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Adsorption of chlorotriazine herbicide onto unmodified and modified kaolinite: Equilibrium, kinetic and thermodynamic studies

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ABSTRACT

In the recent time, adsorption is a commonly economical way for removal of pollutants from wastewater. Chlorotriazine has been a serious threat to life of both human and animal. Modified kaolinite clays were separately prepared by chemical impregnation method with 2 M H_2SO_4 and 2 M NaOH respectively in w/v of 1:2 for a period of 24 h to give unmodified kaolinite (UKC), 2 M H_2SO_4 modified kaolinite (2-AKC) and 2 Mm^3 NaOH modified kaolinite clays (2-BKC) respectively. The UKC with maximum intake value (125.3 mg/g) was derived at equilibrium of 1100 mg/L while 96.65 mg g^{-1} of 2-AKC was obtained at equilibrium of 500 mg L^{-1} and that of 2-BKC was found at equilibrium of 700 mg/L. The Langmuir isotherm best explained the removal of Chlorotriazine onto various kaolinite clays while pseudo 2nd order kinetics fitted best. Thus, kaolinite clays have been proved as a potential adsorbent for the removal of chlorotriazine molecules.

Introduction

Water is a vital resource for life which requires much value in growth and sustainability of our ecosystem and covers 71% of the earth surface. Due to its importance, the rapid growth of the world population and technology advancement has recently brought about increase in the demand of water. Pollution of water is a challenge in Africa and entire world due to limited available good water (Pimental et al., 1997; Miller et al., 2000).

Chlorotriazine is an herbicide, (a pesticide) which contributes to environmental problem and cause adverse effect on aquatic organisms and human and It is also called Atrazine and its IUPAC name is 6-chloroN^2-ethyl-N^4-isopropyl-1, 3, 5-triazine-2, 4-diamine or simply chlorotriazine. It has been commonly utilized in agriculture, thereby contributing environmental problems. For an instance, pesticide is indispensable in agricultural production because almost one-third of the agricultural products are produced by using pesticides (Jinap and Shahzad, 2016). Generally, crops only utilize only 1% of pesticides while remaining 99% find their way into water bodies and the environment (WenJun and FuBin, 2011).

United States utilized atrazine as pre emergence and post emergence herbicide (Trochimsowicz et al., 2001; Mae and Mayra, 2009). The prevention of weeds from growing on both highway and railroad by use of chlorotriazine via principal mode of action of inhibition of photosynthesis (Mae and Mayra, 2009).

Furthermore, the use of chlorotriazine (atrazine) for prevention of loss of fruits, vegetables and cereals from pest destruction has been reported to be 78%, 54% and 32% respectively. The increased use of atrazine in environment might cause diseases like cancer, tumors and endocrine disruption in aquatic and terrestrial organisms (Hayes et al., 2003; WenJun and FuBin, 2011; Feng et al., 2013).

The use of atrazine as a herbicide is prominent in the African countries and United States (Kauffmann et al., 2000). This chlorotriazine herbicide is washed as runoff into the soil and water bodies resulting into a high BOD/COD, a malodorous or irritating odour and difficult to degrade (Jones et al., 1982; Feng et al., 2013). Water bodies that receive such effluents become unfit for drinking and require extra cost of treatment (Sibel et al., 2006; Feng et al., 2013). Chlorotriazine uptake from black soil was enhanced with incorporation of biochars while microbial transformation in biochars amended black soils. The adsorption process of chlorotriazine had been reported to reach equilibrium within 24 h and its kinetic data were accurately described by pseudo second-order kinetic model. The adsorption isotherm data was fitted well with the Freundlich model (Yang et al., 2018).

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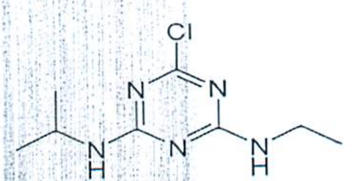

Fig. 1. 6-ChloroN[2]-ethyl-N[4]-isopropyl-1, 3, 5-triazine-2, 4-diamine structure.

Recently, there are increasingly tight restrictions on the organic content of industrial effluent to minimize, or eliminate contaminants from wastewater before it is discharged. This present work is aimed at using the kaolinite clay as a nonconventional, natural low cost adsorbent for the removal of chlorotriazine molecules from aqueous media via adsorption principles.

Materials and method

Adsorbents preparation

The kaolinite clay utilized in this study was collected from Ijapo area Akure, Nigeria, with latitude and longitude of 5°59-07.7 and 6°56-24.2-N respectively. The raw kaolinite clay was purified and

