It has been reported that recently, doxycycline, with other drugs have been used to minimize COVID-19-induced inflammation [3, 4]. As a result of complicated physical and chemical behaviour of doxycycline, it makes its existence in the ecosystem very dangerous [2]. Doxycycline is soluble in water which makes its residue highly toxic in aquatic environment and increases antimicrobial resistance [4].

One of the most abundant components of earth's crust is silica. It is naturally produced from various sources including corn cobs, sugarcane, rice husk, bamboo stems and leaves and barley. A number of researches have been directed either to reduce, reuse or minimize the negative impacts of agricultural wastes on the environment [5]. Some wastes have been applied in many fields such as adsorbent in environmental technologies, low-cost reinforced filter, additives to cement in structural materials and filter materials [6]. As a results of the unique properties of silica and its compounds, many researches showing the various applications of silica and silica-based materials in different fields have been documented [7].

Previous works have been carried out on the use of silica and silica-based materials for removal of antibiotics from solution. For example, removal of antibiotics in water usage cycle using silica-clay nanocomposite was documented [8]. Also, the use of rice husk ash (silica) for removal of doxycycline was reported in the literature [3]. This research has shown the efficiency of extracted silica without modification for doxycycline removal from aqueous solution.

The aim and objective of this research is to investigate the interaction of doxycycline with silica extracted from corn cobs via sol-gel method in comparison with naturally occurring silica in kaolin. The adsorption isotherms, kinetics and potential mechanism of adsorption were analyzed. The effect of pH, contact time, initial concentration, adsorbent dosage and temperature were studied to determine adsorption process.

MATERIALS AND METHODS

Materials

The reagents used for this research are of analytical grade; Doxycycline (Jiangxi Pharmaceutical China), Hydrochloric acid, Sodium hydroxide (BDH) and deionized water. The stock solution of 1000 mg/L doxycycline was prepared. The working concentrations of 50 – 500 mg/L were prepared from the stock solution and kept in refrigerator. The kaolin used for this research was collected from a deposit in Auchi (Edo State, Nigeria).

Adsorbent preparation

Corn cobs were obtained from research farm of Federal University of Technology, Akure, Ondo State, Nigeria. The cobs were washed (to remove sand and other dirt) and dried. The sun-dried cobs were reduced to ash in a carbolite muffle furnace at 620 ^{o}C for 6 hours and was allowed to cool overnight. Silica was extracted from corn cob ash by sol-gel method as reported by Kamath and Proctor [9]. The ash was heated with 1 M NaOH for 1 h, filtered through 110 mm filter paper (Equation 1). The silica was precipitated out by adjusting the pH of filtrate to 7 with 1 M HCL (Equation 2). The resulting silica was washed with distilled water and dried in an oven at 105 ^{o}C for 24 hours. Kaolin was first purified by soaking in water to make a slurry, sieved to remove stones and other particles. It was allowed to settle, decanted and dried in an oven at 105 ^{o}C for 72 hours.

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O \quad (1)$$

$$Na_2SiO_3 + 2HCl \rightarrow SiO_3 + 2NaCl + H_2O \quad (2)$$

Adsorbent characterization

The functional groups and surface properties of the silica and kaolin adsorbents were examined with Perkin Elmer Fourier Transform Spectrometer (FTIR 3000 MX USA) from the range of 4000 – 400 cm^{-1} at room temperature using a KBr disc which contained 1% of ground sample. This mixture was pressed into the wafer of KBr under vacuum. XRD analysis of silica and kaolin were carried out using a Philips X' pert X-ray Diffractometer. The XRD patterns were obtained at 40 kV and30 mA and monochromatic high-intensity Cu Kα 1 (λ = 0.15405 nm) and was used as the source of radiation. The surface area of both adsorbents were analyzed using Brunauer Emmett Teller (BET) analyser (Quantachrome Instruments, Boynton Beach, USA) by nitrogen

adsorption at 77 K using micrometrics Trista II from where surface area was determined and calculated. The surface morphology and elemental composition were determined by Transmission Electron microscope (JEM-2100 USA).

Adsorption experiments

Adsorption measurements was performed via batch experiments by adding 0.02 g of the prepared silica and kaolin each into 20 cm^3 100 mg/L doxycycline solution under stirring condition. This procedure was continued at different time intervals of 2, 5, 7, 10, 15, 20, 25, 30, 60, 90, 120, 180, 240, 300 and 360 min. The pH between 2-10, temperature of 301, 313, 323 and 333 K, concentrations (50, 100, 150, 200, 250, 300, 350, 400, 450 and 500 mg/L) and dosage of 0.01, 0.02, 0.03, 0.04 and 0.05 g. The solution was centrifuged and analyzed using UV-Visible Spectrophotometer (UV-Visible Shimadzu 1800). Also, point zero charge of the adsorbents were determined by weighing 0.02 g of silica and kaolin each into 20 ml of deionized water and pH measured after 48 h. The pH was plotted against change in pH to get the point of zero charge.

