



## 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%;  $\text{pK}_a$ : 6.23 at  $25^\circ\text{C}$ ;  $\log K_{ow}$ : 3.69; water solubility at  $25^\circ\text{C}$ :  $0.80 \text{ g L}^{-1}$ ) 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%  $\text{H}_2\text{O}_2$  solution (Diagboya et al., 2015a). This was followed by washing with distilled water, drying at  $105^\circ\text{C}$ , 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 ( $300^\circ\text{C}$  for 6 h). This was followed by washing to remove residual NaOH and then drying at  $105^\circ\text{C}$ . 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 ( $\text{pH}_{\text{PZC}}$ ) 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  $50 \text{ mg L}^{-1}$  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  $25^\circ\text{C}$  (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  $150 \text{ mg L}^{-1}$  and equilibrating for 1440 min, while the effect of temperature was carried out at 20, 35 and  $50^\circ\text{C}$ . 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 ( $\text{mg g}^{-1}$ ), 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

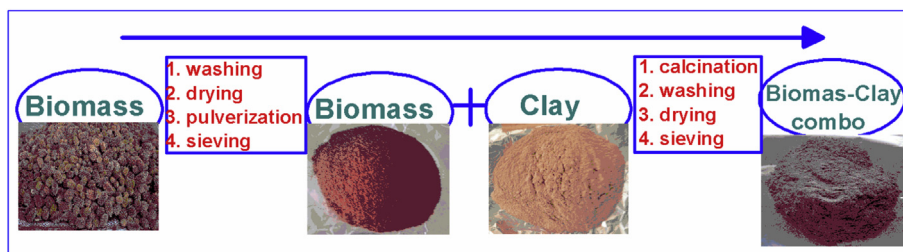


Fig. 1. Schematic diagram of clay modification with biomass.

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