



Research article

Adsorptive removal of 2,4,6-trichlorophenol in aqueous solution using calcined kaolinite-biomass composites



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ABSTRACT

Synergistically combined low-cost composites may be effective for the potential treatment of effluents containing organic pollutants. Hence, preparation of *Carica-papaya*-modified-kaolinite (CPK) and pine-cone-modified-kaolinite (PCK) composites via calcination of pure kaolinite (KAC), *Carica-papaya* and pine-cone seeds is demonstrated. The composites' specific surface areas were reduced by more than 57% but no structural modification in KAC lattice d-spacing, indicating impregnation of calcined biomass on clay surfaces and pores. However, composites' cation exchange capacities were enhanced over 4-fold, indicating higher potential for adsorption. Adsorption of 2,4,6-trichlorophenol on composites and KAC showed that CPK and PCK attained equilibrium relatively faster (30 min) compared to KAC (60 min). Modeling studies showed that 2,4,6-trichlorophenol removal mechanisms involved electrostatic interactions on sites of similar energy. Modification enhanced adsorption by 52 and 250% in PCK and CPK, respectively, and adsorption increased with temperature.

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1. Introduction

Water pollution by toxic substances is ubiquitous and an enormous challenge. This is because over 3.3 billion people of the global population lack reliable access to clean water or live in water-stressed areas, and this number is projected to rise by 52 percent in 2025 (Hejazi et al., 2011; Okoli et al., 2017). Recent high agricultural productivities have complicated the global water challenge because of its immense reliance on chemical substances which are vital for protecting food and fiber from damage by pests (Kellogg et al., 2002; USEPA, 2007). Several reports have indicated that the environmental concentrations and toxic effects of these substances are increasing and may be amplified by biomagnification up the food chain, inducing human health disorders (Eisler, 1989; Fisher, 1991; Kellogg et al., 2002; USEPA, 2007).

A common group of chemical substances— chlorophenols (pentachlorophenol, tetrachlorophenol, trichlorophenol, dichlorophenol and monochlorophenol) are ubiquitous in the

environment due to their wide-spread use in industry and agriculture, their formation during pulp bleaching and the incineration of organic materials in the presence of chloride (Antizar-Ladislao and Galil, 2004). Specifically, they are used in pesticides, wood preservatives, personal care formulations, fungicides, glue preservatives, insecticides, bactericides, defoliant, herbicides, anti-mildew agent for textiles, disinfectant and antiseptic in the treatment of Guinea worm ulcers, fungicides and molluscicides (IARC, 1979; HSDB, 2009; Xing et al., 2012). Chlorophenols are believed to be carcinogenic and thus have been listed as EPA priority pollutants (Wightman and Fein, 1999). Due to their presence in surface and ground waters, wastewater, sludge and drinking water (Xing et al., 2012), 2,4,6-trichlorophenol (2,4,6-T) has been used as a model chlorophenol in this study.

Adsorption-based methods of water treatment are techniques of choice due to several associated technological, economical and environmental benefits. These include low cost of materials and processing, no need for expert training, availability in abundance, good efficiency and environmental friendliness (Okoli et al., 2017). Synergistic combination of low cost sorbents (Unuabonah et al., 2013; Olu-Owolabi et al., 2016), a recent breakthrough in adsorption science has made possible the use of low-cost adsorbents

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which hitherto had one or more flaws in water treatment applications. The composites usually become enhanced by exploring the individual useful properties in the low-cost materials. Such composites are known to possess better physicochemical properties such as high cation exchange capacity (CEC), reduced/eliminated bleeding, enhanced mechanical strength, pore size, better stability and durability, re-usability, sometimes larger specific surface area, and consequently higher adsorption efficiency. The successful use of these composites for removal of aqueous inorganic pollutants (Unuabonah et al., 2013; Olu-Owolabi et al., 2016) is an indication that they may be useful for aqueous organic pollutants removal such as 2,4,6 trichlorophenol. Hence, the objective of this study is to prepare calcined kaolinite-biomass composites from kaolinite clay, *Carica papaya* and pine cone seeds, and use the composites for the removal of 2,4,6 trichlorophenol in aqueous solution.