RESULTS AND DISCUSSION

The results of characterization of silica with FTIR showed absorption band O-H stretching (3441 cm^{-1}), C-H bending (1647 cm^{-1}), O=C=O (2356 cm^{-1}) and Si-O-Si (1136 cm^{-1}) before adsorption while that of kaolin O-H stretching at 3622 cm^{-1}, C-H bending (1648 cm^{-1}), O=C=O (2356 cm^{-1}), Si-O-Si (978 cm^{-1}) and Al-O at 532 cm^{-1}. There were little shift in the absorption bands after adsorption of doxycycline on to the surface of silica and kaolin adsorbent as shown in Figures I and II. It has been documented in the literature that the major component of corn ash is silicon which exists in the form of SiO_2 [10]. After, adsorption, it was observed that the peak patterns of silica loaded with doxycycline changed from 1136 cm^{-1} to 1014 cm^{-1} which confirmed deformation of Si-O-Si and that of O-H as it changed from 3441 cm^{-1} to 3406 cm^{-1} [11].

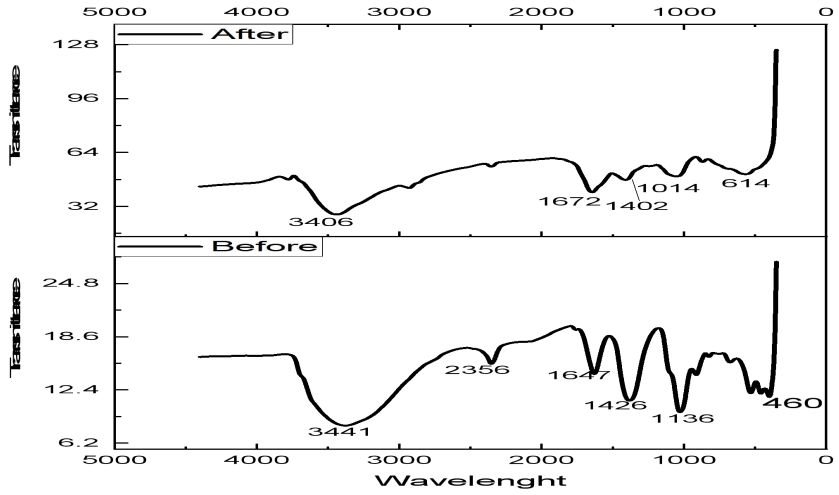

Figure I: FTIR spectra of silica before and after adsorption of doxycycline

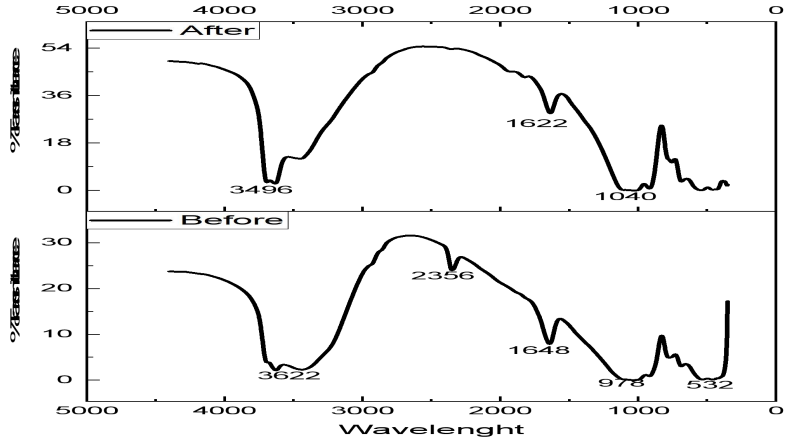

Figure II: FTIR spectra of kaolin before and after adsorption of doxycycline

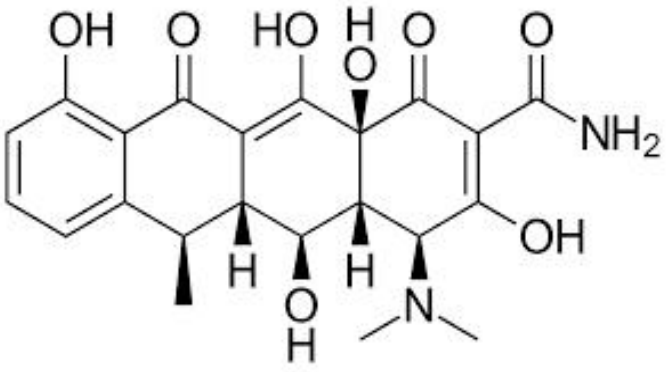

Figure III: Chemical structure of doxycycline

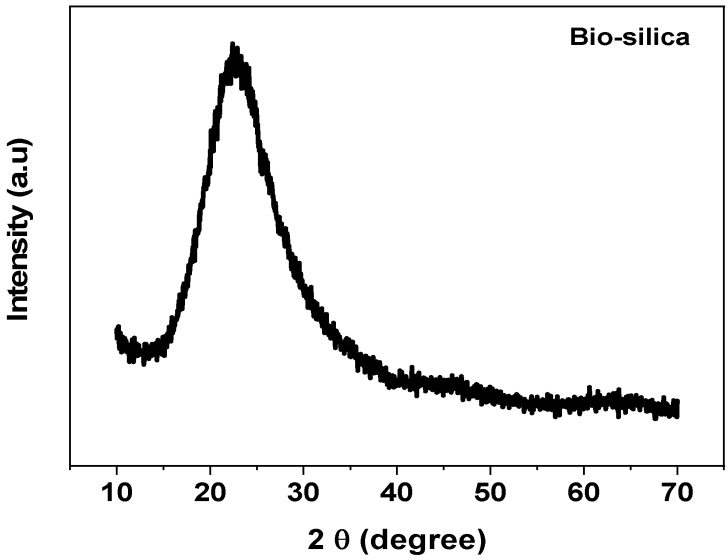

Figure IV: XRD pattern of silica

