

# Sorption Modeling And Soil–Property Controls On Imidacloprid Adsorption In Organically Amended Soils

\*Anyim, P.B.,<sup>1</sup> Tukura, B.W.,<sup>2</sup> Anifowose, O.,<sup>2</sup> Okibe, P.O.,<sup>1</sup> Bello, Z.S.,<sup>1</sup> Alozie, A.C.<sup>2</sup>

1. National Research Institute for Chemical Technology, Basawa Zaria, Kaduna State, Nigeria.

2. Chemistry Department, Nasarawa State University, Keffi, Nasarawa State, Nigeria.

**ABSTRACT:** This study investigated how organic amendments, specifically biochar, poultry manure, and cow dung, affect the adsorption behaviour of imidacloprid in agricultural soils from the Lafia region of Nasarawa State, Nigeria. Surface soil collected from 0–15 cm was amended at 10% (w/w) and assessed using batch equilibrium techniques across imidacloprid concentrations ranging from 10 to 50 mg/L. Physicochemical properties, including pH, organic carbon, cation exchange capacity, and electrical conductivity, were quantified using standard laboratory methods. Adsorption parameters ( $C_e$ ,  $q_e$ , and  $K_d$ ) were evaluated using the Freundlich and BET isotherm models. The findings showed that biochar-amended soil achieved the greatest adsorption capacity and highest distribution coefficients, followed by poultry manure and cow dung, with all amended treatments demonstrating superior performance relative to the unamended control. Adsorption efficiency decreased at higher imidacloprid concentrations, suggesting progressive saturation of available binding sites. The BET model provided an excellent fit for all treatments ( $R^2 = 0.957–0.983$ ), confirming that multilayer adsorption dominated, whereas the Freundlich model was less representative. Correlation analysis further indicated strong positive relationships between adsorption indices ( $q_e$  and  $K_d$ ) and both organic carbon and cation exchange capacity, highlighting their critical role in enhancing pesticide retention. In contrast, electrical conductivity and pH were negatively associated with adsorption performance, suggesting an inhibitory effect on sorption.

**Keywords:** Imidacloprid; soil amendments; biochar; poultry manure; cow dung; adsorption isotherms; multilayer adsorption

## 1.0 INTRODUCTION

Imidacloprid is among the most commonly used systemic insecticides worldwide, and its persistence in agricultural soils has raised concerns regarding mobility, bioavailability, and potential groundwater contamination (6). The behaviour of imidacloprid in soil is strongly controlled by physicochemical properties such as pH, cation exchange capacity (CEC), organic carbon (OC), electrical conductivity (EC), and texture, which influence sorption–desorption processes [1, 2, 3]. Organic amendments, including biochar, poultry manure, and cow dung, are increasingly promoted as low-cost soil conditioners that are capable of enhancing pesticide retention by improving soil structure, supplying reactive functional groups, and increasing organic matter content [4,5,6]. Biochar has been widely recognized for its high sorption potential due to its porous structure, aromatic carbon matrix, and large specific surface area, which facilitate strong interactions with organic contaminants [7]. In contrast, poultry manure and cow dung primarily enhance sorption by increasing organic carbon and cation exchange capacity, although their soluble organic fractions may also influence desorption dynamics [8,9]. Because these amendments differ in composition, stability, and functional group density, their effects on imidacloprid mobility may vary significantly [10,11]. Understanding these interactions is critical, as adsorption governs imidacloprid transport, persistence, and environmental risk [12]. This study evaluates the adsorption dynamics of imidacloprid in unamended soil and soil amended with biochar, poultry manure, and cow dung. Adsorption capacity, distribution coefficients, and isotherm behaviour were assessed across treatments, as shown in Tables 2–7. By integrating equilibrium measurements with Freundlich and BET modelling, the study provides insight into how organic amendments modify soil–pesticide interactions. The findings contribute to improved selection of soil amendments to mitigate pesticide mobility and enhance environmental quality.

## 2.0 MATERIALS AND METHODS

### 2.1 Sampling and Sample Collection

Surface soil was collected from the Lafia area of Nasarawa State, Nigeria, using a composite sampling approach. Samples were taken from 0–15 cm depth with a hand trowel, air-dried for five days, and passed through a 2mm sieve to remove coarse debris. The prepared samples were transported to the laboratory in covered aluminum containers to prevent contamination.

### 2.2 Soil Sample Preparation

The soil was amended with organic materials, cow dung, poultry manure, and biochar, each applied at 10% (w/w) on a dry weight basis. For each treatment, triplicate 5kg soil portions were thoroughly mixed with 500 g of the respective amendment, while an unamended portion served as the control [13]. The amended soils were homogenized and allowed to stabilize for two weeks before analysis, following the procedure described by Carpio et al [14].

