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PH and Thermodynamic Modelling on Endosulfan Adsorption using Activated and Unactivated Boiler Fly Ash and Maize Cob

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Abstract

The persistence of endosulfan, a toxic organochlorine pesticide and persistent organic pollutant (POP), in aquatic environments presents serious ecological and human health risks due to its bioaccumulative and endocrine-disrupting properties. Conventional removal methods, such as advanced oxidation, membrane filtration, and biological degradation, often suffer from limitations including high cost, energy intensity, and secondary pollution. Adsorption using low-cost, abundant biomass-based materials has emerged as a sustainable alternative. In this study, the effects of pH and thermodynamic parameters on the adsorption of endosulfan from aqueous solutions were investigated using activated and unactivated boiler fly ash (BFA) and maize cob (MC). Adsorbents were prepared, characterized, and applied under varying pH (2–12) and temperature (30–110 °C) conditions to evaluate adsorption efficiency. Results indicated that pH significantly influenced adsorption behavior. For BFA, adsorption decreased with increasing pH, while for MC, adsorption increased with fluctuations, with maximum uptake observed at pH 10. Activation of the adsorbents enhanced adsorption capacity, attributable to increased surface area and modification of surface functional groups. Thermodynamic studies revealed distinct mechanisms: adsorption on BFA was exothermic with negative ΔH° values, while adsorption on MC was endothermic with positive ΔH°. Negative ΔG° values for BFA indicated spontaneous adsorption, whereas positive ΔG° values for MC suggested non-spontaneity under the studied conditions. The entropy changes (ΔS°) were negative for both adsorbents, implying decreased randomness at the solid–liquid interface. Sticking probability analysis further showed physisorption predominance for MC and unfavorable sticking on BFA. Overall, the study demonstrates that both boiler fly ash and maize cob, particularly in their activated forms, are effective low-cost adsorbents for endosulfan removal, though with different thermodynamic behaviors. These findings contribute to the development of sustainable, waste-derived adsorbents for pesticide remediation and highlight the importance of pH and thermodynamics in optimizing adsorption processes.

Keywords: Agricultural by-products; Biomass adsorbents; Contaminants; Environmental Remediation; Pesticides; Pollutants

1 Introduction

Endosulfan with chemical name 6,7,8,9,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,3,4-benzodioxathiepin-3-oxide, has been reported to be used on a variety of fruits, vegetables and many other plants. It is described as a broad spectrum contact insecticide. It is a widely used agricultural pesticide as a broad-spectrum insecticide on cotton, tea, sugarcane, vegetables, and fruit crops [51] despite its life-threatening toxic effects [45]. It has been reported that it is classified as a toxicity category 1 pesticide [50], and also described as a persistent organic pollutant (POP). Acute, accidental or intentional ingestion of large amounts of endosulfan has resulted to death in humans [17]. Some of the problems associated with POPs are their uptake by plants, resulting to increased food contamination and their persistence in the environment even when their application in the environment has been discontinued for a long time. Residues of a previously used pesticide, such as endosulfan, have been reported to occur around the world, giving rise to various toxicity problems [10, 9]. It became a highly controversial agricultural chemical due to its acute toxicity, potential for bioaccumulation, and role as an endocrine disruptor.

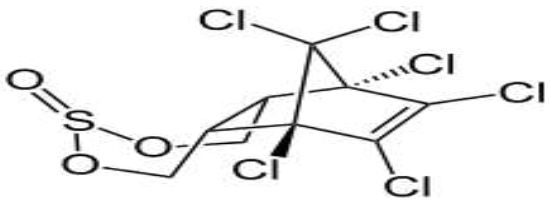


Figure 1: Chemical structure of Endosulfan pesticide [66]

Pesticides are common water pollutants and their major sources includes wastewaters from agricultural runoff, pesticides & insecticides production [48]. The mobility of pesticides is very high because most of them are highly water soluble, hence, the probability of their reaching and contaminating water sources downstream is very high. The mechanisms involved in the adsorption of endosulfan and the prediction of its movement in soils have been reported [37, 66]. Therefore, very high levels of Endosulfan concentrations in the environment can result to both acute and chronic toxicity. Hence, it is very important to find ways to remove endosulfan pesticide from the environment.

Processes such as advanced oxidation, Fenton's reaction, photochemical degradation, chlorination, biological treatment and membrane filtration [43, 57, 62, 5, 33] have been investigated for the removal of pesticides and other contaminants from aqueous solutions. These processes have some advantages and disadvantages, but their disadvantages, far outweigh the advantages. Such disadvantages include, sludge formation, formation of by-products, energy and cost intensive process, etc. [13]. The best method that has been recommended for the decontamination of wastewater such as pesticide contaminated wastewater, is adsorption because it is easy and cheap to carry out, it is cost effective and highly efficient. Also, there is wide availability of adsorbents, large surface area of adsorbents, high adsorption capacity and the existence of some surface functional groups, which enhances adsorption [6, 42, 21]. The only disadvantage reported for the use of adsorption method is that pesticides are transferred form one medium to another and not destroyed [6, 42]. This problem can be solved by follow-up regeneration after adsorption.

Activated carbon has been reported as the major conventional adsorbent used in adsorption [1]. Adsorption of pesticides from aqueous solutions using activated carbon has been reported [28, 20, 44, 48, 23]. As a result of the expensive nature of conventional activated carbon, adsorbents derived from waste biomass, can be a great asset to reduce the cost of wastewater treatment. Hence, in this study, boiler fly ash and maize cob biomass, both abundant agricultural wastes, were applied for the removal of Endosulfan pesticide from aqueous solutions. In this case, the use of adsorbent materials from agricultural wastes serves also as a means of waste reduction, increase in utilization of natural resources, sustainable development and increase in resource proficiency in a circular bioeconomy [22, 3, 14, 46, 31]. The use of maize cob and boiler fly ash as adsorbents for other contaminants have been previously reported [29, 8, 36, 24].

When it comes to adsorption processes, temperature and pH have been reported as very important parameters that affect adsorption reactions [12, 55]. Investigation of the effect of temperature helps to elucidate the classification of adsorption as either physisorption or chemisorption process. An increase in adsorption with increasing temperature suggests strong interaction between the [27]. Also, to understand the spontaneity and energy changes during adsorption reactions, a knowledge of the effect of temperature and thermodynamic parameters must be well understood. Again, it is a reported fact that the pH of adsorption solutions, usually affects the adsorption studies and most adsorption reactions are pH dependent [2, 68, 41]. During adsorption reactions, solution pH greatly affects the degree of ionization of the adsorbate and surface charge characteristics of the adsorbent (N'diaye et al. 2019). Therefore, this study investigated the influence of pH and temperature on the sorption capacity of boiler fly ash and maize cob waste biomass for the removal of Endosulfan pesticide from aqueous solutions.

