

Introduction

There has been increased use of pesticides, fungicides, herbicides, and other chemicals in recent years for pest control and improved agricultural productivity, resulting in massive occurrences of pesticide residues and their metabolites in the environment [1-3]. DDT (dichlorodiphenyltrichloroethane), an organochlorine pesticide, belongs to the group of halogenated aromatic hydrocarbons and is transformed into its metabolites: 1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene (DDE) and 1,1-dichloro-2,2-bis(p-chlorophenyl)ethane (DDD) (Fig. 1) under reductive dechlorination conditions [3-4]. Although the application and production of DDT were banned worldwide during the 1970s by the Stockholm resolution because of ecological concerns, it was reintroduced in the 2000s in some tropical countries, which include Africa, for malaria, dengue fever, and yellow fever vector control by the World Health Organization [2-4].

In this study, the adsorbent was employed in a batch adsorption system for the sequestration of DDT, DDD, and DDE. An optimization study of the effects of adsorption conditions: adsorbent weight, pH, contact time and process temperature on the uptake capacity of pesticide on acid-modified adsorbent (ATCPP) was conducted.

The equilibrium behaviour of the adsorption process was exploited via adsorption isotherm models. Kinetic models (pseudo-first and second-order, intraparticle diffusion, Boyd model) were applied to the adsorption data to understand the mechanism of the adsorbate-adsorbent interaction.

In addition, the thermodynamics of adsorption processes was studied at different temperatures. The differential behaviour of pesticide (DDT, DDD, and DDE) adsorption was further studied through density functional theory (DFT), the Monte Carlo theory, and molecular dynamics (MD) simulations. The novelty associated with this research is embedded in the use of computational studies, that is, DFT Calculation, Monte Carlo Theory, MD Simulations for the study of DDT, DDD, DDE in the environment alongside low-cost plantain peel biosorbent for the first time in time in literature to the best of our knowledge.

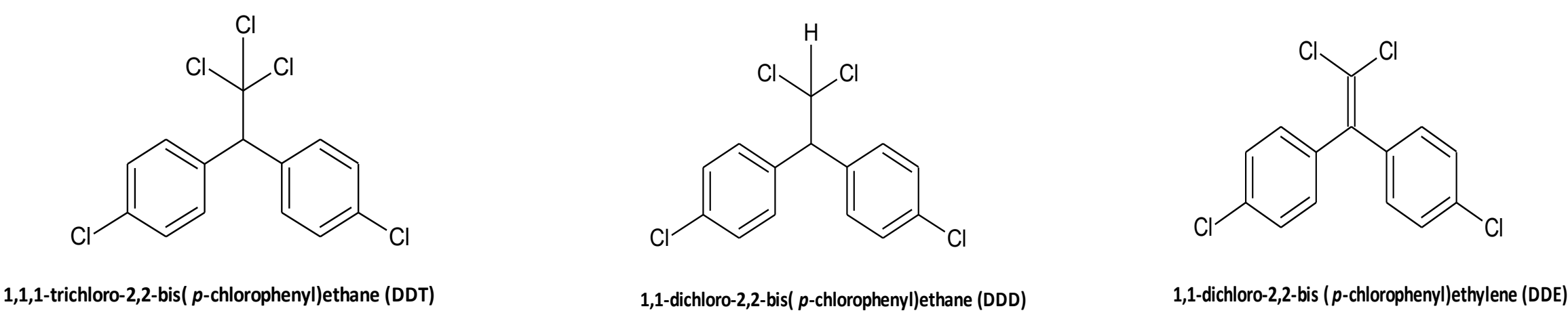


Fig. 1. Structure of DDT and its metabolites DDE, DDD

Preparation of Adsorbents

The carbonization process was carried out according to the procedure described by Umukoro et al. [5] in which case the oven-dried plantain peels were loaded into a covered earthenware pot and heated at high temperatures.

For activation, an equal mass/volume ratio of UPPC and 0.2 M sulphuric acid were mixed in a crucible. The mixture was allowed to stand for 24 h, after which it was filtered [6], repeatedly washed with deionized water until the filtrate reached a circumneutral pH and was oven-dried at 105°C to a constant weight. The activated biochar was labelled TPPC.