2. Materials and methods

2.1. Materials and pretreatments of the sorbents

All reagents used for this study were analytical grade. 2,4,6-T (Chemical formula: $\text{Cl}_3\text{C}_6\text{H}_2\text{OH}$; molecular weight: $197.45 \text{ g mol}^{-1}$; purity: 98%; pK_a : 6.23 at 25°C ; $\log K_{ow}$: 3.69; water solubility at 25°C : 0.80 g L^{-1}) was obtained from Sigma–Aldrich (St. Louis, MO, USA). Absolute ethanol (HPLC grade) and milliQ water (1:1) were used in preparing the 2,4,6-T stock solution, while the working solutions were prepared from this stock using milliQ water only. Locally sourced *Carica papaya* and the pine cone seeds were sun-dried and subsequently oven dried to remove moisture. The seeds were then separately pulverized to fineness using a steel blender, and stored in air-tight containers for the study. Kaolinite (KAC) clay (from the clay reserve of Federal Institute of Industrial Research Oshodi (FIRO), Lagos, Nigeria) was pretreated by suspending in deionized water in order to remove sand and heavy non-clay materials. Organic matter in the clay was then removed by treatment with 30% H_2O_2 solution (Diagboya et al., 2015a). This was followed by washing with distilled water, drying at 105°C , sieving using a 230 mesh size sieve, and storage for the study.

2.2. Preparation of calcined clay-biomass combo

Preparation of the calcined clay-biomass combo followed similar methods reported by Olu-Owolabi et al. (2016) and Unuabonah et al. (2013). In summary, the treated clay and either of *Carica papaya* or pine cone seeds were weighed (1:1) into a beaker containing 0.1 M NaOH solution. The mixture was stirred and heated to dryness. The dry mass was placed in a crucible and calcined (300°C for 6 h). This was followed by washing to remove residual NaOH and then drying at 105°C . This process was carried out using KAC with either *Carica papaya* or pine cone seeds. The resulting adsorbents were labeled as *Carica papaya*-KAC (CPK) and pine cone-KAC (PCK). A schematic diagram of the modification

process is shown in Fig. 1.

2.3. Characterization of clay-biomass combo and 2,4,6-T adsorption study

The X-ray diffractogram (XRD) and infra-red (IR) spectra of the adsorbents were obtained using Bruker phaser X-ray diffractometer system and Fourier transform infrared (FTIR) spectrometer (Perkin Elmer Instruments Co. Ltd., USA), while specific surface areas were determined using Micromeritics ASAP 2020 M+ accelerated surface area analyzer (Micromeritics Instrument Corporation, USA). The pH of the adsorbents was determined in deionized water (ratio 1:1), while the pH at point of zero charge (pH_{PZC}) and Cation Exchange Capacity (CEC) were determined using the pH drift method and sodium saturation method, respectively, as described by Olu-Owolabi et al. (2016).

All adsorbents (KAC, CPK and PCK) were used for the adsorption study. Adsorption experiments were carried out in duplicate by adding 20 mL solution of 50 mg L^{-1} concentration of aqueous 2,4,6-T (except for effect of 2,4,6-T concentrations on adsorption) into the vials containing 100 mg of the adsorbent. The adsorbent and aqueous 2,4,6-T mixtures were then equilibrated in a controlled shaker at 100 rpm and 25°C (except where otherwise stated) until equilibrium. The pH of the experimental medium was adjusted as required during the study by adding drops of either 0.1 M HCl or 0.1 M NaOH solutions. The effects of time and pH on adsorption were investigated by varying the time from 15 to 1440 min and the pH from 2 to 10, respectively. The effects of 2,4,6-T concentrations were carried out by varying concentration from 30 to 150 mg L^{-1} and equilibrating for 1440 min, while the effect of temperature was carried out at 20, 35 and 50°C . The vials were centrifuged at equilibrium (3000 rpm for 10 min) and the concentrations of 2,4,6-T remaining in solution were determined using a UV–Visible spectrophotometer (Perkin Elmer, USA) at wavelength of 286 nm.