2 Methodology

Boiler fly ash was obtained from an oil mill located at Uturu, Abia state, while maize cob was obtained from a refuse dump site at Eke market Okigwe, Imo State Nigeria. All reagents used were of analytical grade, purchased and used without further purification. InstakillEndosulfan pesticide ($C_9H_6Cl_6O_3S$), (6,7,8,9,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,3,4-benzodioxathiepin-3-oxide), 350g/L, manufactured by Zibo Nab Agrochemicals Ltd China was purchased and used without further purification. The chemical structure of the Endosulfan pesticide is shown in Figure 1 [66], while the properties of the pesticide are shown in Table 1 [52]. Doubly distilled-deionized water was used in all dissolutions and dilutions.

Table 1: Properties of Endosulfan pesticide [52].

Chemical formula	**Molar mass**	**Appearance**	**Odour**	**Density**
$C_9H_6Cl_6O_3S$	406.90 g mol^{-1}	Brown crystals	Slight sulphur dioxide odour	1.745 g/cm^3
Melting point	**Boiling point**	**Solubility in water**	**Vapour pressure**	
70 to 100 °C	decomposes	0.33 mg/L	0.00001 mmHg (25 °C)	

2.1 Preparation of adsorbents and adsorbates

The maize cob was washed thoroughly with water and then with de-ionized water, ground to powdered form and air dried. Big lumps in the boiler fly ash were removed and both maize cob and boiler fly ash were sieved using a test sieve shaker (EFL IMK3 model made by Endecotts England). The meal that was retained on the 250 µm was used. The adsorbents were divided into two parts each. One part each was dissolved in 2% (v/v) nitric acid for 24hrs, filtered and air dried. These were stored as activated boiler fly ash (Act-BFA) and activated maize cob (Act-MC) for experimental studies. The remaining parts each were left unactivated and labelled as unactivated boiler fly ash (Unact-BFA) and unactivated maize cob (Unact-MC). The physicochemical characteristics of the adsorbents and other characterizations such as FT-IR, XRD, SEM, have been reported. Stock solutions of known concentrations of Endosulfan were prepared. Different concentrations were obtained from the stock solutions by serial dilutions. A 200-960 nm wavelength UV/vis spectrophotometer was used to determine concentrations of pesticide in the solution after adsorption. A calibration curve using Beer Lambert principle was used to obtain residual Endosulfan concentrations.

2.2 Effect of pH

The effect of pH of the endosulfan pesticide solutions was determined for each adsorbent for one hour at constant temperature. 100 mL of a known concentration of pesticide solution and 1g of each adsorbent of 250 µm particle size were used. The pH of each solution was adjusted to 2, 4, 6, 8, 10 and 12 respectively using 0.1M HCl or 0.1M NaOH. Each solution was placed in a rotary shaker and agitated for one hour after which the content of each flask was filtered using Whatman No.41 filter paper. The pesticide concentration in the filtrate was also determined using a UV-vis absorption spectrophotometer model SP-300.

2.3 Effect of Temperature

Sorption studies at different temperatures were carried out according to the procedure described by [30]. The effect of temperature of adsorption of the Endosulfan pesticide solutions were determined for each adsorbent for 1hr at constant pH of 7.5. 100 mL of a known concentration of pesticide solution and 1g of each adsorbent of 250 µm particle size were used. The temperature of each solution was adjusted to 30, 50, 70, 90 and 110 °C using a water bath. Each solution was placed in a water bath at regulated temperature and agitated for 1hr after which the content of each flask was filtered using Whatman No.41 filter paper. The pesticide concentration in the filtrate was also determined using a UV-vis absorption spectrophotometer model SP-300.

3 Results And Discussion

The activation of the boiler fly ash and maize cob biomass with 2% (v/v) nitric acid was to possibly open up the microspores of the adsorbent and make them ready for adsorption. Also, activation helps to wash off any soluble biomolecule that might interfere with the adsorption process. The amount of Endosulfan pesticide adsorbed for each of the parameters; pH and temperature were plotted to find the variation in the adsorption capacity for the effect of each of the parameters. The amount of pesticide adsorbed from solution was calculated by a mass balance equation as shown below:

$$q_e = \frac{V(C_0 - C_e}{m} \tag{1}$$

where, q_e is the amount adsorbed (mg/g); V is the volume of the solution (L); C_0 is the initial pesticide concentration (mg/L); C_e is the pesticide concentration in the filtrate (mg/L) and m is the mass of adsorbent used (g).

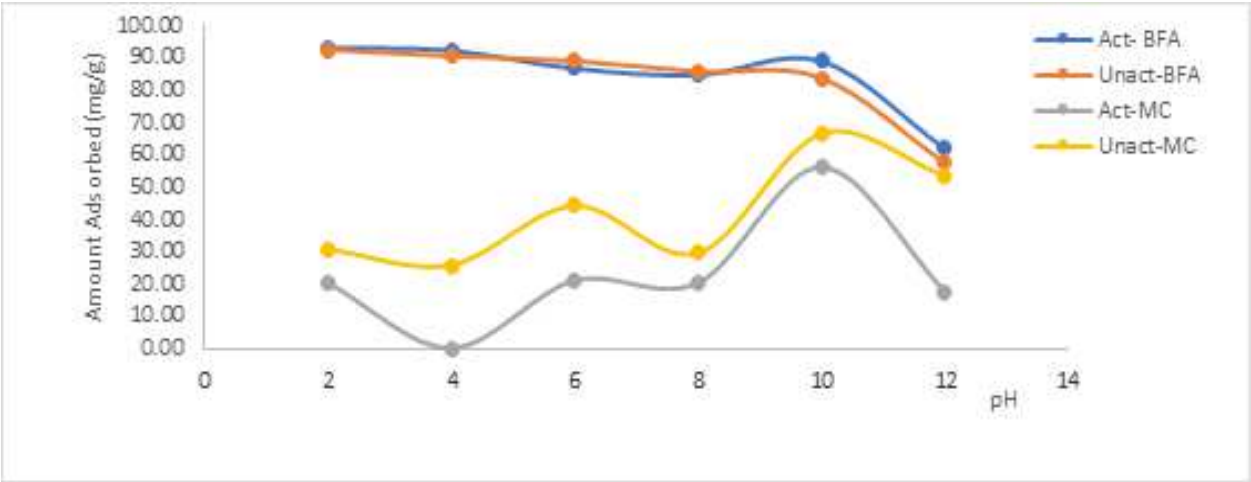


Figure 2: Amount adsorbed against pH for adsorption of Endosulfan pesticide using activated and unactivated boiler fly ash and maize cob

3.1 Effect of pH of Solution

adsorbate and surface charge characteristics of the adsorbent is greatly influenced by solution pH [53]. Therefore, the initial solution pH plays a pivotal role in the adsorption process by altering the adsorbent's surface charge via the point of zero charge and influencing the speciation, hydrogen bonding potential, and interfacial behavior of the adsorbate. These pH-dependent changes affect electrostatic attraction or repulsion, hydrophobic partitioning, and surface hydrogen-bonding interactions—all of which critically determine adsorption efficiency across different adsorbents and pesticides [4, 58]. The results for the effect of pH of solution are shown on Figure 2 for Endosulfan adsorption.