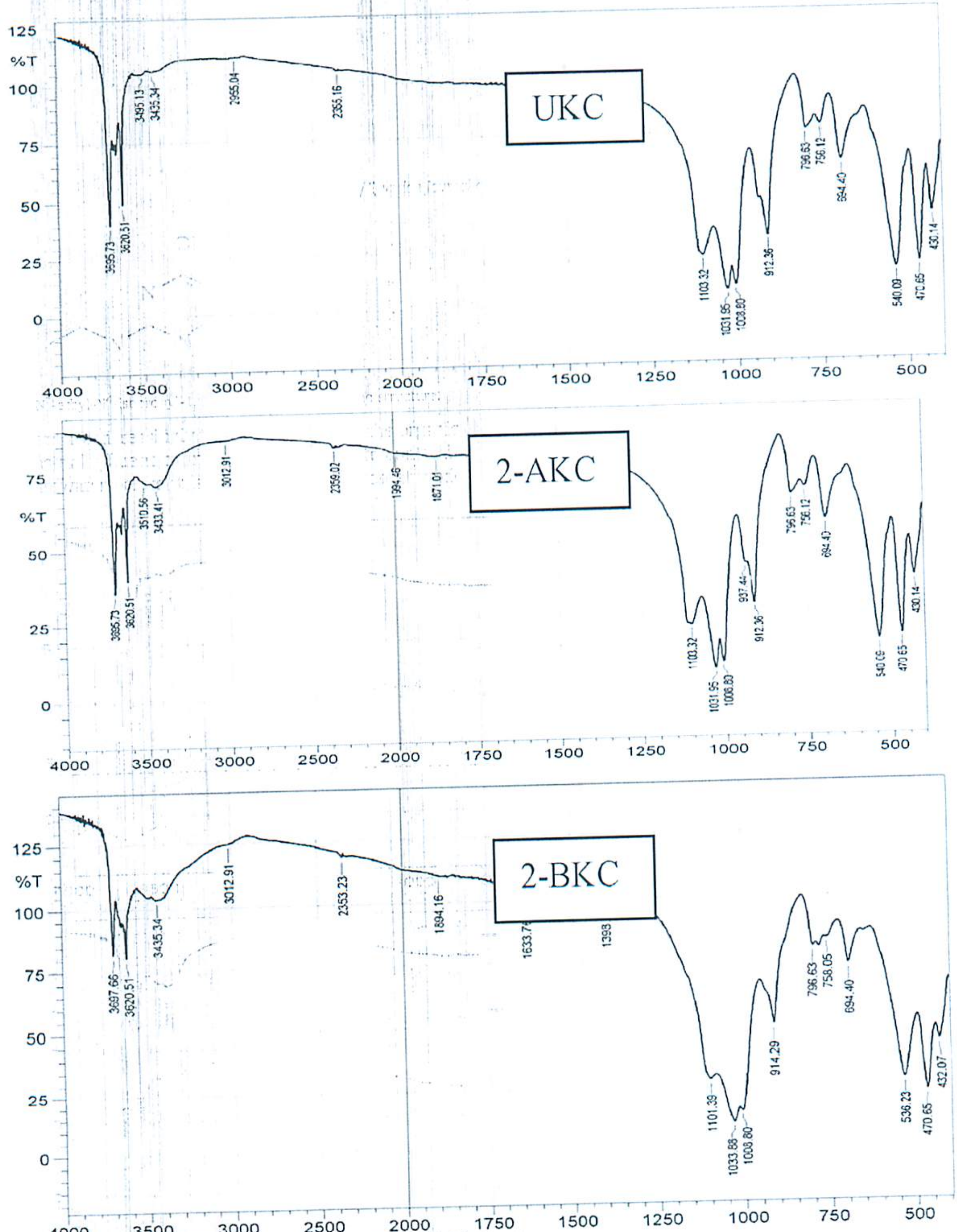

Fig. 2. FTIR spectra of various kaolinite clays.

modified to produce Unmodified kaolinite clay (UKC), 2 M H_2SO_4 modified kaolinite clay (2-AKC) and 2 M NaOH modified kaolinite clay (2-BKC). It was washed with distilled water filtered with vacuum and dried in oven at 376 K (8 h) (Gomez-tamayo et al., 2008; Ajala et al., 2018; Nwosu et al., 2018).

Adsorbents characterization

The surface morphology and Infrared spectrum of kaolinite clay types were characterized using Scanning Electron microscope (SEM) and Fourier transform infrared (FTIR) respectively.

Preparation of adsorbate

Stock solution of chlorotriazine, known as 6-chloroN^2-ethyl-N^4-isopropyl-1, 3, 5-triazine-2, 4-diamine (Fig. 1) was prepared by dissolving 1 g of the atrazine in 1 L of distilled water to give a concentration of 1000 mg L^{-1} solution.

Batch adsorption experiment

The experiments were performed in a 25 mL plastic bottle with a constant concentration of chlorotriazine, shaken in water bath shaker at 30 °C and centrifuged at 150 rpm to remove the residual aqueous concentration. Their initial and final concentrations were obtained using BECHMAN UV – visible spectrophotometer at λ max (273 nm). Working aqueous solutions of desired concentrations were prepared and calibration curve was determined. Equilibrium q_e of the atrazine uptake was calculated using this expression:

$$q_e = \frac{(C_o - C_f)\,v}{m} \quad (1)$$

where q_e is the amount of Chlorotriazine molecules uptake in mg g^{-1} at equilibrium, C_o and C_f are the initial and final concentrations in mg L^{-1} respectively and v is volume (L).

Effect of variable factors

The effect of variable factors of adsorption capacities of UKC, 2-AKC and 2-BKC were studied. Effects of initial concentration varied within ranges of (100–1500 mg L^{-1}), contact time (5–200 min), adsorbent dose (0.05–0.35 g), pH (1–12) and temperature (308–333 K) have been studied by variation of one parameter while other variables were kept constant (Ajala et al., 2018).