DFT calculations and Computational details

The computational calculations and the simulations have been performed through BIOVIA Materials Studio 2020 [7]. The Density Functional Theory calculation of DDT and its metabolites, DDD and DDE, has been performed to obtain the optimized geometry and understand their reactivity and physicochemical properties using the DMol3 module of Materials Studio[6].

MD simulation of the amorphous cellulose with the pesticide molecules adsorbed over its surface was performed to understand the equilibrium behaviour of the system. For MD simulation, the Forcite module of Materials Studio 2020 was utilized[8].

Results and Discussion

Characterisation of Adsorbents

The SEM micrograph and FT-IR analysis of the untreated carbon from plantain peel (UCPP) and acid-treated carbon from plantain peel (ATCPP) discussed in this study (Fig. 2) [8]. The increase in specific surface area and the formation of vacant active sites for adsorption influence the high adsorption capacity attributed to the acid-treated biosorbent [8].

The FT-IR analysis of the carbon adsorbents was observed in the spectral range of 400–4000 cm⁻¹ as shown in Fig. 3. The peak found at 657.73 cm⁻¹ may be associated with aromatic vibration. The other peaks at the wavenumbers 1065.85 cm⁻¹ and 1380.11 cm⁻¹ are linked to C-O in the aromatic ring and CH₃ bending vibration, respectively. The band at 3354 – 3248.13 cm⁻¹ is delegated to the stretching modes of the hydroxyl functional clusters O–H and H–O–H, confirming the presence of moisture [9].

Effects of Operational Parameters on Pesticide Adsorption

Influence of Adsorbent Weight. The result showed an initial increase in the percentage removal of DDT, DDD, and DDE on the activated carbon adsorbent (ACTPP) from 87.60% to 98.56%, as the adsorbent dose increased from 2-5 g/100mL (Fig. 3a).

Influence of Solution pH, This result showed that optimum adsorption efficiency occurred at pH 3 (Fig. 3b).

Impact of Temperature, The percentage adsorption of the pesticides slightly decreases with temperature (Fig. 3c), as the working temperature rises from 30 to 40°C; hence, maximum adsorption was achieved at 30°C.

Effect of Contact Time, The result showed that the removal efficiency of the pesticides increased with agitation time (Fig. 3d). This suggests that continuous bombardment of the organochlorine pesticide molecules on the surface of the adsorbent enhances the adsorption process. Rapid adsorption occurred over the first 60 min of adsorption, followed by a gradual uptake until equilibrium was reached at 120 min [8].