Figure 2 shows that increase in the pH from 2 to 12 resulted to a decrease in adsorption of Endosulfan on activated (Act-BFA) and unactivated (Unact-BFA) boiler fly ash. For activated (Act-MC) and unactivated (Unact-MC) maize cob, it increased but fluctuated. Maximum adsorption for Endosulfan was observed at pH of 10. Activation of the adsorbents also affected their adsorption capacity with respect to solution pH. Most adsorbents (activated carbon, metal oxides, biochars, geopolymers) have surface functional groups (–OH, –COOH, $–NH_2$) whose protonation changes with pH. Changes in electrostatic interactions with anypolar or ionized species at the interface can influence orientation and packing of neutral hydrophobic molecules at the surface. For endosulfan (neutral), changes in surface polarity and hydrogen-bond donor/acceptor behavior have been reported to be very important [39, 32, 25]. This indicates that at high pH the adsorbent surface was charged negatively, while at low pH the adsorbents surface was charged positively [69].

Optimal pH levels for adsorption has been reported to vary depending on the particular pesticide and adsorbent, but generally, pH around neutral value (6.5-7.5) have been reported [64, 38]. Although, a slightly acidic to neutral pH (around 5-7) have also been reported as often observed to be beneficial [38, 32]. For Endosulfan-a technical mixture of $\alpha-$ and $\beta-$ isomers, it has been reported as a largely neutral, hydrophobic organochlorine pesticide. Because it is non-ionizable, pH does not change it's charge directly; instead pH may affect adsorption largely by (1) changing the surface charge and protonation of the adsorbent, (2) altering hydrogen-bonding capability and site availability, (3) controlling competition with OH^- and other ions for adsorption sites, and (4) changing the chemical stability of endosulfan by alkaline hydrolysis, which reduces initial concentration and can be mistaken for reduced adsorption [47, 39, 25]. Therefore, endosulfan adsorption often depends on hydrophobic partitioning into non polar regions of the adsorbent (carbonaceous domains, organic matter). Acidic pH that keeps surface functional groups protonated can increase hydrophobic character and favour adsorption in some adsorbents. Conversely, deprotonation (higher pH) increases surface polarity and can reduce hydrophobic partitioning. Hydrogen bonding, that is, adsorbent –OH with endosulfan O/Cl sites, can also be pH-sensitive [47, 39]. At high pH (alkaline), abundant OH^- competes for and screens active sites, and deprotonated surfaces repel polar adsorbates or reorganize the interfacial water, often lowering adsorption. Several experimental studies report decreased removal efficiency as pH rises beyond neutral [39, 32, 25]. Activated adsorbents (Act−MC and Act−BFA) behaved differently from their unactivated forms. Activation by chemical treatment modifies the surface area, porosity, and functional groups on the adsorbent.This

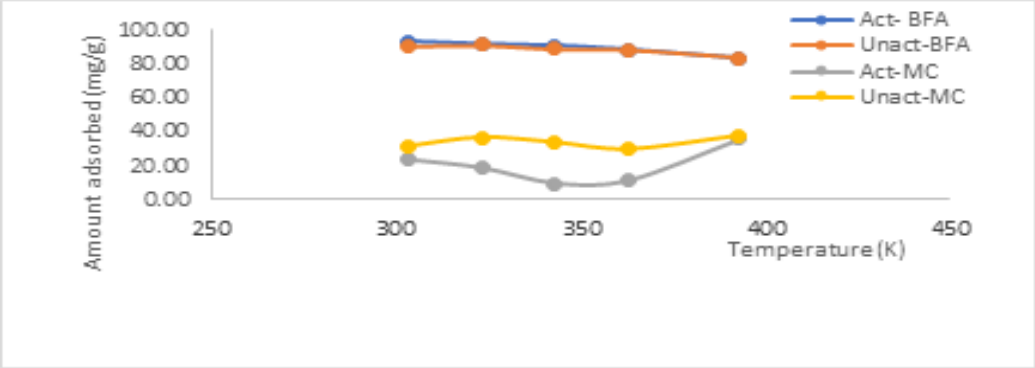


Figure 3: Amount adsorbed against Temparature (K) for adsorption of Monocrotophos pesticide using activated and unactivated boiler fly ash and maize cob

affects how the adsorbent interacts with pesticide molecules under different pH conditions. Activation generally enhances adsorption, but its effect is pH dependent [65, 18]. At low pH, adsorbent surfaces are protonated, carrying a positive charge.At high pH, they become deprotonated, carrying a negative charge. Endosulfan, though largely neutral, has polar groups and can interact with charged sites through-Van der Waals forces, Hydrogen bonding and electrostatic interactions if partial ionization occurs [35, 15]. Thus, the solution pH affected both the surface charge of the activated and unactivated boiler fly ash and maize cob and the hydrophobic partitioning of the pesticide into non polar regions of the adsorbent

3.2 Effect of Temperature of Solution

The importance and role of temperature in adsorption studies has been described as crucial because it helps to classify adsorption as either physical or chemical. When adsorption increases with increase in temperature, it depicts strong interaction between the adsorbent surface and adsorbate, which suggests chemisorption [27]. For proper understanding of the spontaneity and changes in energy during the entire sorption process, adequate knowledge of the thermodynamic parameters for the equilibrium process is very important [11, 16]. The results of the effects of varying temperature of the sorption system are shown in Figure 3.