Results and discussion

Adsorbents characterization

The FTIR spectra of UKC, 2-AKC, and 2-BKC are presented in Fig. 2 respectively. The spectrum displays diagnostic sharp peak at 3702.31 cm^{-1} and 3623.22 cm^{-1} are assigned to hydroxyl group and inner surface N–H stretching respectively and are corresponding to 3697 cm^{-1} and 3620 cm^{-1} in literature (Georges-IVO, 2005; Liliana et al., 2006).

The SEM micrographs (×500 and ×1000 magnifications) were depicted in Fig. 3 and showed numerous pores with irregular shapes that suggested high effect of contact area during the adsorption (Patel and sudhakar, 2008).

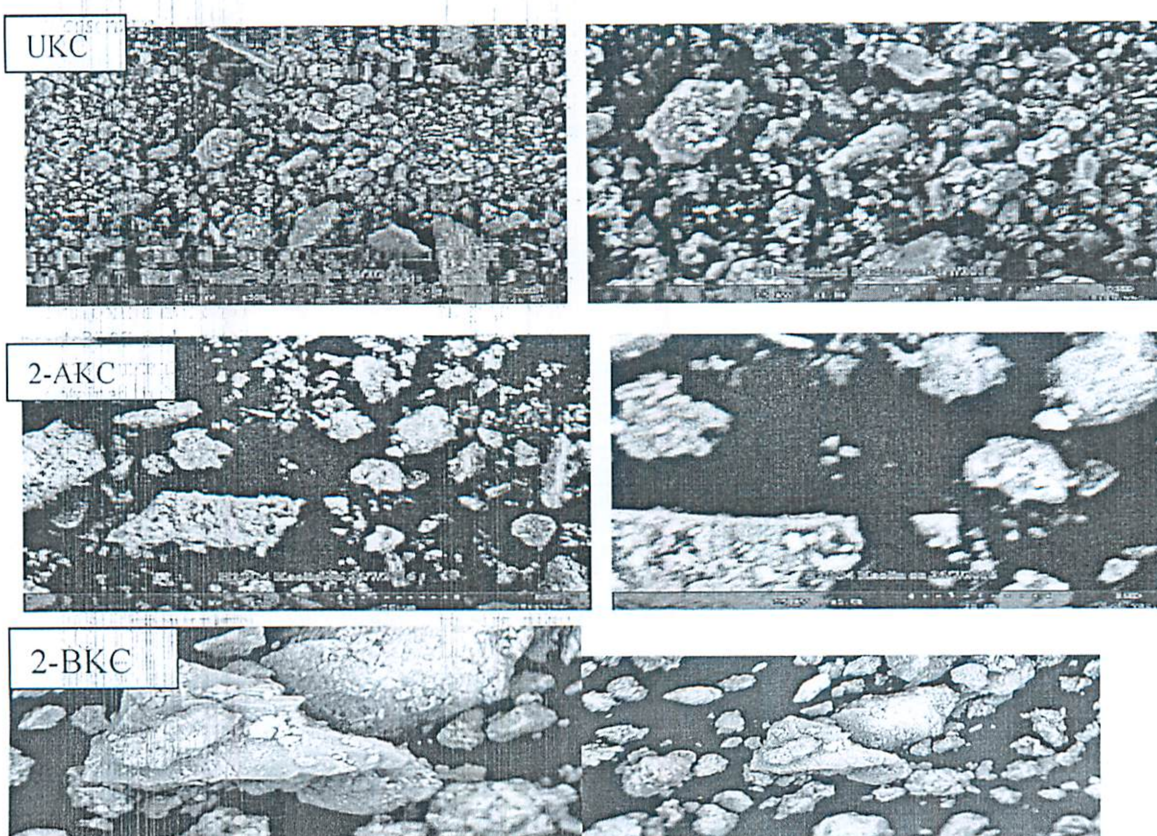

Fig. 3. Scanning electron microscope images at magnification ×500 and ×1000.

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Influence of various parameters onto atrazine adsorption

Effect of initial chlorotriazine concentration on Chlorotriazine adsorption

The amount adsorbed atrazine molecules increased within ranges (20.00–125.30 mg g^{-1}), (20.00–96.65 mg g^{-1}) and (20.00–161.06 mg g^{-1}) as initial concentration increased within ranges (100–1100 mg L^{-1}), (100–500 mg L^{-1}) and (100–700 mg L^{-1}) for UKC, 2-AKC and 2-BKC respectively (Fig. 4a). It has been observed that increase in the initial atrazine concentration led to mass transfer resistances of adsorbate (Weng et al., 2009). Equilibrium concen-