The initial (C_0) and final (C_e) concentrations of 2,4,6-T in solution were employed to estimate the amount of 2,4,6-T adsorbed at equilibration using the equation $q_e = (C_0 - C_e)v/m$; where q_e , v and m are the 2,4,6-T adsorbed (mg g^{-1}), volume of the solution (mL) and mass (g) of used adsorbent, respectively. The experimental data have been described using three kinetic models [Lagergren (1898) Pseudo–First Order (PFO) and Pseudo–Second Order (PSO), and the Weber and Morris (1963) Intra-Particle Diffusion (IPD) kinetic models], two adsorption isotherm models [Langmuir (1916) and Freundlich (1906)] and their thermodynamic parameters (details in Supporting Materials–SM 1).

3. Results and discussion

3.1. Clay and combo characterizations

The physicochemical characterization results are shown in Fig. 2 and Table 1. It was observed that upon the calcination of KAC with

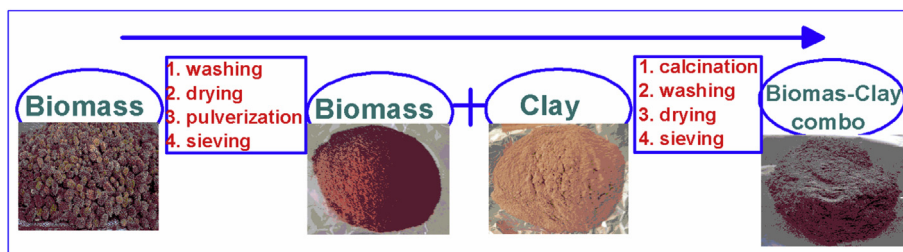


Fig. 1. Schematic diagram of clay modification with biomass.

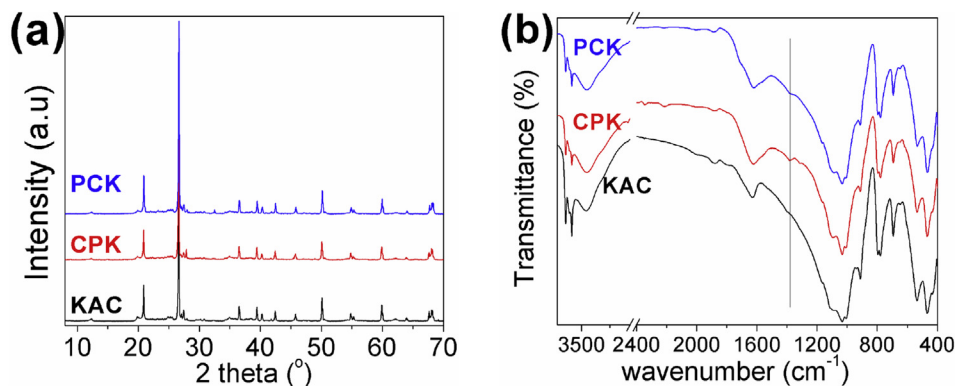


Fig. 2. (a) XRD and (b) FTIR spectra of KAC adsorbents.

Table 1
Physicochemical parameters of treated and modified KAC adsorbents.

	pH (H ₂ O)	pH (KCl)	CEC (meq 100g ⁻¹)	pH _{PZC}	Specific surface area (m ² g ⁻¹)
PC ^a	4.8	4.4	125.7	5.0	–
CP ^a	5.6	5.3	194.8	5.3	–
KAC	7.1	7.2	9.6	7.5	25.6
CPK	8.5	7.9	48.3	7.8	10.9
PCK	8.7	7.6	37.8	7.7	10.0

^a PC – Pine cone; CP – Carica papaya.