The XRD pattern of silica and kaolin are shown in Figures IV and V respectively. The absence of sharp peaks in the XRD pattern indicated the amorphous nature of the materials. This is because the pattern matches Joint Committee on Powder Diffraction Standards (JCPDS) card number 29-85 which confirms amorphous silica while the peak pattern of kaolin matched card number 3-52, having triclinic structure. Additionally, the intense broad peak at $2\theta = 22^{o}$ was observed, which indicated the presence of silica nanoparticle [12].

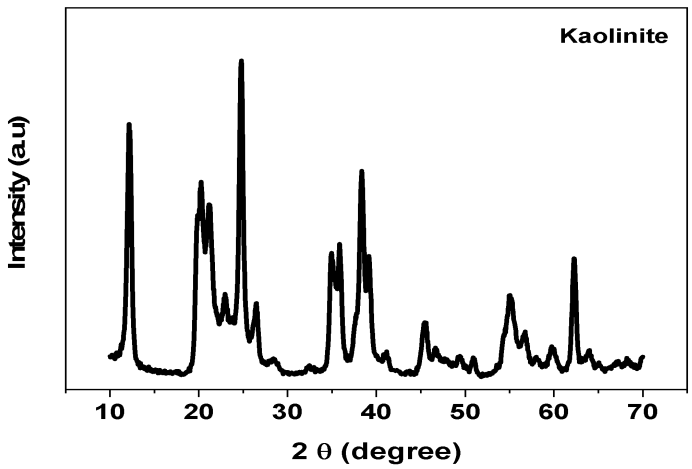

Figure V: XRD pattern of kaolin

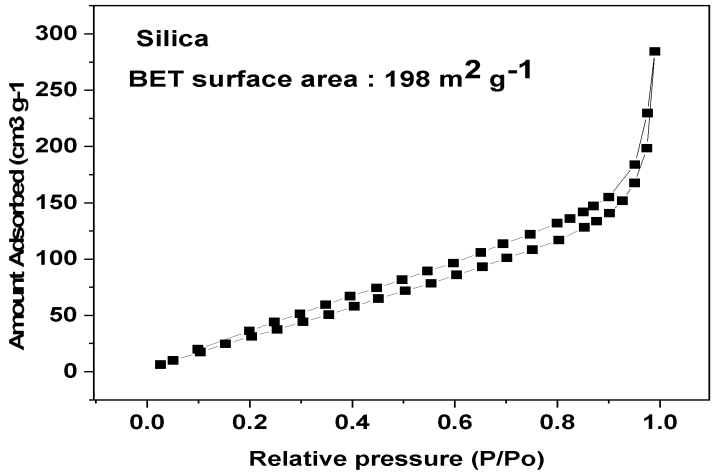

Figure VI: BET analysis of silica

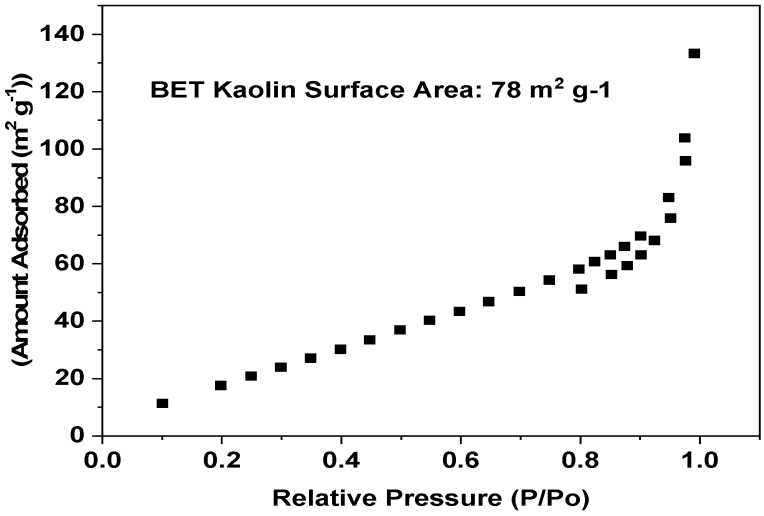

Figure VII: BET analysis of kaolin

The surface area of silica and kaolin were analyzed using Brunauer Emmett Teller (BET) analyser. The adsorption-desorption isotherm of the adsorbents are shown in Figures VI and VII. Brunauer–Emmett–Teller (BET) theory is used to measure the surface area of solid or porous materials. It gives important information on their physical structure as the area of a material's surface affects how that solid will interact with its environment. The surface area of silica is 198 m^2 g^{-1} which played prominent role in the adsorption of doxycycline [13] while kaolin has surface area of 78 m^2 g^{-1}.