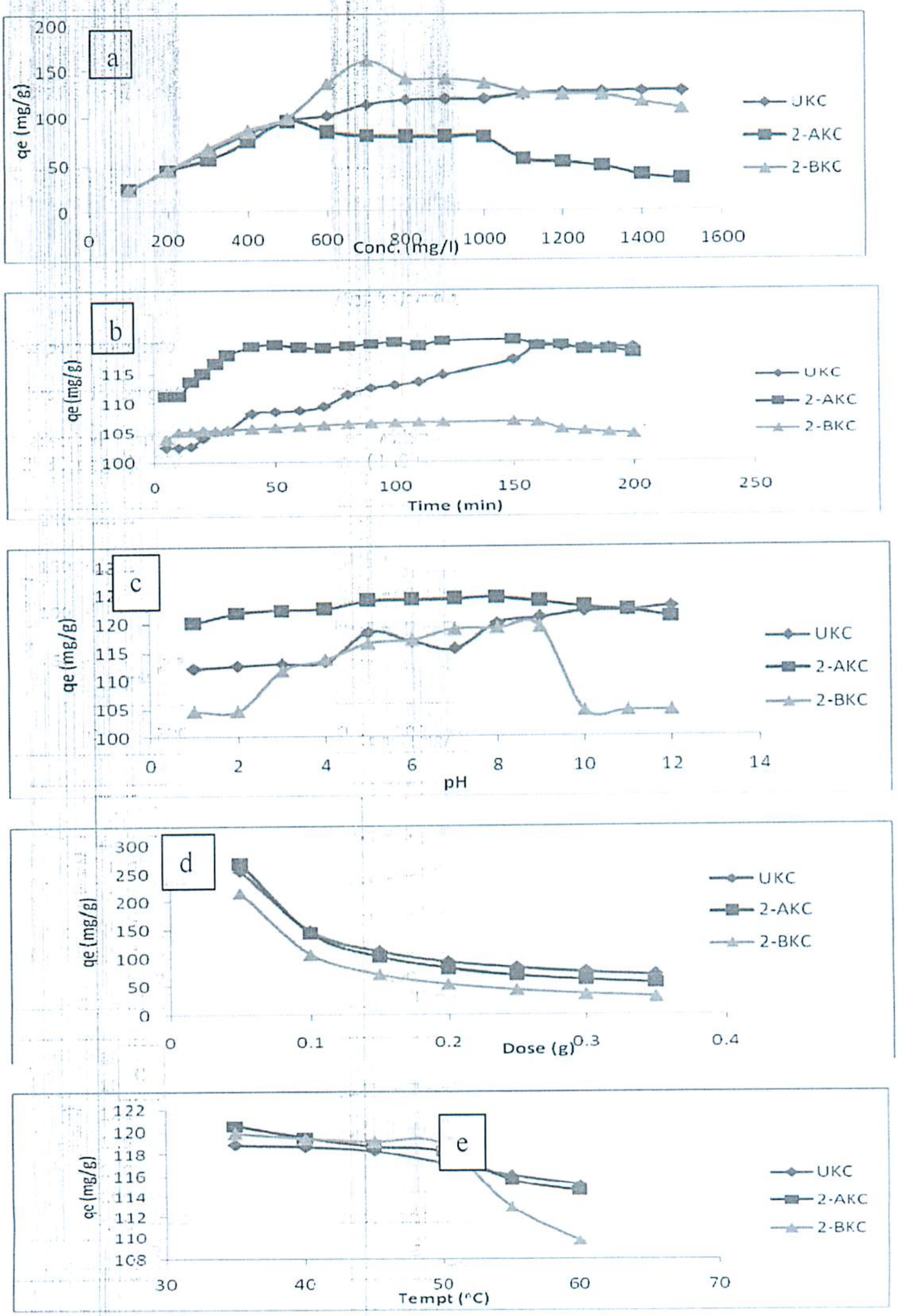

Fig. 4. Effect of different adsorption parameters of sorption capacities of various kaolinite clay types. (a) Initial concentration; (b) contact time; (c) pH; (d) adsorbent dosage; (e) temperature; percentage error for all plots is less than 5%.

trations were found to be 1100, 500 and 700 mg L^{-1} for UKC, 2-AKC and 2-BKC respectively.

Effect of contact time on chlorotriazine adsorption

Fig. 4(b) explained the importance of the effect of clay types contact time on adsorption process of atrazine molecules. As contact time increased, the adsorption of atrazine increased rapidly at the beginning until after 50 min with adsorption capacity of 120 mg/g for 2-AKC and later slowed down until the adsorption capacity remained virtually constant at about 180 min. This may be due to many available vacant sites surface on the clay types at the beginning (Alnmedw et al., 2007; Sathishkumar et al., 2007). Similar trend was observed for UKC and 2-BKC though their adsorption capacities were lower.

Effect of solution pH on chlorotriazine adsorption

Fig. 4(c) showed the removal of adsorbate molecules onto UKC, 2-AKC and 2-BKC as pH increased from 1 to 12. The adsorptivity value of cations always tend to pHpzc value towards acidity region of the pH scale while that of anion tends towards alkali region of the pH scale (Mall et al., 2006; Maleki et al., 2007). It was observed in the three systems that the lowest uptake capacity was determined at pH 1 while its climax was determined at pH 12 (122.95 mg/g) for UKC, at pH 8 (124.45 mg/g) for 2-AKC and at pH 9 (119.3 mg/g) for 2-BKC. These results are similar with the result of the research of atrazine on the performance of pig manure biochars by Zhang et al. (2013).