the biomasses, the specific surface area of the composite materials was reduced by more than 57% when compared with the pristine treated clay (Table 1). However, the XRD diffraction spectra of the pure and composite adsorbents (Fig. 2a) showed no significant changes in the position of the diffraction peaks of the adsorbents (Olu-Owolabi et al., 2016; Unuabonah et al., 2013); this strongly suggest that calcination of the clay with biomasses did not promote any structural modification in the basic d-spacing on the lattice of the clay, but that these biomaterials were only impregnated on the clay surfaces and pores or crevices. This assumption is supported by the reduction in the composites' specific surface areas upon impregnation as noted above (Table 1). The pH_{PZC} of the composite adsorbents increased for both *Carica papaya* and pine cone seeds calcined clay; though the *Carica papaya* modification was slightly higher. The pH_{PZC} of the pulverized biomasses (PC and CP) were much lower than those of the pristine clay and composite adsorbents; the higher pH_{PZC} of the composites may be attributed to delocalized π-electrons in lewis bases of oxygen-containing functional groups, such as pyrones or chromenes, formed during calcination of the biomass materials (Olu-Owolabi et al., 2016; Rivera-Utrilla and Sanchez-Polo, 2003). In accordance with the pH_{PZC}, the composites exhibited higher pH values than the pristine clay. The CEC of the treated clays increased upon calcination (Table 1); an indication that the composites may be effective in the adsorption of pollutants in aqueous solutions.

Fig. 2b show the infra-red spectra peaks between 4000 and 400 cm⁻¹ for the pure and modified clay. The spectra bands between 3700 and 3440 cm⁻¹ have been assigned to –OH groups vibrations lying between the tetrahedral and octahedral sheets of the clay, as well as the octahedral surface –OH groups which form hydrogen bonds with the oxygen of Si–O–Si bonds on the lower surface of the upper layer (Unuabonah et al., 2013; Johnston et al., 1990). The peaks between 1633 and 1626 cm⁻¹ were linked to the stretching and bending vibrations of H–O–H and –NH groups (Okoli et al., 2014; Unuabonah et al., 2013). The peaks around 1043 and 910 cm⁻¹ have been attributed to Si–O and Al–OH in plane bending vibrations, respectively, while the doublet between 807

and 782 cm⁻¹ were due to Si–O–Si inter-tetrahedral bridging bonds in SiO₂ and –OH deformation bands of gibbsite. Other peaks between 1110 and 450 cm⁻¹ confirm the presence of Si–O stretching and bending as well as –OH bending vibrations usually observed in pure kaolinite clay (Unuabonah et al., 2013). The modified adsorbents showed a new peak at 1390 cm⁻¹ which was attributed to –C–N band (Rivera-Utrilla and Sanchez-Polo, 2003); presence of this peak suggests that this may be the position of active interaction between the calcined biomass and the clay.

3.2. Rate and kinetic of 2,4,6-T removal from aqueous solution

The rate of a pollutant removal from aqueous solution is an important parameter that needs to be determined in order to ascertain the efficiency of an adsorbent for water treatment (Diagboya et al., 2015b). Hence, the rates of 2,4,6-T removal by the various adsorbents were determined in the time range of 15–1440 min and results are shown in Fig. 3a. It was observed that the 2,4,6-T (Fig. 3a insert) removal rates were very high in the initial 15 min of starting the process, and equilibrium was attained within 30 min for CPK and PCK, while the pure clay (KAC) equilibrium was attained after a longer time (60 min). The faster equilibrium observed in CPK and PCK may be attributed to the modification which resulted in faster 2,4,6-T removal rates. There were no significant increases in the removal of this pollutant upon equilibrium attainment. Increase in 2,4,6-T removal with time follows from the fact that at the beginning of the process, there are numerous vacant adsorption sites/pores which have high affinity for 2,4,6-T and thus the initial rapid increases after which little or no removal takes place as observed in Fig. 3a.