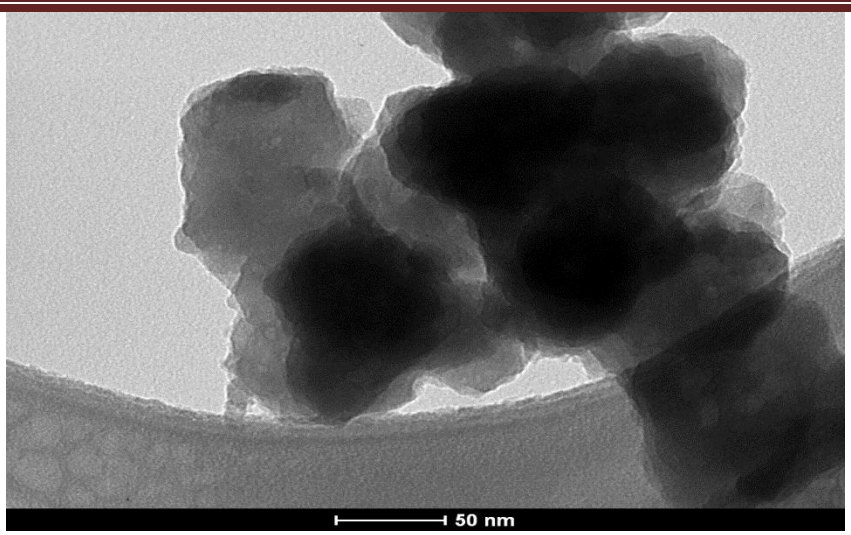

Figure VIII: TEM image of silica

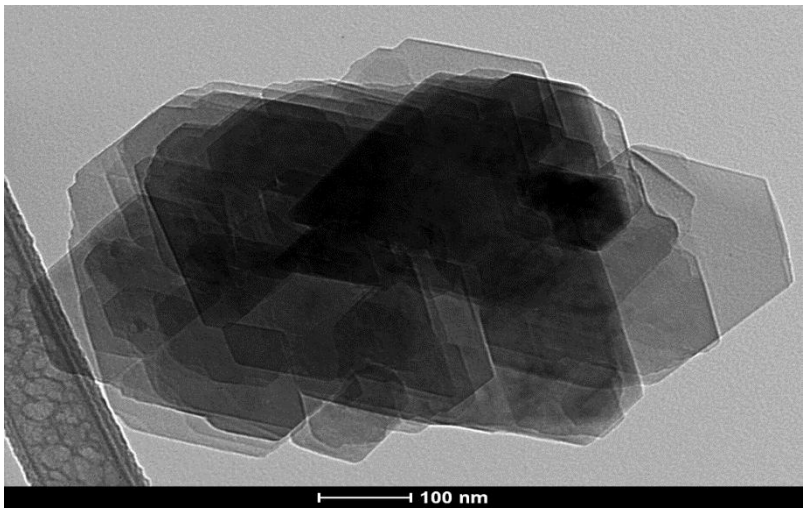

Figure IX: TEM analysis of kaolin

Transmission electron microscopic analysis of silica and kaolin was analyzed using TEM. The micrographs (Figures VIII and IX) revealed that particle of silica was formed with homogenous distribution having spherical shape and that of kaolin exhibited a hexagonal symmetry. Similar observation was reported in the literature [11].

Effects of pH on adsorption

The influence of pH on adsorption of doxycycline using silica and kaolin adsorbents were studied at pH range 2-10. There were more adsorption at basic pH (pH 8 for silica and kaolin

respectively) than what was observed at lower pH (Figures X and XI). The maximum percentage removal of doxycycline by adsorption was 90.01% from initial concentration of 100 mg/L and 29.26% for kaolin at the same concentration. The reason for this was that doxycycline being an amphoteric molecule has different functional groups which can ionize into anions, cations and zwitterion at different pH [12]. At, at pH ≤ 3, doxycycline is protonated which makes it exist as cation [14]. The amine group on doxycycline is protonated making the antibiotic exist as cation. The surface charge of the adsorbent becomes more negative above pzc. Therefore, there was electrostatic interaction between positive amine group and negatively charged adsorbent at higher pH. This interaction actually accounted for higher uptake with silica recorded highest adsorption capacity [15].