Effect of adsorbent dose on chlorotriazine adsorption

Fig. 4(d) represents the profile diagram of the doses for UKC, 2-AKC and 2-BKC used for removal of adsorbate. The adsorption capacity of chlorotriazine onto various kaolinite clay types decreased with increasing adsorbent dose as per 254.9 mg g^{-1} down to 71.10 mg g^{-1}, 269.89 mg g^{-1} to 55.71 mg g^{-1} and 215.20 mg g^{-1} to 30.74 mg g^{-1} for UKU, 2-AKC and 2-BKC respectively as the dose of adsorbent increased within range of 0.05 g–0.35 g. Thus, 0.1 g dose of the adsorbents was obtained as the optimum (Nwosu et al., 2017).

Effect of temperature on chlorotriazine adsorption

Fig. 4(e) depicted the effect of temperature on atrazine adsorption onto UKC, 2-AKC and 2-BKC. It was noted that the capacity of the adsorption decreased as the temperature increased which implied adsorption process is exothermic. This is due to reduction in diffusion within the pores of the adsorbent materials and high solubility as temperature increased (Hatem et al., 2013). The adsorptivity value ranged 120.55 mg g^{-1}–114.55 mg g^{-1},

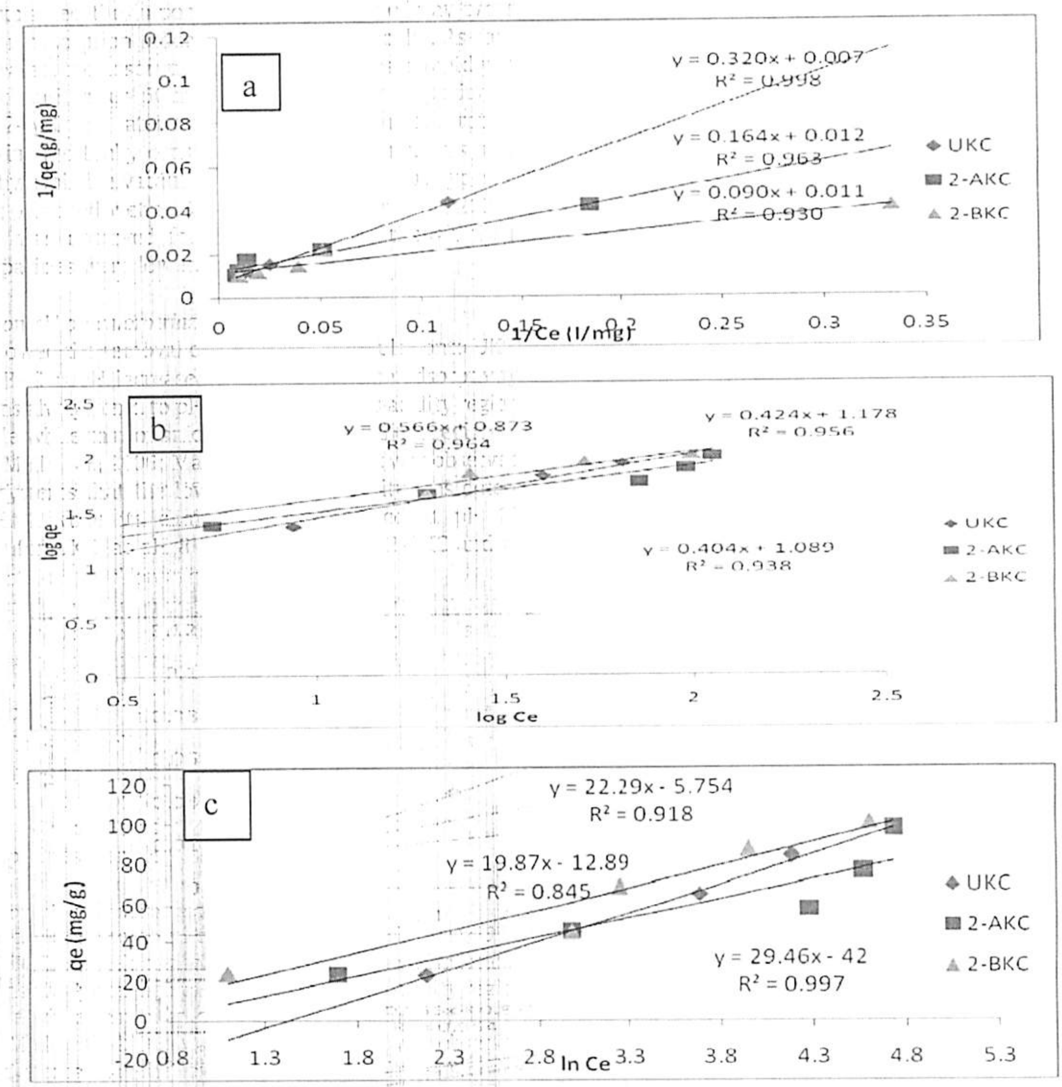

Fig. 5. Different Adsorption isotherms for adsorption of Atrazine from aqueous solution. (a) Langmuir; (b) Freundlich; (c) Temkin. Percentage error is less than 5%.

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119.85 mg g^{-1}–109.75 mg g^{-1} and 118.85 mg g^{-1}–115.2 mg g^{-1} for 2-AKC, 2-BKC and UKC respectively.