The data for the rates of 2,4,6-T removal from aqueous solution were subjected to the PFO, PSO and IPD kinetic models in order to identify the kinetic mechanism(s) involved in the adsorption process. All calculated model parameters are shown in Table 2. Comparison of the calculated PFO and PSO kinetic models parameters (adsorption capacity (q_e) and the closeness to unity of the correlation coefficient (r²) values) showed that the PSO was more

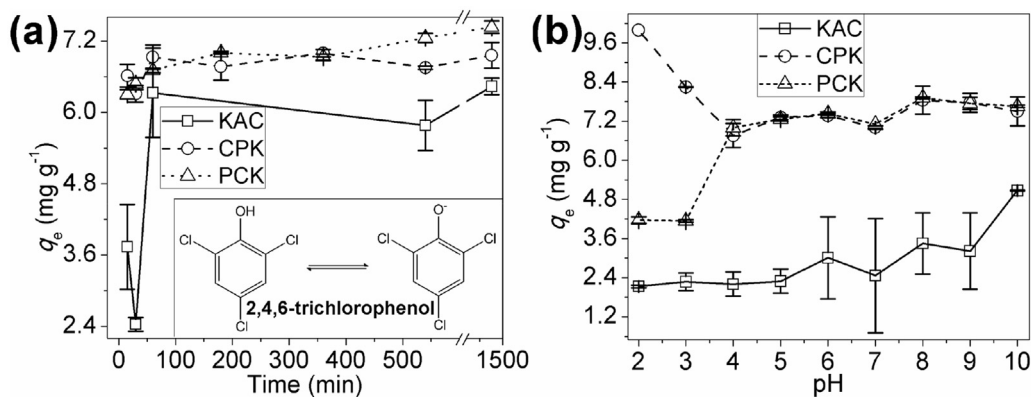


Fig. 3. Effects of (a) time (Insert: unionized and ionized 2,4,6-T) and (b) pH on KAC, CPK and PCK, on 2,4,6-T adsorption.

Table 2

Kinetic models parameters for 2,4,6-T adsorption on KAC, CPK and PCK.

Kinetic models	Parameters	KAC	CPK	PCK
PFO	q_e (mg g^{-1})	1.61	2.61	1.04
	k_1 ($\times 10^{-4}$) (min^{-1})	16.60	6.40	16.60
	r^2	0.479	0.253	0.928
PSO	q_e (mg g^{-1})	6.54	6.99	7.46
	k_2 ($\times 10^{-2}$) ($\text{g g}^{-1} \text{min}^{-1}$)	0.52	4.31	1.29
	r^2	0.997	0.999	0.999
IPD	C (mg g^{-1})	3.70	6.58	6.38
	k_1 ($\times 10^{-2}$) ($\text{g g}^{-1} \text{min}^{-1/2}$)	7.90	1.10	3.10
Experimental	q_e (mg g^{-1})	6.33	6.93	6.74
Pore adsorption ^a	%	41.6	5.1	5.4
Surface adsorption ^a	%	58.4	94.9	94.6

^a These values were obtained using experimental q_e and IPD q_e values.

appropriate in describing the data than the PFO. The PSO q_e values correlate better with the experimental q_e values while the r^2 values were closer to unity (≥ 0.997). The PFO showed gross underestimations for both the q_e and r^2 values, and thus cannot be used to describe the experimental data. The good fits of the experimental data to the PSO model suggests that the 2,4,6-T removal mechanism involves electrostatic interactions between the aqueous 2,4,6-T species and the adsorption sites (Okoli et al., 2017). The IPD model (Table 2) is another invaluable model used in describing adsorption processes because the magnitude of the parameter C (mg g^{-1}) gives an idea of the thickness of the adsorbed 2,4,6-T species on the various adsorbents' surfaces. When the value of C is the same as the experimental q_e value, it suggests that the bulk of the pollutant (2,4,6-T) was adsorbed on the surface of the adsorbent while lower values indicate partitioning within pores or internal spaces (Olu-Owolabi et al., 2015; Weber and Morris, 1963). The C values in Table 2 indicated that $\geq 58\%$ of the 2,4,6-T removal is surface adsorption on the pure KAC adsorbent while the rest $\approx 41\%$ is partitioning within pores. Upon modification, however, percentage surface adsorption became $\geq 94\%$; the trend in surface adsorption is KAC ($\geq 58\%$) > PCK \geq CPK ($\approx 94\%$). This is an indication that calcination of KAC with biomass blocks the pore spaces within the pristine clay, hence the observed reduction in specific surface area above (Table 1).