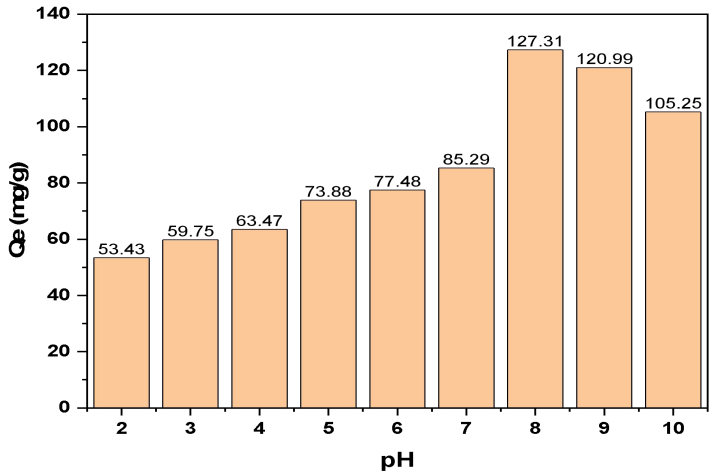

Figure X: Effects of pH on adsorption of doxycycline using Silica

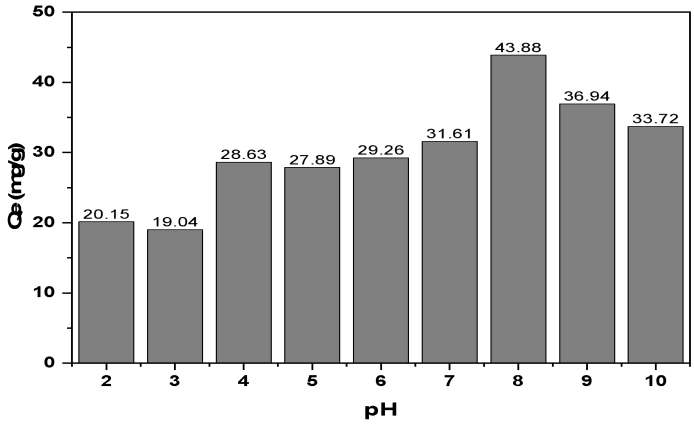

Figure XI: Effects of pH on adsorption of doxycycline using Kaolin

Concentration and adsorption isotherms of doxycycline

Adsorption isotherms are used to represent equilibrium relationship between the adsorbents surface and adsorbate concentration in the liquid phase at a given condition [16]. In this study, four adsorption isotherms were employed to describe adsorption equilibrium relationship. They are: Langmuir, Freundlich, Dubinin-Radushkevich and Liu (Equations 3 & 4, 5, 6 & 7 respectively). The adsorption of doxycycline using silica and kaolin were subjected to these four adsorption isotherms as presented in Figures XII and XIII.

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (3)$$

$$R_L = \frac{1}{1 + K_L C_o} \quad (4)$$

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad (5)$$

$$q_e = q_{max} \exp - K_{D\text{-}R} \varepsilon^2 \quad (6)$$

$$q_e = q_m (K_g C_e)^{nL} / 1 + (K_g C_e)^{nL} \quad (7)$$

where q_e is the amount of doxycycline adsorbed (mg/g), q_{max} is the maximum adsorption capacity (mg/g), C_e is equilibrium concentration of solution (mg/L), K_L is Langmuir constant (L/mg), R_L is favourability factor, K_F is adsorption capacity (L/mg), E is energy of adsorption, ε is Polanyi potential, ß is Dubinin-Radushkevich constant, K_g is Liu constant (L/mol) and 1/n and n_L are adsorption intensities. Langmuir isotherm predicted that the active sites on the adsorbent are energetically similar hence monolayer adsorption do occur. Freundlich assumed that concentration of adsorbate on the adsorbent surface increases with the adsorbent concentration, therefore infinite adsorption can occur. Dubinin-Radushkevich provides information on physiosorption or chemisorption of adsorption process. Liu combines both Langmuir and Freundlich isotherms where both monolayer and infinite adsorption were eliminated stating that adsorbent surface cannot possess the same energy [17].

The concentration and isotherm studies were performed at temperature range of 301 – 333 K with initial concentrations of 50 – 500 mg/L. The experiments were studied at pH 8 for adsorption of doxycycline using silica and kaolin (Figures XII and XIII), agitation time of 180 min and mass of adsorbent (0.02 g). As the temperature increases, the uptake rate reduces due to exothermic nature of adsorption. The Langmuir isotherm assumes monolayer coverage of adsorbed molecules on homogeneous adsorbent surface [18, 19].

This study investigated the relevance of the isotherm model to adsorption of adsorbate with silica and kaolin. It was observed that Liu isotherm was found more fitted to explaining the adsorption process which suggested that the active sites of the adsorbents possess different energy when considered the values of SD and R^2. Also, the downward trend in temperature values of q_{max} and K_g depicts an exothermic adsorption process. For example, adsorption of doxycycline with silica has adsorption capacity reduced from 443.33 mg/g at room temperature (301 K) to 286.34 mg/g at 343 K while that of kaolin reduced from 120.70 – 66.57 mg/g (Tables I & II).

The nature of adsorption was also determined by non-linear plot of Dubinin-Raduskeviech (D-R). The values observed were all less than 8 KJ mol^{-1} (Tables III and IV) which showed that doxycycline was physically adsorbed to silica and kaolin adsorbents. Similar observation was reported in the literature [20].