Equilibrium isotherms studies

The data obtained from equilibrium studies were subjected to Langmuir, Freundlich, and Temkin adsorption isotherm models

The Langmuir model

The linear equation for this model is stated as follows (Varank et al., 2012):

$$\frac{1}{q_e} = \left(\frac{1}{C_e}\right)\left(\frac{1}{bq\max}\right) + \left(\frac{1}{q\max}\right) \quad (2)$$

$1/q_e$ versus $1/C_e$ is the plot for Langmuir model for three adsorbents as explained in Fig. 5(a). The data derived from the slope and intercept on the Fig. 5(a) are shown in Table 1. Correlation coefficient, R^2 values of 0.998, 0.963 and 0.930 were obtained for UKC, 2-AKC and 2-BKC respectively.

Table 1 revealed that UKC has an adsorptivity value (142.86 mg g^{-1}) which is more than that of the 2-BKC (90.90 mg/g) and 2-AKC (83.33 mg/g). Also, the equation for R_L (dimensionless separation factor) is shown in Eq. (3):

$$R_L = \frac{1}{1 + K_L C_e} \quad (3)$$

R_L in Eq. (3) explains important features in the process and its value ranges from 0 to 1 (Table 1) which affirmed the removal of chlorotriazine molecules (Meenaa et al., 2005).

Freundlich model

For this isotherm, monolayer formation cannot be regulated (Halif et al., 2007). Its linear equation is:

$$\log\frac{x}{m} = \log K + \frac{1}{n}\log C_e \quad (4)$$

Log q_e versus Log C_e; is the plot for Freundlich isotherm (Fig. 5b) with intercept and slope of K_F and 1/n respectively as well as the correlation coefficient value, R^2 for UKC, 2-AKC and 2-BKC (Table 1).

The data had shown that removal process of chlorotriazine molecules on UKC, 2-AKC and 2-BKC adsorbents obey Langmuir and Freundlich adsorption isotherms with high R^2 values greater than 95%. The Freundlich constant, K_F of 15.07 mg/g for 2-BKC is greater than the Freundlich constant (K_F) for 2-AKC (K_F = 12.27 - mg/g) and UKC (K_F = 7.464 mg/g). It showed that the adsorption affinity for 2-BKC is greater than that of 2-AKC and UKC. The value for adsorption intensity implied appreciable adsorption as 1/n values are between 0 and 1(Halif et al., 2007).

Temkin Model

This is characterized by binding energies which is uniform distribution up to to the climax of binding energy (Tempkin and Pyzhev, 1940; Smitha et al., 2017). The linear equation of this isotherm is represented in Eq. (5):

$$q_e = \frac{RT}{b_T}\ln A_T + \left(\frac{RT}{b_T}\right)\ln C_e \quad (5)$$

$$\text{And } B = \frac{RT}{b_T} \quad (6)$$

Fig. 5(c) suggests that the Temkin model plots for the adsorbate adsorption onto UKC, 2-AKC and 2-BKC. From Table 1, the B_T (energies of adsorption) values were found to be 85.51, 126.78 and 109.72 for UKC, 2-AKC and 2-BKC respectively while A_T (equilibrium binding energy) values are 0.2403, 0.5227 and 0.7725 L mg^{-1} for UKC, 2-AKC and 2-BKC respectively. Therefore, adsorption rate of atrazine molecules are more strongly bonded to the sites of 2-AKC than to the surfaces of UKC and 2-BKC (Table 1).

The R^2 obtained indicated experimental data obtained in this study fitted well into the various adsorption isotherms data. On basis of R^2, the three isotherm models could be arranged in decreasing order of favoured adsorption isotherm as follows: Langmuir > Freundlich > Temkin for UKC, 2-AKC and 2-BKC.

Table 1
Equilibrium experimental data.

Isotherm		UKC	2-AKC	2-BKC
Langmuir	q_{max} (mg/g)	142.86	83.33	90.90
	K_L	0.02	0.07	0.12
	R_L	0.31	0.12	0.08
	R^2	0.99	0.96	0.93
Freundlich	K_F (mg g^{-1})	7.46	12.27	15.07
	n^{-1}	0.56	0.40	0.42
	R^2	0.96	0.94	0.96
Temkin	B	29.46	19.87	22.29
	b_T	85.5	126.8	109.7
	A_T (L/mg)	0.24	0.52	0.77
	R^2	0.99	0.85	0.92

Adsorption kinetics studies

The kinetic studies for the removal of this adsorbate onto UKC, 2-AKC and 2-BKC were illustrated by pseudo-1st order, pseudo-2nd order, intra-particle diffusion and Elovich kinetic models.

Pseudo-1st order and pseudo-2nd order kinetic models

The pseudo-first order and pseudo-second order kinetic models linearized forms are as Eqs. (7) and (8) respectively.

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (7)$$

Table 2
Adsorption kinetic parameters.