3.3. Effect of pH on 2,4,6-T adsorption

Another major parameter used for establishing the efficiency of an adsorbent for a pollutant is the response to variation in aqueous pH. This is vital because the extent of an ionizable pollutant's removal depends on the magnitude of charge density surrounding

either the pollutant or adsorbent, or both (An et al., 2010). Thus, the effect of pH on the adsorption of 2,4,6-T by these adsorbents has been carried. Fig. 3b shows the changes in 2,4,6-T removal with variation in the solution pH. It was observed that the adsorption on KAC and PCK increased with increase in pH until \approx pH 8 (which was the optimum pH of 2,4,6-T adsorption on all adsorbents as well as the pH_{pzc}). Though adsorption on KAC and PCK increased with pH, the variability for PCK was low while it was high for KAC between pH 6 and 9. This high variability observed for KAC may be an indication that weaker adsorption forces were involved in 2,4,6-T adsorption on KAC around this pH region.

The 2,4,6-T adsorption trends on the adsorbents were attributed to effects of pH on the adsorption sites as well as the 2,4,6-T species in aqueous solution. Recall that the calcination process resulted in the formation of surface amide II groups with delocalized π -electrons (Rivera-Utrilla and Sanchez-Polo, 2003; Olu-Owolabi et al., 2016; Unuabonah et al., 2013). The degree of formation of these groups may vary depending on the type of biomass used in the calcination process; here the results indicate that the quantity of these groups added to the CPK was far higher than for PCK. Hence, the adsorption trend of CPK and PCK may be explained. At pH < pH_{pzc} and with decreasing solution pH, the surface of the CPK becomes increasingly protonated. This can contribute to increase positive charge density within the adsorption surfaces; in this case, increasing the electrostatic attraction between 2,4,6-T species and adsorption surfaces resulting in enhanced adsorption (Fig. 3b). However, at pH \geq pH_{pzc} and with increasing solution pH, the surface of the CPK becomes deprotonated. This leads to decreased positive charge density within the adsorption surfaces; and hence, increased electrostatic repulsion between 2,4,6-T species and adsorption surfaces leading to lower adsorption. On the other hand, PCK with limited quantity of the added surface functional groups had lower 2,4,6-T adsorption especially at acidic pH region.

The adsorption trend on KAC was rather different. At lower solution pH, the 2,4,6-T species in solution and the adsorption sites on KAC were protonated. Thus, adsorption via electrostatic interactions was almost eliminated but removal of 2,4,6-T might have occurred through other forces as well as by partitioning within the pores of KAC. However, with increasing solution pH, these surfaces become protonated and adsorption occurred via electrostatic interactions between 2,4,6-T and the adsorption surfaces; hence, the increased adsorption.

3.4. Trichlorophenol adsorption dynamics

The effects of 2,4,6-T concentration and temperature on adsorption on all three adsorbents are shown in Fig. 4a–c. It was