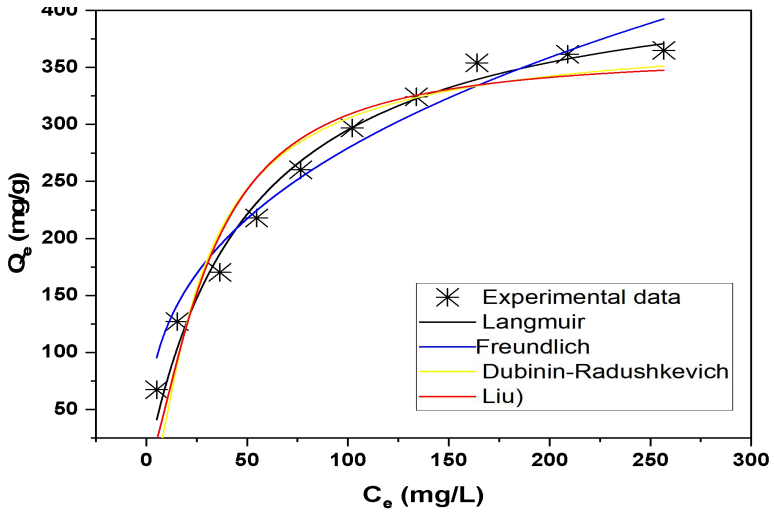

Figure XII: The Langmuir, Freundlich, Dubinin-Radushkevich and Liu plots for adsorption of doxycycline using Silica

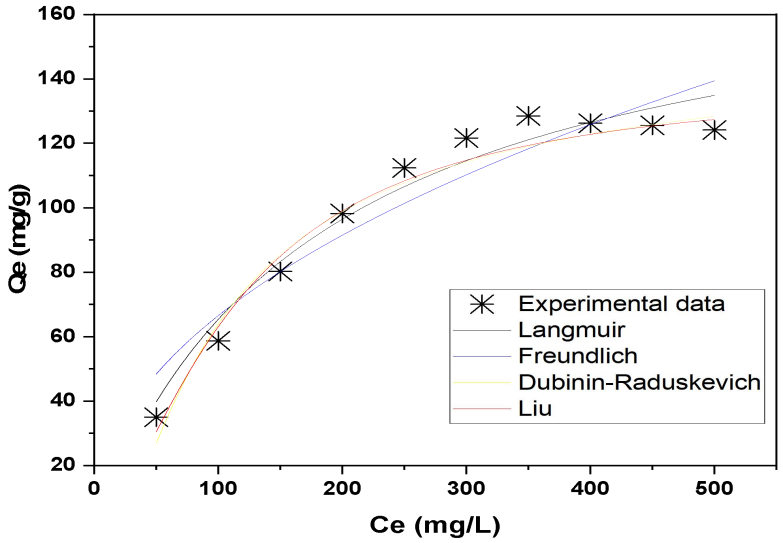

Figure XIII: The Langmuir, Freundlich, Dubinin-Radushkevich and Liu plots for adsorption of doxycycline using Kaolin

Table I: Isotherm parameters for adsorption of doxycycline using silica at different temperatures

	Parameters	*301K*	*313K*	*323K*	*333K*
Langmuir	Q_{max} (mg/g)	443.33	408.98	368.08	286.34
	K_L (L/mg)	0.03	0.02	0.05	0.03
	R_L (min^{-1})	0.35	0.32	0.29	0.29
	SD	6.50	8.02	7.80	8.22
	R^2	0.95	0.96	0.95	0.93
Freundlich	K_f (mg/g)	40.69	39.24	36.99	35.60
	1/n	4.26	3.86	4.40	4.59
	SD	3.68	6.79	5.98	4.67
	R^2	0.96	0.94	0.93	0.93
	Q_{max}	172.76	166.70	151.18	132.07
Dubinin-	K_{ad} (mol_2kJ^{-2})	0.01	0.05	0.03	0.08
Radushkevich	*E* (kJ/mol^{-1})	5.96	6.43	6.74	7.37
	SD	5.15	8.48	8.64	6.56
	R^2	0.93	0.87	0.86	0.88

Liu	Q_{max}	168.89	161.92	147.77	129.39
	Kg	0.02	0.03	0.04	0.03
	nL	1.26	1.35	1.30	1.27
	SD	0.22	0.87	0.62	0.40
	R^2	0.99	0.99	0.98	0.97

Table II: Isotherm parameters for adsorption of doxycycline using kaolin at different temperatures

	Parameters	301K	313K	323K	333K
Langmuir	Q_{max} (mg/g)	120.704	101.836	86.17	66.57
	K_L (L/mg)	0.06	0.07	0.08	0.09
	R_L (min^{-1})	0.39	0.37	0.35	0.28
	SD	7.58	8.57	7.63	2.51
	R^2	0.95	0.94	0.95	0.98
Freundlich	K_f (mg/g)	20.11	13.21	10.95	8.00
	1/n	2.18	2.44	2.67	3.96
	SD	2.17	3.06	3.86	2.53
	R^2	0.90	0.86	0.85	0.83
	Q_{max}	154.13	150.88	145.03	99.89
Dubinin-	K_{ad} (mol_2kJ^{-2})	0.02	0.04	0.03	0.01
Radushkevich	*E* (kJ/mol^{-1})	5.41	5.74	6.09	7.86
	SD	7.35	6.67	6.21	2.26
	R^2	0.97	0.96	0.95	0.93
Liu	Q_{max}	140.05	136.95	132.91	97.95
	Kg	0.02	0.04	0.01	0.02
	nL	1.56	1.67	1.68	1.71
	SD	2.68	2.84	3.69	2.31
	R^2	0.99	0.98	0.97	0.98