Kinetic Model		UKC	2-AKC	2-BKC
Pseudo 1st	k_1 (1/min)	0.0115	0.0576	0.0069
	q_e (mg g^{-1})	18.79	14.49	6.95
	R^2	0.90	0.94	0.81
Pseudo 2nd	k_2 (g mg^{-1} min^{-1})	0.0135	0.0107	0.0810
	q_e (mg g^{-1})	111.11	125.00	111.11
	R^2	0.99	0.99	1.00
Intra-particle diffusion	k_i (mg/gmin$^{1/2}$)	1.47	1.19	0.44
	C	97.9	109.6	103.3
	R^2	0.96	0.82	0.87
Elovich	A (mg/g/min)	52.142	7.49×10^{13}	1.02×10^{50}
	B (gm g^{-1})	0.181	0.293	1.122
	R^2	0.90	0.91	0.94

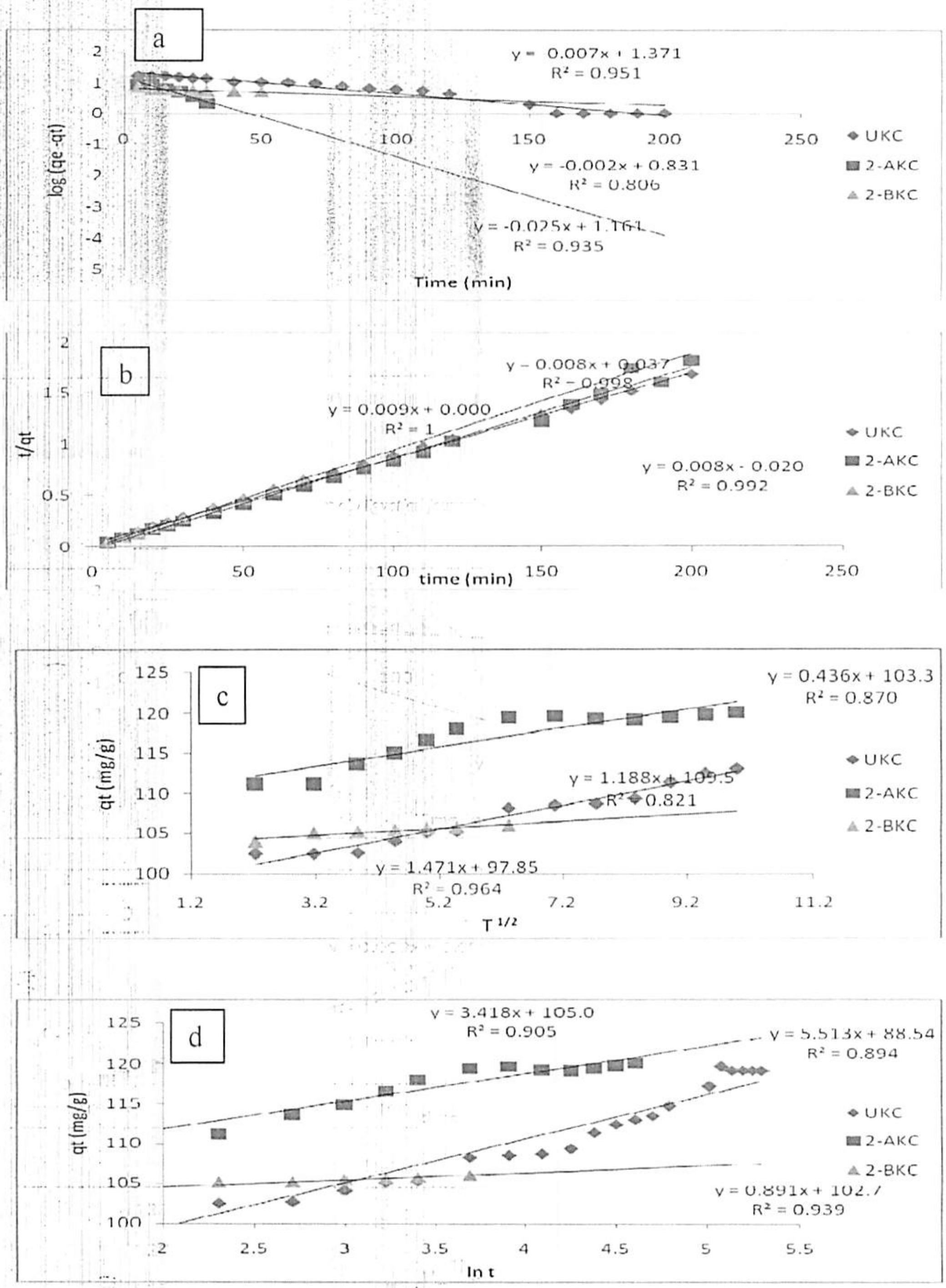

Fig. 6. Kinetic Studies for the removal of atrazine onto various kaolinite clays. (a) Pseudo-1st; (b) Pseudo-2nd; (c) Intra-particle; (d) Elovich. Percentage error is less than 5%.

Table 3
Thermodynamics parameters.