3.3 Thermodynamic Modelling

Thermodynamic analysis provides insights into the feasibility, spontaneity, and nature of adsorption. Parameters such as Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) are commonly evaluated. Negative ΔG° values confirm spontaneous adsorption, while positive ΔH° values suggest endothermic processes, indicating that higher temperatures enhance adsorption efficiency [19]. Thermodynamic parameters such as enthalpy change (ΔH°) and entropy change (ΔS°), were calculated from the van't Hoff equation (Eq. 2); the Gibbs free energy change (ΔG°) for the adsorption process were calculated using equation 3 [49]; while activation energy (E_A) and sticking probability (S^*) were evaluated from the sticking probability plot (Eq. 4) [29].

$$InK = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \tag{2}$$

$$\Delta G^{\circ} = -RTInK \tag{3}$$

$$S^* = (1-\theta)\exp^{-\frac{E_A}{RT}} \tag{4}$$

where R is the molar gas constant; T is absolute temperature, K is the equilibrium constant for the adsorption process and θ is the fractional attainment to equilibrium, given by the equation below:

$$\theta = 1 - \frac{C_e}{C_o} \tag{5}$$

The graph of the linear form of Eq. 4 was used to evaluate the sticking probability (S^*) values. The Van't Hoff plots are shown on Figure 4, while the sticking probability plots are shown on Figure 5.

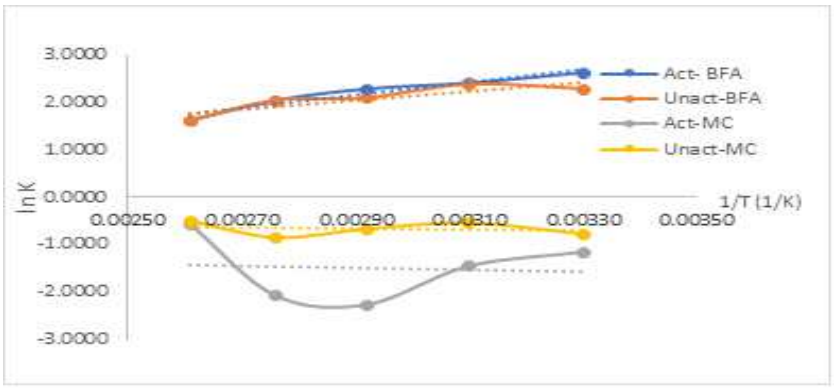


Figure 4: Vant Hoff plot for adsorption of Endosulfan pesticide using activated and unactivated boiler fly ash and maize cob

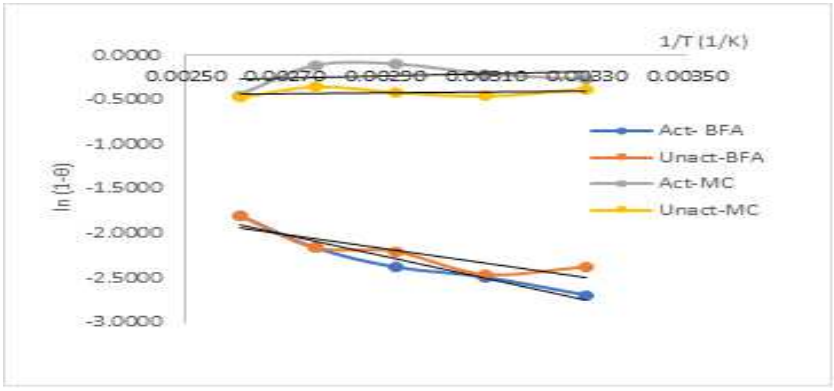


Figure 5: Sticking probability plot for adsorption of Endosulfan pesticide using activated and unactivated boiler fly ash and maize cob

For Endosulfan pesticide studied, boiler fly ash gave higher adsorption as temperature increased than maize cob. Temperature may affect endosulfan adsorption in three major ways: (1) it changes the rate, that is, the kinetics of the adsorption process- higher temperature usually speeds mass transfer and diffusion to adsorbent sites; (2) it changes the equilibrium capacity depending on the adsorption mechanism, that is, if the adsorption is endothermic or exothermic; and (3) it affects competing loss processes, that is, alkaline hydrolysis, volatilization, or biodegradation, that can reduce initial pesticide concentration [7]. Raising the temperature increases molecular diffusivity and often reduces the thickness of the stagnant boundary layer at particle surfaces, so endosulfan reaches adsorption sites faster and shorter equilibration times are observed. Many batch studies therefore report faster approach to equilibrium at higher temperatures [39]. If the adsorption process is endothermic ($\Delta H^\circ > 0$), increasing temperature increases equilibrium adsorption capacity because heat supplies the energy for the interaction (commonly observed when adsorption involves chemical bond formation, structural re-arrangements in the adsorbent, or displacement of strongly bound water) [66]. It has also been reported that if the adsorption is primarily physisorption (van der Waals/hydrophobic partitioning) it is often exothermic ($\Delta H^\circ < 0$); therefore adsorption capacity may decrease with increasing temperature From Figure 3, it could be seen that the adsorption process is exothermic for adsorption of endosulfan on boiler fly ash and endothermic for adsorption of endosulfan on maize cob, influenced by hydrophobic interactions and hydrogen bonding [63]. Several adsorption studies reported increasedendosulfan uptake with temperature and computed positive ΔH° values, indicating endothermic sorption [67, 60, 25]. Also, different adsorbents have been reported to show either trend-endothermic or exothermic [59, 56, 54], the direction depends on adsorbent surface chemistry, porosity and the dominant sorption mechanism. Thermodynamic parameters, ΔH° , ΔS° , E_A and the sticking probability (S*) were evaluated and recorded in Table 2. The Gibbs free energy (ΔG°) for the sorption process were calculated and shown in Table 3. The values of ΔH° are negative for boiler fly ash and positive for maize cob and large values were obtained suggesting exothermic for adsorption of Endosulfan on boiler fly ash and endothermic for adsorption of Endosulfan on maize cob. Also, the values of ΔS° were all negative for Endosulfan on boiler fly ash and maize cob. The negative values of ΔS° suggest a reduced randomness at the adsorbent/solution interface during the sorption process. On the other hand, positive and high values of ΔS° suggest an increased randomness. Other authors have reported similar results [34, 61]. Calculation of activation energy helps distinguish diffusion-controlled from chemically-controlled adsorption. Low activation energies typically indicate physisorption/diffusion control; higher values indicate chemisorption. Several endosulfan adsorption papers report activation energies and use them to interpret whether adsorption is mainly physical or chemical. All the values of ΔG° were negative and large for adsorption of Endosulfan on boiler fly ash, but positive for maize cob, indicating that the sorption of the pesticide on boiler fly ash was spontaneous but was not spontaneous on maize cob. Higher negative value of ΔG° (above -40 KJ $gmol^{-1}$) involve charge sharing from the biomass surface to the pesticide to form a coordinate bond (Chemisorption), while a lesser negative value of ΔG° (up to -20 KJ $gmol^{-1}$) are consistent with physisorption, i.e. electrostatic interaction between pesticide molecules and sorption sites. The decrease in ΔG° (i.e. increased negative) values with increase in temperature indicated more efficient adsorption at higher temperature.The values of thermodynamic equilibrium constant range from 0.76 to 0.86. This shows that a greater amount of the pesticides was removed because their values were greater than 0.5. Also, the potential sticking probability model was used to ascertain whether the sorption process was of physiosorption or chemisorption mechanism. It was also used to confirm the probability of the pesticide molecules remaining on the surface of the adsorbent. The values of the activation energy EA were very high and negative for adsorption of Endosulfan on boiler fly ash but positive for adsorption using maize cob.