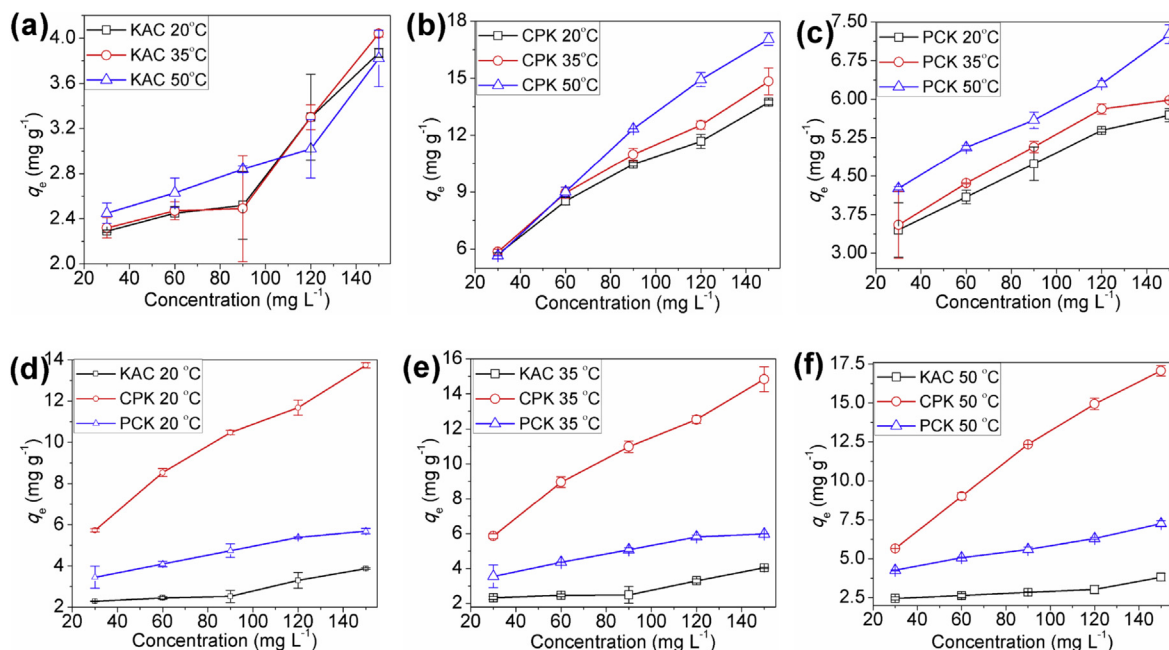


Fig. 4. *a–c* Trichlorophenol adsorption trend for each adsorbent as concentration and temperature increased; *d–f* Comparison of 2,4,6-T adsorbed on all adsorbents at each temperature studied.

observed that adsorption was concentration dependent, increasing as concentration increased. Fig. 4a showed that there was no significant difference in adsorption on KAC as temperature increased from 20 to 50 °C. However, adsorption increased with temperature (Fig. 4b–c) on the modified adsorbents following the trend 50 > 35 > 20 °C. The increased adsorption at higher temperature was attributed to the fact that the repulsive forces which act as barriers to the adsorption process are eliminated as temperature increased leading to easier adsorption.

Comparing the adsorption at the same temperature for the various adsorbents (Fig. 4e–f) showed that CPK had better performance than PCK and KAC at all temperatures. The adsorption trend for the adsorbents is CPK >> PCK >> KAC. The higher adsorption of 2,4,6-T on CPK may be attributed to the relatively higher CEC value (Table 1), higher surface amide II groups and apparently to the higher carbon content (Unuabonah et al., 2013) of *Carica papaya* modified clay. These are believed to provide more adsorption surfaces than the pristine clay for adsorption of non-polar organics. Multi-layer adsorption may occur through the π – π interaction between the already adsorbed 2,4,6-T and 2,4,6-T species in solution (Olu-Owolabi et al., 2014); and this may be the reason for the increased adsorption observed with increase in concentration (Fig. 4).

The experimental data at 20 °C was fitted to the Langmuir and Freundlich adsorption isotherm models (Table 3). Comparing the predicted adsorption by both isotherm models (Q_0 and q_e) to the experimental adsorption capacity (q_e) showed that the experimental data fit more to the Langmuir adsorption isotherm than the Freundlich. The correlation coefficients (r^2) of the Langmuir (≥ 0.87) also showed better correlation than the Freundlich (≥ 0.70). The better fit of the experimental data to the Langmuir is indication that the adsorption occurred on the adsorption surfaces of similar energy. Although the r^2 for adsorption on CPK and PCK suggested good fits to the Freundlich adsorption isotherm (≥ 0.96), this may be explained according to Weber et al. (1992). They showed that when adsorption occurs on dissimilar sites having different adsorbate affinities or adsorption energies, adsorption on the

Table 3

Calculated parameters for adsorption isotherm models.