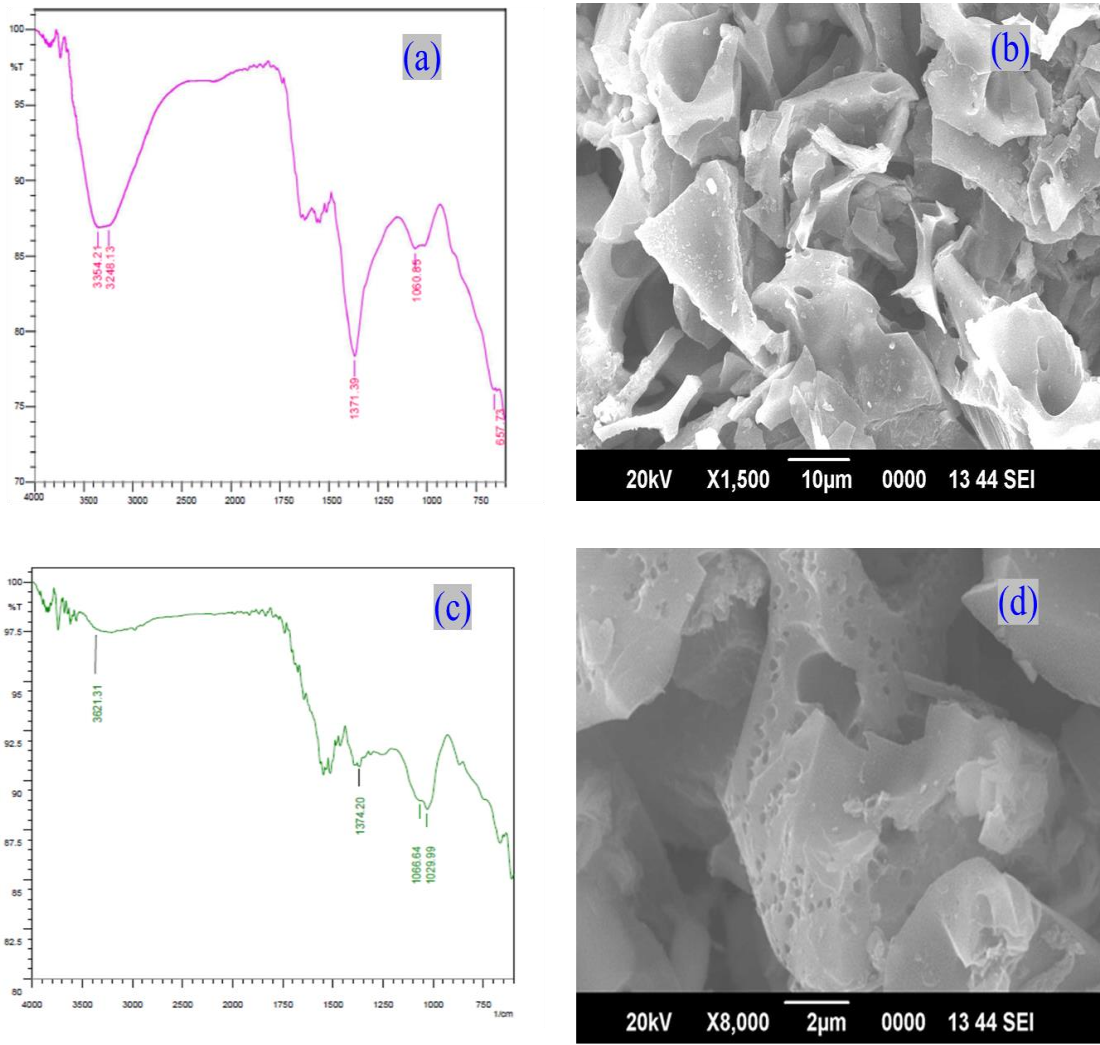


Fig. 2. FT-IR spectrum (a) and SEM micrograph (b) of Unactivated carbon from plantain peel (UPPC); FT-IR spectrum (c) and SEM micrograph (d) of Acid-treated carbon from plantain peel (ATCPP).