Table 2: Thermodynamic constants for adsorption of Endosulfan pesticide using activated and unactivated boiler fly ash and maize cob

Constants	**Boiler fly ash (BFA)**		**Maize Cob (MC)**	
	Unactivated BFA	**Activated BFA**	**Unactivated MC**	**Activated MC**
ΔS^0	-5.63	-15.03	-2.27	-7.85
ΔH^0	-7809.34	-11329.49	1132.37	1618.65
R^2	0.7680	0.9315	0.0674	0.0058
S^*	1.25	3.55	0.57	0.55
E_A	-6872.93	-10114.81	407.59	1038.00
R^2	0.7719	0.9393	0.0767	0.0582

Also, the potential sticking probability (S^*) which is used to ascertain the mechanism of adsorption, was em-

ployed according to the following conditions: (1) $S* > 1$: Adsorbate unsticking to adsorbent no sorption; (2) $S^* = 1$: Linear sticking relationship between adsorbate and adsorbent-possible mixture of physiosorption and chemisorption; (3) $S^* = 0$: Indefinite sticking of adsorbate to adsorbent chemisorption mechanism predominant and (4) $0 < S^* < 1$: Favourable sticking of adsorbate to adsorbent physiosorption mechanism predominant. It was also used to confirm the probability of the pesticide molecules remaining on the surface of the adsorbent. As seen from the results of the sticking probability on Table 2, S^* values were 1.25 and 3.55 for unactivated BFA and activated BFA respectively, showing conforming to condition (1) $S* > 1$: Adsorbate unsticking to adsorbent no sorption. On the other hand, the S^* values for unactivated and activated MC were 0.57 and 0.55 respectively, agreeing to condition (4) $0 < S^* < 1$: Favourable sticking of adsorbate to adsorbent physiosorption mechanism predominant. Sticking probability model has been used to evaluate the mechanism of adsorption processes [29].

Table 3: Values of change in standard Gibbs free energy (ΔG^0) for adsorption of Endosulfan pesticide using activated and unactivated boiler fly ash and maize cob

	$\Delta G^0 KJgmol^{-1}$			
	Activated BFA	**Unactivated BFA**	**Activated MC**	**Unactivated MC**
303	-6775.4	-6103.5	3996.6	1820.2
323	-6474.8	-5990.9	4154.2	1865.6
343	-6174.2	-5878.3	4311.2	1911.0
363	-5873.6	-5765.7	4468.2	1956.4
383	-5573.0	-5653.1	4625.2	2001.8

Again, for intraparticle diffusion to occur [26], then it means that the adsorbate diameter is smaller than the adsorbents pore size, hence, the adsorbate ion can easily be trapped on the adsorbent surface in the micropores and mesopores of the adsorbent [40]. But only the surface area and filling of pores, cannot determine the adsorbate adsorption during the process of adsorption. The SEM analysis shows that the surface morphology of the adsorbent changes after adsorption, indicating that pesticides partially adsorbed on the adsorbents outside surfaces through the process of diffusion [70]. This means that both surface diffusion and intraparticle diffusion took place during the sorption process.

4 CONCLUSIONS

This study has shown that activated and unactivated boiler fly ash (BFA) and maize cob (MC) can serve as effective, low-cost adsorbents for the removal of endosulfan pesticide from aqueous solutions. Adsorption was strongly influenced by pH, with BFA exhibiting higher uptake at acidic conditions while MC favored alkaline conditions. Activation improved performance in both cases, underscoring the role of surface modification in enhancing adsorption sites. Thermodynamic analysis revealed different mechanisms of adsorption. For BFA, the process was spontaneous and exothermic, suggesting a favorable physical adsorption pathway. In contrast, MC adsorption was endothermic and non-spontaneous within the studied range, indicating dependence on external energy input. The negative entropy changes for both adsorbents point to decreased randomness at the solid–liquid interface during endosulfan binding. Overall, the findings demonstrate that agricultural and industrial wastes such as maize cobs and boiler fly ash can be valorized into environmentally friendly materials for pesticide remediation. Their distinct adsorption behaviours also provide useful insights for tailoring conditions to optimize removal efficiency in real water treatment applications. It is recommended that (1) Optimization of operating conditions: Since adsorption efficiency is strongly influenced by pH and temperature, water treatment systems employing BFA or MC should be designed to operate under conditions that maximize removal efficiency; (2) Scaling up for field application: Pilot-scale studies are needed to assess the performance of these adsorbents under real wastewater conditions, where multiple contaminants and fluctuating water chemistries may interact with adsorption processes; (3) Further material modification: Surface functionalization of maize cob and boiler fly ash using green activation methods could enhance their adsorption capacity and selectivity for pesticides and related organic pollutants; and (4) Integration with treatment technologies: BFA and MC adsorbents can be combined with biological or advanced oxidation processes to develop hybrid, cost-effective, and sustainable remediation systems.

5 ACKNOWLEDGMENTS

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6 DECLARATION OF CONFLICT OF INTEREST

The authors confirm that they have no conflicts of interest to declare.

7 FUNDING INFORMATION

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8 AUTHOR CONTRIBUTION

Conceptualization, Funding acquisition: B. O. Osu; data collection: Statistical analysis: J. C. Igwe, B. O. Osu; data interpretation: J. C. Igwe, C. Olunkwa, K.E. Onwuka; writing the first draft: J. C. Igwe, B. O. Osu; Manuscript editing and reviewing: J. C. Igwe, C. U. Aghalibe., B. O. Osu C. Olunkwa, K.E. Onwuka ; Project administration: B. O. Osu, J. C. Igwe.

9 DATA AVAILABILITY STATEMENT

The datasets generated during the current study are not publicly available as the study is ongoing; however, they are available from the corresponding author upon reasonable request.