Time and adsorption kinetics

The equilibrium time for adsorption of doxycycline using silica and kaolin were 180 and 240 min with 84.710% and 40.41% removal respectively. Kinetic models such as the pseudo-first order, pseudo-second order and Elovich (Equations 8, 9 and 10 respectively) were used to investigate the adsorption processes. The non-linear kinetic plots of adsorption of doxycycline is presented in figures XIV and XV. The q_e experimented and q_e calculated values showed that the adsorption fitted to pseudo-second order model than pseudo-first order. Also, the low SD values for pseudo second order when compared to that pseudo first order agreed with above assertion. Additionally, the correlation coefficient (R^2) suggested that the adsorption were fitted to pseudo-second order kinetics (Table III). Similar observation has been previously reported [21].

$$q_t = q_e\left\{1-\exp\left(-k_1 t\right)\right\} \quad (8)$$

$$q_t = q_e - \frac{q_e}{1+k_2 q_e t} \quad (9)$$

where k_1 and K_2 (min^{-1}) are rate constant of the pseudo-first-order and second order adsorption, qt (mg/g) denotes the amount of metal ions adsorbed on adsorbent mass at time t (min) and q_e (mg/g) is the amount of metal ions adsorbed at equilibrium.

The Elovich equation has been proven to be useful in describing chemisorption on heterogeneous adsorbent surfaces.

$$qt = 1/ß\, ln(\alpha\, ß) + 1/ß\, lnt \quad (10)$$

Where qt is uptake of adsorbate, α is adsorption rate (mg/g/min), ß is desorption rate constant (g/mg) and t is time (min).

In this study, (Table III), it was observed that the adsorption rate (α) were small (0.060 and 0.200 mg/g/min for adsorption of doxycycline using silica and kaolin adsorbents), while ß which is desorption rate were very large. Therefore, the adsorption process is physiosorption unlike chemisorption where there is exchange of ion leading to formation of chemical bond [16].

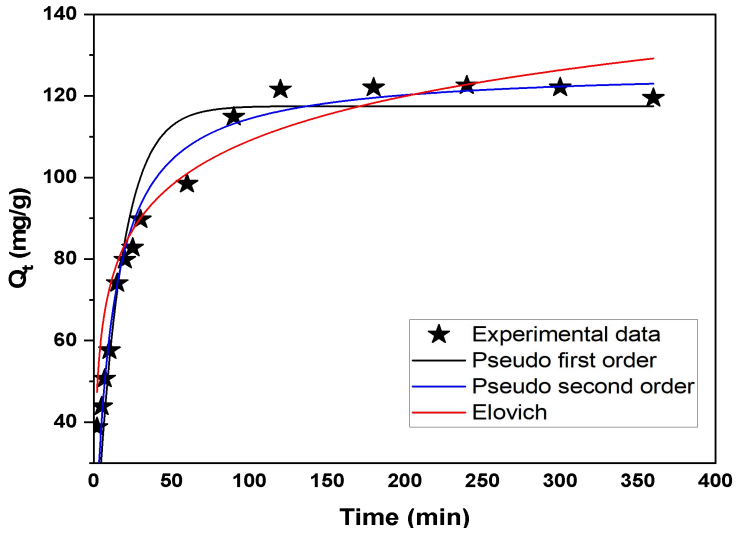

Figure XIV: Kinetics studies for adsorption of doxycycline using silica

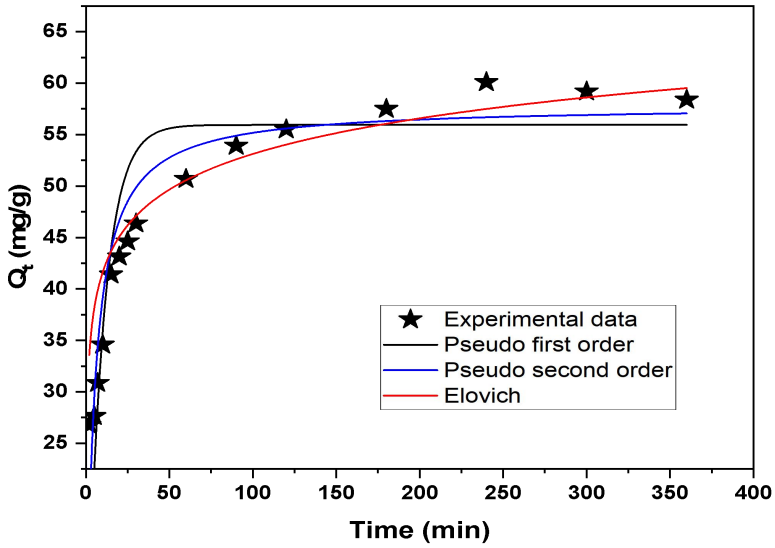

Figure XV: Kinetics studies for adsorption of doxycycline using kaolin

Table III: Kinetics parameters for adsorption of doxycycline using silica and kaolin adsorbents