Adsorbent Temp. (K)	ΔH (kJ mol^{-1})	ΔS (J/mol)	ΔG (kJ mol^{-1})					
			303	313	318	323	328	333
UKC	−265.2	−0.663	−4033	−4011	−3904	−3535	−3207	−2894
2-AKC	−444.9	−1.211	−4898	−4379	−4097	−3966	−3078	−2791
2-BKC	−590.7	−1.681	−4509	−4354	−4303	−4252	−2322	−1626

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \tag{8}$$

From the plot linear plot (Fig. 6a), k_1 (rate constant) of adsorption of chlorotriazine at equilibrium q_e and its R^2 for pseudo first-order are shown in Table 3. The data for three adsorbents for pseudo first order kinetics model fell within ranges of R^2 (0.806–0.935) which were lesser than their corresponding value range of pseudo second order kinetics model R^2 (0.999–1.000). The experi-

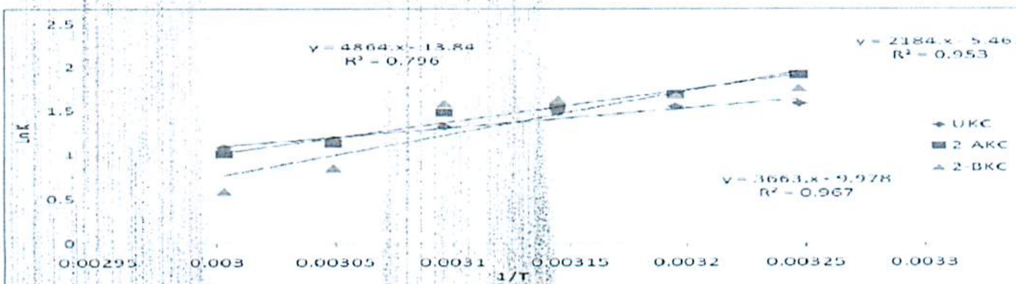

Fig. 7. The plot of thermodynamics for the removal of atrazine onto various kaolinite clays. Percentage error is less than 5%.

mental values of q_e were very close to the calculated values q_e for UKC, 2-AKC and 2-BKC.

The movement of adsorbate molecule onto the adsorbent surface from the aqueous solution diffusion (Khan et al., 2012) explained the rate of chemical reaction in intra-particle diffusion and is expressed in Eq. (9) (Bohli et al., 2013):

$$q_t = k_{id}t^{1/2} + C \tag{9}$$

where, k_{id} is intra-particle diffusion rate constant and C is the boundary layer thickness. The plot of q_t versus $t^{1/2}$ (Fig. 6c) explained effect of diffusion of the pores. The bulk diffusion is the important features attributed to initial linear portion; equilibrium is represented by plateau portion and intra-particle diffusion when it passes through origin. The rate constant of pore diffusion k_{id} values of 1.47, 1.188 mg/g min$^{1/2}$ and 0.436 mg/g min$^{1/2}$ obtained for UKU, 2-AKC and 2-BKC respectively showed that the diffusion of atrazine is substantial onto all the three adsorbents. This study showed that the linear line did not go through zero indicating that controlling step is not only intra particle diffusion but boundary surface effects are involved (Hatem et al., 2012).

The linearized form of Elovich equation is given as (Varank et al., 2012):

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \tag{10}$$

where, α (mg/g min) is the initial adsorption rate constant and β (g mg^{-1}) is the rate constant for desorption. The Kinetics study of removal of atrazine onto UKC, 2-AKC and 2-BKC also corresponded with Elovich of the linear form (q_t versus ln t) with high R^2 (Fig. 6d). The Elovich constants α and β computed from the plots are 52142 mg/g min, (0.181 g mg^{-1}), 7.49 × 10^{12} mg/g min, (0.293 g mg^{-1}) and 1.02 × 10^{50} mg/g min (1.122 g mg^{-1}) for UKC, 2-AKC and 2-BKC respectively (Table 2). These data could help to interpret the reason for longer time in reaching equilibrium during adsorption process.

From the studies, α, β values has been reported as 1.10 mg/g min and 1.05 g mg^{-1} respectively which were obtained for the removal of methyl orange using Bamboo Sawdust and 2.23 mg/g min and 0.58 g mg^{-1} when applied acid treated Bamboo Sawdust indicating that the treatment improved the capacity of the adsorbent (Khan et al., 2012). The comparison of pseudo 2nd order kinetic model R^2 range (0.99–1.00), illustrated that the process of adsorption is preferred for pseudo 2nd order kinetic model to Elovich model R^2 (0.895–0.939) (Table 2).

Thermodynamics studies

Enthalpy (ΔH), entropy (ΔS) and free energy (ΔG) changes explained the thermodynamic data for adsorption process which were calculated by:

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{11}$$

$$\Delta G = RT\ln K \tag{12}$$

where, T means absolute temperature in Kelvin, R means gas constant (8.314 J mol^{-1} K^{-1}). The plots of thermodynamic derived from Eqs. (11) and (12) are represented in Fig. 7 while the result for ΔH, ΔS, and ΔG are presented in Table 3.

Table 3 revealed that the enthalpy, entropy and free energy changes data are negative values which suggested exothermic process, decreased in the degree of disorderliness and spontaneous. (Varank et al., 2012; Hatem et al., 2013).

Conclusion

The experimental condition influenced the adsorption capacity of chlorotriazine molecules adsorbed by the three adsorbents. Langmuir isotherm best explained the removal of chlorotriazine onto UKC, 2-AKC, and 2-BKC while the kinetic studies was best described by pseudo-2nd order kinetic model which fitted the data of the experiment of the three kaolinite clays. Intra particle diffusion plus boundary surface mechanism contributed to mechanism of adsorption process. The process was exothermic and spontaneous. Thus, kaolinite clay has a high potential for the removal of atrazine from any aqueous media and could be recommend for industrial effluents removal.

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