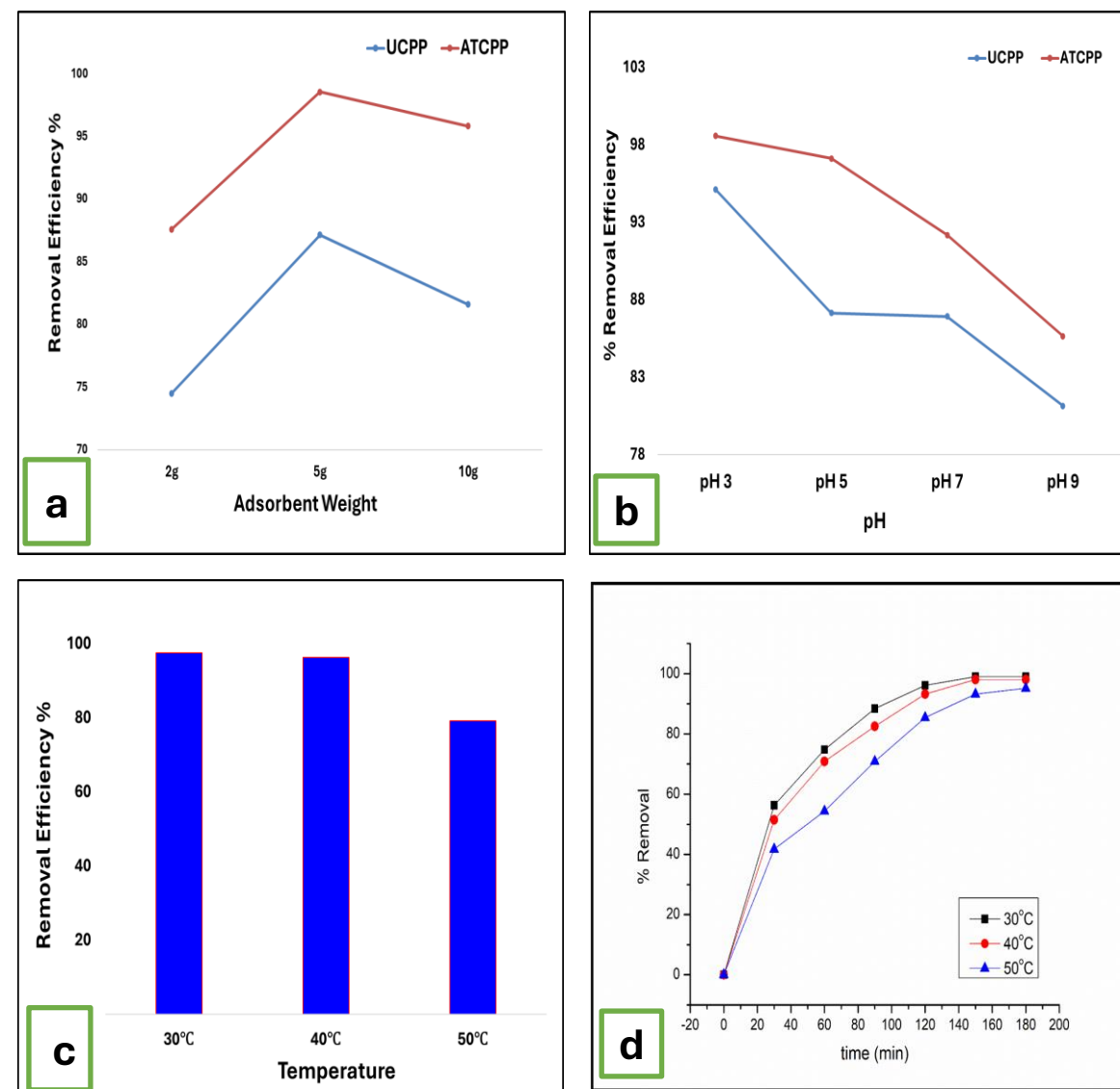


Fig. 3. Optimization study of the effects of adsorbent weight (a), solution pH (b), temperature (c), and contact time (d) on the pesticides' adsorption onto ACTPP.

Table 1. Energies of frontier molecular orbitals, dipole moment, and calculated physicochemical descriptors of pesticide molecules

Pesticide	E _H (eV)	E _L (eV)	dipole moment (Debye)	ΔE _{H-L} (eV)	η	χ	μ	ω	S
DDD	-5.861	-5.363	2.4495	0.498	0.249	5.6120	-5.612	3.921071	2.008032
DDE	-5.806	-3.811	4.4046	1.995	0.9975	4.8085	-4.8085	11.53193	0.5012
DDT	-5.930	-5.504	0.8699	0.426	0.213	5.7170	-5.7170	3.480855	2.347418

Footnote: E_H = E_{HOMO}; E_L = E_{LUMO}

DFT Computations and Monte Carlo

The DFT computations were performed to gain insights into the electronic properties and the reactivity of the pesticide molecules. The optimized structures of the pesticide molecules, their frontier molecular orbitals (FMO), highest occupied molecular orbital (HOMO), and lowest unoccupied molecular orbital (LUMO) are represented in Fig. 4. The energy of the FMOs provides a key insight into their reactivity, with the help of physicochemical descriptors which are chemical hardness (η), electronegativity (χ), electrophilicity index (ω), chemical potential (μ), and softness (S), which are obtained using Eq. 1 – 5 [8-10].

$$\eta = \frac{(E_{\text{LUMO}} - E_{\text{HOMO}})}{2}$$

$$\chi = \frac{-(E_{\text{LUMO}} + E_{\text{HOMO}})}{2}$$

$$\omega = \frac{\mu^2}{2\eta}$$

$$\mu = \frac{(E_{\text{LUMO}} + E_{\text{HOMO}})}{2}$$

$$S = \frac{1}{2\eta}$$

The HOMO-LUMO energies of the pesticides are the key indicator of their reactivity; the lower the energy of HOMO, the lower the donor ability. DDT exhibited the lowest E_H (-5.930 eV), suggesting it to be the most stable, among its metabolites. DDE exhibited the highest E_L of -3.811 eV, indicating its highest tendency to accept electrons among the three pesticide molecules.

The ΔE_{L-H} is the indicator of the chemical reactivity of the molecule. DDT possesses the smallest DE of 0.426 eV, implying its higher chemical reactivity and low kinetic stability, followed closely by DDD (0.498 eV). In contrast, DDE showed a significantly higher energy gap in their comparison (1.995 eV), suggesting its higher stability and lower reactivity [8, 9].