Models		*Silica*	*Kaolin*
Pseudo- First Order	q_{exp} (mg/g)	127.06	63.09
	q_{cal} (mg/g)	117.50	55.94
	K_L (min^{-1})	0.06	0.10
	SD	10.88	6.65
	R^2	0.89	0.74
Pseudo-Second Order	q_{exp} (mg/g)	127.06	63.10
	q_{cal} (mg/g)	126.68	61.82
	K_L (min^{-1})	0.04	0.02
	SD	6.95	1.66
	R^2	0.96	0.91
Elovich	α (mg/g/min)	0.07	0.20
	β (g/mg)	159.47	2063.25
	SD	5.19	2.49
	R^2	0.89	0.83

Adsorbent dosage

One of the advantages of study on adsorbent dosage is to prevent wastage of materials after the equilibrium has been reached [15]. The results obtained from the effect of dosage as presented in Figure XVI showed the impact of variation on amount of adsorbate that was adsorbed from the initial concentrations of 100 ppm concentration for the adsorbates used between the range of 0.02 and 0.10 g. It was observed that adsorption of doxycycline with the two adsorbents increased significantly from 79.26 – 87.02% and 27.02 – 47.93% for silica and kaolin respectively. This implied that increasing the adsorbent dosage beyond the 0.02 g resulted in more uptake of the antibiotics [22].

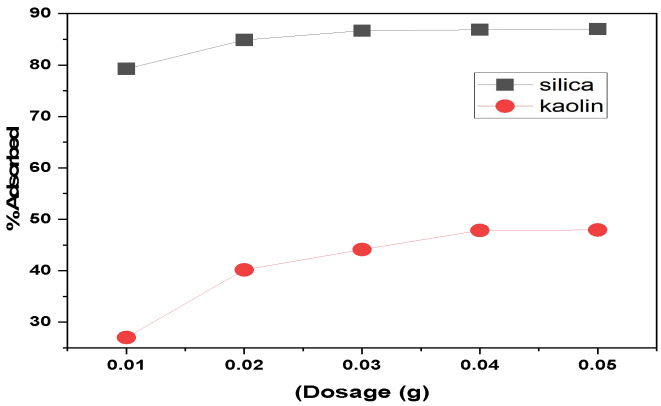

Figure XVI: Effect of adsorbents dosage on doxycycline adsorption

Adsorption thermodynamics

Thermodynamics parameters for the adsorption of doxycycline using silica and kaolin adsorbents such as enthalpy ΔH^o (kJ/mol), entropy ΔS^o (J (molK) and Gibb's free energy ΔG^o were determined from equations 11, 12 & 13 below;

$$\Delta G^o = \Delta H - T\Delta S \quad (11)$$

$$\Delta G^o = -RT\ln(K) \quad (12)$$

The two equations when combined, gave

$$\ln(K_g) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (13)$$

Where K_g (L/mol) is a dimensionless thermodynamic equilibrium constant was derived from Liu equilibrium constant being the most nonlinear fitted isotherm in the adsorption process; T is the temperature in Kelvin and R is the gas constant (8.314 J/mol/K). According to Van't Hoff equation (Equation 13), thermodynamic parameters can be calculated from the variations of the thermodynamic equilibrium constant K_e [23].

The slope and intercept of the plot of ln K_g versus $1/T$ were used to determine the values of ΔH^o and ΔS^o respectively.

The values of enthalpy (ΔH^o) for doxycycline was negative which actually confirmed the exothermicity and spontaneity of the adsorption process [24]. The positive values observed for entropy (ΔS^o) depicted an increase in the rate of disorderliness of the system at the interface of the adsorbents and adsorbate [25]. The negative values of ΔG showed that the adsorption process of the adsorbates were feasible and spontaneous Table IV).

Table IV: Thermodynamic parameters for adsorption of doxycycline.

Adsorbents	**ΔH^o (KJ/mol)**	**ΔS^o (J/mol)**	**ΔG^o (KJ/mol)**			
			301 K	313 K	323 K	333 K
Silica	-4.73	64.56	-24.16	-24.94	-25.58	-26.23
Kaolin	-9.69	39.64	-21.63	-22.10	-22.48	-22.89

CONCLUSIONS

Silica was extracted from corn cobs using sol-gel method while naturally occurring kaolin was prepared and dried. The silica and kaolin were characterized using Fourier Transform Infrared Spectrophotometry (FTIR), XRD, BET and TEM which revealed the functional groups, nature of adsorbents, surface area and morphology respectively. The adsorption process was determined using pseudo first and second order kinetics and Elovich modelling with experiment data fitted more into pseudo second order kinetic model. Additionally, the adsorption studies fitted more to non-linear Liu adsorption isotherm. Adsorption was pH dependent and equilibrium reached at 180 and 240 min for silica and kaolin respectively. The thermodynamic studies revealed that the enthalpy change (ΔH^o) was negative, indicating that exothermic process was involved. Entropy change, ΔS^o was positive, which implies increase in the rate of disorderliness of the system. The negative values of ΔG^o showed that the adsorption process of the adsorbate was feasible and spontaneous.

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