10 ETHICS APPROVAL DECLARATION

This study was approved by the Ethics Committee of the Tertiary Education Trust Fund (TETFUND), Nigeria.

11 CONSENT TO PARTICIPATE

Informed consent was obtained from all individual participants included in this study.

12 CONSENT TO PUBLISH

Participants provided informed consent for the publication of their data.

References

[1] O. Abdia and M. Kazemi. A review study of biosorption of heavy metals and comparison between different biosorbents. *J. Mater. Environ. Sci.*, 6(5):1386–1399, 2015.

[2] R. Agarwala and L. Mulky. Adsorption of dyes from wastewater: A comprehensive review. *ChemBioEng Rev.*, 10(3):326–335, 2023.

[3] F.A. Ahmad. The use of agro-waste-based adsorbents as sustainable, renewable, and low-cost alternatives for the removal of ibuprofen and carbamazepine from water. *Heliyon*, 9:e16449, 2023.

[4] M.B. Ahmed, J.L. Zhou, H.H. Ngo, and W. Guo. Adsorptive removal of pesticides from water and wastewater: Thermodynamics and kinetic modeling perspectives. *Journal of Hazardous Materials*, 389:121928, 2020.

[5] Y. Ahmed, A.A.S. Maya, P. Akhtar, H. AlMohamadi, A.W. Mohammad, S.M. Ashekuzzaman, A.I. Olbert, and M.G. Uddin. Advancements and challenges in fenton-based advanced oxidation processes for antibiotic removal in wastewater: From the laboratory to practical applications. *Journal of Environmental Chemical Engineering*, 13(1):115068–115089, 2025.

[6] T.O. Ajiboye, A.T. Kuvarega, and D.C. Onwudiwe. Recent strategies for environmental remediation of organochlorine pesticides. *Appl. Sci.*, 10:6286, 2020.

[7] I. Alacabey. Endosulfan elimination using amine-modified magnetic diatomite as an adsorbent. *Front. Chem.*, 10:907302, 2022.

[8] J. Bayuo, M.J. Rwiza, and K.M. Mtei. Applicability of bio-adsorbents synthesized from maize/corn plant residues for heavy metals removal from aquatic environments: an insight review. *EQA - International Journal of Environmental Quality*, 56(1):15–35, 2023.

[9] A. Berdowska and K. Bandurska. Health hazards associated with exposure to endosulfan: A mini-review. *Toxics*, 13(6):455, 2025.

[10] L. Beyger, R. Orrego, J. Guchardi, and D. Holdway. The acute and chronic effects of endosulfan pulse-exposure on jordanella floridae (florida flagfish) over one complete life-cycle. *Ecotoxicology and Environmental Safety*, 76:71–78, 2012.

[11] F. Bouhamed, Z. Elouear, J. Bouzid, and B. Ouddane. Multi-component adsorption of copper, nickel and zinc from aqueous solutions onto activated carbon prepared from date stones. *Environ Sci Pollut Res*, 23:15801–15806, 2016.

[12] T.M. Budnyak, M. Błachnio, A. Slabon, A. Jaworski, V.A. Tertykh, A. Deryło-Marczewska, and A.W. Marczewski. Chitosan deposited onto fumed silica surface as sustainable hybrid biosorbent for acid orange 8 dye capture: Effect of temperature in adsorption equilibrium and kinetics. *J Phys Chem C Nanomater Interfaces*, 124(28):15312–15323, 2020.

[13] I.B. Bwatanglang, S.T. Magili, and I. Kaigamma. Adsorption of phenol over bio-based silica/calcium carbonate (cs-sio2/caco3) nanocomposite synthesized from waste eggshells and rice husks. *Peer J Physical Chemistry*, 3:1–20, 2021.

[14] M. Duque-Acevedo, L.M. Ulloa-Murillo, L.J. Belmonte-Ureña, F. Camacho-Ferre, F. Mercl, and P. Tlustoš. Sustainable and circular agro-environmental practices: A review of the management of agricultural waste biomass in spain and the czech republic. *Waste Manag Res.*, 41(5):955–969, 2023.

[15] Y. El-Nahhal and I. El-Nahhal. Adsorption, leaching and degradation of chlorpyrifos in soil under mediterranean conditions. *Environ. Nanotechnol., Monit. Manag.*, 13:100287, 2020.

[16] G. Enaime, K. Ennaciri, A. Ounas, A. Baçaoui, M. Seffen, T. Selmi, and A. Yaacoubi. Preparation and characterization of activated carbons from olive wastes by physical and chemical activation: Application to indigo carmine adsorption. *J Mater Environ Sci*, 8:4125–4137, 2017.

[17] H. Eun, G. Choi, D-S. Choi, and S-M. Hong. Performance evaluation for endosulfan removal by carbon-based adsorbents. *Korean J. Pestic. Sci.*, 25(2):111–118, 2021.

[18] J. Gao, H. Liu, Y. Liu, and X. Fang. ph-dependent adsorption behavior of pesticides on biochars and the implications for environmental risk assessment. *Sci. Total Environ.*, 806:150564, 2022.

[19] C.R. Girish. Determination of thermodynamic parameters in adsorption studies: A review. *Chemical Papers*, 79(9):5687–5706, 2025.

[20] P. González-Garcia. Activated carbon from lignocellulosics precursors: A review of the synthesis methods, characterization techniques and applications. *Renewable and Sustainable Energy Reviews*, 82:1393–1414, 2018.

[21] G. Göktepeli, S. Yıldız, and E. Esra, Yel. Phenol adsorption on magnetic biochar derived from olive pomace: Equilibrium, kinetic and thermodynamics. *Hacettepe J. Biol. & Chem.*, 49(2):133–145, 2021.

[22] G.A.K. Gürdil, M. Mengstu, and A. Kakarash. Utilization of agricultural wastes for sustainable development. *Black Sea Journal of Agriculture*, 4(4):146–152, 2021.

[23] S. Harabi, S. Guiza, A. Alvarez-Montero, A. Gomez-Aviles, M. Bagane, C. Belver, and J. Bedia. Adsorption of pesticides on activated carbons from peach stones. *Processes*, 12:238–255, 2024.

[24] B. Haryanto, R. Tambun, O.M. Sitohang, S.Y. Sidauruk, G.E. Naomi, and V. Alexander. Competence of corncob (zea mays l.) powder with hcl activation as adsorbent to purify waste cooking oil: Reference in the batch adsorption process. *South African Journal of Chemical Engineering*, 52:48–60, 2025.