Model	Parameter	KAC	CPK	PCK
Langmuir	Q_0 (mg g^{-1})	4.4	14.1	6.3
	β	0.03	0.12	0.06
	r^2	0.87	0.97	0.99
Freundlich	$1/n$	0.24	0.20	0.23
	K_f	1.04	5.19	1.87
	r^2	0.70	0.96	0.96
	q_e (mg g^{-1}) ^a	0.5	1.1	0.7
Experimental	q_e (mg g^{-1})	3.6	12.7	5.5

^a q_e – these values were obtained by inserting the calculated Freundlich adsorption isotherm parameters (Table 3) into the Freundlich equation.

various sites follow the Langmuir adsorption isotherm model. But if the sites have approximately equal adsorption energies, combination of their various Langmuir isotherms gives close approximation to the Freundlich adsorption isotherm model; hence, the good fit.

The experimental adsorption isotherm curves for 2,4,6-T adsorption obtained by plotting the q_e vs C_e data (SM Fig. 1) showed that the data at all three temperatures fitted better to the L-type (Langmuir type) isotherm (Giles et al., 1960). This is indicative of 2,4,6-T species adsorbed flat on the surface or sometimes, of vertically oriented species with particularly strong intermolecular attractions. This supports the prediction above that the experimental data is better described by the Langmuir adsorption isotherm model.

The calculated thermodynamic parameters (ΔG° , ΔH° and ΔS°) are shown in Table 4. The positive ΔS° values suggest an increase in randomness of 2,4,6-T species in solution as the adsorption process proceeded towards equilibrium due to increased degree of freedom for the molecules in solution. The ΔH° values for KAC and PCK were positive in conformity with experimental observation, an indication that the adsorption process was endothermic, thus increase in temperature would enhance the adsorption of 2,4,6-T on these adsorbents. The ΔH° values for CPK is however negative suggesting

Table 4
Thermodynamic parameters for 2,4,6-T adsorption.

Adsorbent	ΔH°	ΔS°	ΔG° (kJ mol ⁻¹)		
	kJ mol ⁻¹	J mol ⁻¹ K ⁻¹	293 K	308 K	323 K
KAC	9.32	15.71	4.51	4.94	3.99
CPK	-11.17	21.18	-4.29	-6.14	-3.50
PCK	12.81	34.64	1.61	4.48	0.34

an exothermic process; this notwithstanding, CPK exhibited better adsorption relative to PCK and KAC (Fig. 4d–f; Table 3) and this indicates that higher temperature might have contributed to reducing repulsive forces which act as barriers to the adsorption process (Olu-Owolabi et al., 2012). The magnitude of the calculated ΔH° also suggest that the energy involved in holding the 2,4,6-T species at the adsorption sites is compatible with energy strengths associated with physisorption (<40 kJ mol⁻¹) such as electrostatic interactions, π – π interactions and the Van-der Waals forces (Lavrich et al., 1998).

Negative ΔG° values were observed for CPK, indicating that the process is feasible and spontaneous (Diagboya et al., 2016). However, positive ΔG° values were observed for KAC and PCK. This does not imply that the process is not spontaneous but may be related to the fact that estimation of ΔG° using linear plots of thermodynamic models may introduce errors that could shift values from the borderline of one extreme to another. When such happens, reactions that have small but negative ΔG° could shift to small but positive ΔG° (Olu-Owolabi et al., 2014).

4. Conclusion

The *Carica papaya*-modified kaolinite (CPK) and pine cone-modified kaolinite (PCK) composites showed enhanced the cation exchange capacity of over 4-fold but their specific surface areas were reduced by more than 57%. No structural changes were observed in the clay upon modification indicating that the calcined biomass was mainly impregnation on clay surfaces and pores. The adsorption rates of 2,4,6-T were higher on composites than on pure clay, and removal mechanisms involved electrostatic interactions on sites of similar energy. Relative to KAC, modification enhanced adsorption by over 52 and 250% in PCK and CPK, respectively. The CPK was the best adsorbent and adsorption trend is CPK \gg PCK \gg KAC. Hence, these composites especially, the CPK, may be effective for the removal of 2,4,6-T from aqueous solution.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jenvman.2017.01.055>.

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