[25] M.A. Hussain, I.G. Murtaza, M. Zia-ur Rehman, M. Shahid, and S. Calero. Evaluating adsorption kinetics of endosulfan on natural and synthetic adsorbents: A comparative study. *Journal of Animal & Plant Sciences*, 35(2):429–444, 2025.

[26] J.C. Igwe and A.A. Abia. Sorption kinetics and intraparticulate diffusivities of cd, pb, and zn ions on maize cob. *African Journal of Biotechnology*, 4(6):509–512, 2005.

[27] J.C. Igwe, A.A. Abia, and H.O. Felix. Kinetic studies on the sorption of ag+ and al3+ from aqueous solutions by coconut fibre. *Terrestrial and Aquatic Environmental Toxicology*, 5(1):19–24, 2011.

[28] J.C. Igwe, A. Ekwuruke, B.C. Gbaruko, and A.A. Abia. Detoxification of copper fungicide using edta-modified cellulosic material. *Afr. J. Biotechnol.*, 8(3):499–506, 2009.

[29] J.C. Igwe, N.E. Okoronkwo, C.U. Aghalibe, K.E. Onwuka, K.O. Achilike, E.E. Joseph, and C.E. Ujarah. Thermodynamics of heavy metals (hg2+, cd2+, fe2+ and ni2+) adsorption using boiler fly ash. *Intern. J. Therm. Chem. Kinetics*, 6(2):25–34, 2020.

[30] J.C. Igwe, N.E. Okoronkwo, and E.A. Okoli. Adsorption studies of chlorpyrifos and endosulfan pesticides from aqueous solution using coconut fibre. *J. Chem. Soc. Nigeria*, 39(2):44–50, 2014.

[31] K.I. John, A.T. Adeleye, S. Munsif, B.O. Odusina, and P.M.O. Omorogie. Perspectives on circular economy and efficient resource utilization of valorized value-added material for sustainable development. *Preprints*, 2025.

[32] K. Kalsoom, Z.A. Khan, S. Khan, N. Muhammad, F. Jabeen, M. Ziad, and A. Khan. Comparative adsorption of selected pesticides from aqueous solutions by activated carbon and biochar. *AQUA-Water Infrastructure, Ecosystems and Society*, 73(10):1994–2012, 2024.

[33] V.R. Keerthika, S. Reshma, John Moses, S. Sadhna, and J. Eunice. Advanced oxidation process: Treating organic pollutant. *International Research Journal on Advanced Engineering Hub (IRJAEH)*, 3(3):330–338, 2025.

[34] A. Kesraoui, T. Selmi, M. Seffen, and F. Brouers. Influence of alternating current on the adsorption of indigo carmine. *Environ Sci Pollut Res*, 24:9940–9950, 2017.

[35] M.H. Khalid, T. Mahmood, K.M. Al-Qahtani, and J. Rinklebe. Adsorptive removal of pesticides from aqueous environment using various adsorbents: A review. *Environmental Pollution*, 254:113026, 2019.

[36] M.A. Lala, Z.O. Olomowewe, A.T. Adeniyi, and A. Giwa. Maize cob-derived activated carbon as an adsorbent for the removal of nickel (ii) cation from aqueous solution: optimization and kinetic studies. *Arab Journal of Basic and Applied Sciences*, 30(1):573–582, 2023.

[37] J.S. Lazarotto, K. da Boit Martinello, J. Georgin, D.S.P. Franco, M.S. Netto, D.G.A. Piccilli, L.F.O. Silva, E.C. Lima, and G.L. Dotto. Preparation of activated carbon from the residues of the mushroom (agaricus bisporus) production chain for the adsorption of the 2,4-dichlorophenoxyacetic herbicide. *J. Environ. Chem. Eng.*, 9:106843, 2021.

[38] C. Li, N. Zhang, J. Chen, J. Ji, X. Liu, J. Wang, J. Zhu, and Y. Ma. Temperature and ph sensitive composite for rapid and effective removal of sulfonylurea herbicides in aqueous solution. *Environmental Pollution*, 255(1), 2019.

[39] I. Luttah, D.O. Onunga, V.O. Shikuku, B. Otieno, and C.O. Kowenje. Removal of endosulfan from water by municipal waste incineration fly ash based geopolymers: Adsorption kinetics, isotherms, and thermodynamics. *Front. Environ. Chem.*, 4:1164372–1164385, 2023.

[40] H. Ma, J. Yang, X. Gao, Z. Liu, X. Liu, and Z. Xu. Removal of chromium (vi) from water by porous carbon derived from corn straw: Influencing factors, regeneration and mechanism. *Journal of Hazardous Materials*, 369:550–560, 2019.

[41] P. Mahdavi, A. Siol, and J. Thöming. Adsorption-based removal of pharmaceutical from water: A critical review on adsorbent performance. *Journal of Environmental Chemical Engineering*, 13(5):117520–117558, 2025.

[42] M. Marton, J. Ilavsky, and D. Barlokova. Adsorption of specific chloroacetanilides on granular activated carbon. *IOP Conf. Ser. Mater. Sci. Eng.*, 867:012031, 2020.

[43] A.A. Mayyahi and H.A.A. Al-Asadi. Advanced oxidation processes (aops) for wastewater treatment and reuse: A brief review. *Asian Journal of Applied Science and Technology (AJAST)*, 2(3):18–30, 2018.

[44] J. McGinley, M.G. Healy, P.C. Ryan, P-E. Mellander, L. Morrison, J.A. Harmon O'Driscoll, and A. Siggins. Batch adsorption of herbicides from aqueous solution onto diverse reusable materials and granulated activated carbon. *Journal of Environmental Management*, 323:116102–116110, 2022.

[45] R.G. Menezes, T.F. Qadir, A. Moin, H. Fatima, S.A. Hussain, M. Madadin, S.B. Pasha, F.A. Al Rubaish, and S. Senthilkumaran. Endosulfan poisoning: An overview. *Journal of forensic and legal medicine*, 51:27–33, 2017.

[46] B. Mishra, Y.K. Mohanta, C.N. Reddy, S.D.M. Reddy, S.K. Mandal, R. Yadavalli, and H. Sarma. Valorization of agro-industrial biowaste to biomaterials: An innovative circular bioeconomy approach. *Circular Economy*, 2(3):100050, 2023.

[47] A. Mudhoo, A. Bhatnagar, M. Rantalankila, V. Srivastava, and M. Sillanpää. Endosulfan removal through bioremediation, photocatalytic degradation, adsorption and membrane separation processes: A review. *Chemical Engineering Journal*, 360:912–928, 2019.

[48] M.A. Murtala, K.R. Aminu, K.A. Sanusi, and B. Abdurrahman. Adsorption of pesticides from aqueous solution using kinkeliba (combretum micranthum g.) derived activated carbon. *International Journal of Sciences: Basic and Applied Research (IJSBAR)*, 63(2):308–319, 2022.

[49] S. Mustapha, D.T. Shuaib, M.M. Ndamitso, M.B. Etsuyankpa, A. Sumaila, U.M. Mohammed, and M.B. Nasirudeen. Adsorption isotherm, kinetic and thermodynamic studies for the removal of pb(ii), cd(ii), zn(ii) and cu(ii) ions from aqueous solutions using albizia lebbeck pods. *Applied Water Science*, 9:142–153, 2019.

[50] M.S. Nader and E.A. Elkhatib. Kinetics and thermodynamics of β-1 endosulfan pesticide adsorption in jordan valley soils. *Global Journal of Science Frontier Research*, 18(B1):1–10, 2018.

[51] M. Narayanan, K. Devarayan, M. Verma, M. Selvaraj, H.A. Ghramh, and S. Kandasamy. Assessing the ecological impact of pesticides/herbicides on algal communities: A comprehensive review. *Aquatic Toxicology*, 268:106851, 2024.

[52] National Center for Biotechnology Information (NCBI). Pubchem compound summary for cid 13940, endosulfan sulfate. https://pubchem.ncbi.nlm.nih.gov/compound/Endosulfan-sulfate, 2024. Retrieved July 1, 2024.

[53] A.D. N'diaye, C. Boudokhane, M. Kankou, and H. Dhaouadi. Potential of rice husk ash in atrazine removal. *Chemistry and Ecology*, 35(7):678–692, 2019.

[54] W. Nyairo, J.B. Njewa, and V.O. Shikuku. Adsorption of heavy metals onto food wastes: a review. *Front. Environ. Chem.*, 6:1526362–1526382, 2025.

[55] O. Ogunlalu, I.P. Oyekunle, K.O. Iwuozor, A.D. Aderibigbe, and E.C. Emenike. Trends in the mitigation of heavy metal ions from aqueous solutions using unmodified and chemically-modified agricultural waste adsorbents. *Current Research in Green and Sustainable Chemistry*, 4:100188–100207, 2021.

[56] Z. Raji, A. Karim, A. Karam, and S. Khalloufi. Adsorption of heavy metals: Mechanisms, kinetics, and applications of various adsorbents in wastewater remediation—a review. *Waste*, 1(3):775–805, 2023.

[57] R. Rajkumar, R.K. Raman, S. Sarves, and S. Swaminathan. Hydrodynamics and phenol adsorption studies in continuous counter current liquid-solid settling column. *Process Safety and Environmental Protection*, 142:350–358, 2020.

[58] R.A. Rashid, L.B.L. Lim, and A. Usman. Temperature-dependent adsorption of pesticides on agricultural waste adsorbents: Thermodynamics and mechanisms. *Journal of Environmental Management*, 307:114534, 2022.

[59] E. Rápó and S. Tonk. Factors affecting synthetic dye adsorption; desorption studies: A review of results from the last five years (2017–2021). *Molecules*, 26(17):5419–5450, 2021.

[60] J.D. Santamaria-Juarez, M.Á. Hernández, G.I. Hernández, K.M. Álvarez, E. Rubio, R. Portillo, M.d.l.Á. Velasco, J.F. Aquino, and V. Petranovskii. Adsorption of the herbicide endosulfan by newly discovered zeolitic tuffs in mexico. *Minerals*, 14:643–675, 2024.

[61] T. Selmi, M. Seffen, F. Brouers, V. Fierro, and H. Sammouda. Adsorption of model dyes onto porous materials: Effect of ph and temperature on the parameters of brouers sotolongo kinetic fractal and generalized isotherm. In *Recent Advances in Environmental Science from the Euro Mediterranean and Surrounding Regions: Proceedings of Euro-Mediterranean Conference for Environmental Integration (EMCEI-1), Tunisia 2017*, pages 1039–1041, Cham, 2018. Springer International Publishing.

[62] J.A. Silva. Advanced oxidation process in the sustainable treatment of refractory wastewater: A systematic literature review. *Sustainability*, 17(8):3439, 2025.

[63] C.S. Sundaram, P. Kumar, and A. Ramesh. Toxicity and environmental risks of endosulfan: An updated review. *Chemosphere*, 271:129494, 2021.

[64] F. Suo, X. Liu, C. Li, M. Yuan, B. Zhang, J. Wang, Y. Ma, Z. Lai, and M. Ji. Mesoporous activated carbon from starch for superior rapid pesticides removal. *Intern. J. Biol. Macromol.*, 121:806–813, 2018.

[65] M.A. Tahir, M.M. Khan, M. Rafiq, and N. Iqbal. Removal of monocrotophos from aqueous solution using chemically activated wheat straw biochar: Adsorption isotherms, kinetics and thermodynamics. *Environ. Technol. Innov.*, 23:101689, 2021.

[66] E.N. Vaikosen, C.M. Davidson, B.I. Olu-Owolabi, L.T. Gibson, F.O. Agunbiade, A.J. Kashimawo, and K.O. Adebowale. Kinetic and isotherm studies on the adsorption–desorption of technical-grade endosulfan in loamy soils under theobroma cacao l cultivation, southwestern nigeria. *Environ. Sci.: Adv.*, 2:257–277, 2023a.

[67] E.N. Vaikosen, R.C. Worlu, S.J. Bunu, E. Dode, and M. Doctor. Liquid-liquid separation and determination of betamethasone, clotrimazole and neomycin in topical cream by uv-visible spectrophotometry. *Int. J. in Pharm. Sci.*, 1(4):170–179, 2023b.

[68] J. Vievard, A. Alem, A. Pantet, N.D. Ahfir, M.G. Arellano-Sánchez, C. Devouge-Boyer, and M. Mignot. Bio-based adsorption as ecofriendly method for wastewater decontamination: A review. *Toxics*, 11(5):404–437, 2023.

[69] Y. Wang, S.L. Wang, T. Xie, and J. Cao. Activated carbon derived from waste tangerine seed for the high-performance adsorption of carbamate pesticides from water and plant. *Bioresource Technology*, 316:123929, 2020.

[70] H. Zheng, Q. Zhang, G. Liu, X. Luo, F. Li, Y. Zhang, and Z. Wang. Characteristics and mechanisms of chlorpyrifos and chlorpyrifos-methyl adsorption onto biochars: Influence of deashing and low molecular weight organic acid (lmwoa) aging and co-existence. *Science of the Total Environment*, 657:953–962, 2019.

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