### 2.3 Batch Equilibrium Experiment

Adsorption of imidacloprid was assessed using the batch equilibration technique described by Yu et al [15]. One gram of soil was combined with 10 cm<sup>3</sup> of 0.01 M CaCl<sub>2</sub> solution containing imidacloprid at initial concentrations of 10, 20, 30, 40, and 50 mg/L. Samples on a rotary shaker for 24 hours at room temperature, and subsequently centrifuged for 60 minutes. The equilibrium concentration of imidacloprid in the supernatant was determined using a UV-Visible spectrophotometer set to 280 nm. Blank controls, containing only the imidacloprid solution without soil, were included to correct for losses during the procedure.

Parameter	Control	Modified soils		
		Biochar	Poultry droppings	Cow dung
CEC (mol/kg)	0.84 ± 0.008	0.96 ± 0.019	0.86 ± 0.009	0.90 ± 0.011
EC (µs/cm)	345.00 ± 0.100	1250.00 ± 2.00	573.00 ± 3.000	201.00 ± 3.000
OC (%)	1.89 ± 0.015	2.32 ± 0.020	2.40 ± 0.400	2.42 ± 0.080
pH	7.10 ± 0.050	7.50 ± 0.200	7.90 ± 0.100	8.00 ± 0.400

The amount of imidacloprid sorbed at equilibrium ( $q_e$ ) by the soil was then calculated as follows:

$$q_e = \frac{(C_0 - C_e) \times V}{m}$$

Where:

$q_e$  = amount of imidacloprid adsorbed at equilibrium (mg/g)

$C_0$  = initial concentration of imidacloprid in solution (mg/L)

$C_e$  = equilibrium concentration of imidacloprid in solution (mg/L)

$V$  = volume of the solution (L)

$m$  = mass of the adsorbent (g)

#### 2.4 Physicochemical analysis of a soil sample

The soil and amended samples were subjected to physicochemical characterization using established laboratory procedures. Soil texture was analyzed with the Bouyoucos hydrometer technique. Soil pH was measured with a glass electrode after preparing a 1:1 soil-to-distilled-water slurry. Organic matter content was quantified using the Walkley-Black wet oxidation procedure. Cation exchange capacity (CEC) was determined through the ammonium acetate extraction and titration method. Electrical conductivity was assessed following standard analytical procedures.

### 3.0 RESULTS

The physicochemical properties of the soil samples are presented in Table 1. The adsorption behaviour of imidacloprid in the unamended soil and amended soils is summarized in Tables 2–5, which detail the equilibrium concentrations ( $C_e$ ), adsorbed amounts ( $q_e$ ), distribution coefficients ( $K_d$ ), and percent improvement for each amendment. The Correlation coefficients ( $r$ ) for soil parameters and the adsorption capacities of imidacloprid are displayed in Table 6. The corresponding adsorption isotherms are illustrated in Figures 1–8, while Figures 9 and 10 show the variations in the percent improvement in adsorption capacity across the different treatments.

Table 1: Chemical properties of modified and control soil

Table 2: Adsorption and distribution coefficient of imidacloprid in unmodified soil

$C_0$ (mg/l)	Absorbance	$C_e$ (mg/l)	$q_e$ (mg/g)	$K_d$ (l/g)
10	$1.043 \pm 0.001$	0.767	0.092	0.120
20	$1.715 \pm 0.010$	1.264	0.187	0.148
30	$1.202 \pm 0.010$	0.885	0.291	0.329
40	$0.843 \pm 0.055$	0.620	0.394	0.635
50	$0.936 \pm 0.020$	0.688	0.493	0.716

$C_0$  = Initial concentration;  $C_e$  = Equilibrium concentration;  $q_e$  = adsorbed amount of imidacloprid;  $K_d$  = distribution coefficient

Table 3: Adsorption, distribution coefficient, and percent improvement of imidacloprid in biochar-amended soil

$C_0$ (mg/l)	Absorbance	$C_e$ (mg/l)	$q_e$ (mg/g)	$K_d$ (l/g)	Improvement (%) $q_e$	Improvement (%) $K_d$
10	$0.495 \pm 0.009$	0.363	0.096	0.266	4.35	121.67
20	$0.658 \pm 0.010$	0.483	0.195	0.404	4.28	173.00
30	$0.503 \pm 0.002$	0.369	0.296	0.804	1.72	144.41
40	$0.441 \pm 0.010$	0.323	0.397	1.229	0.76	93.50
50	$0.549 \pm 0.003$	0.403	0.496	1.232	0.61	72.18

Table 4: Adsorption, distribution coefficient, and percent improvement of imidacloprid in poultry dropping amended soil

$C_0$ (mg/l)	Absorbance	$C_e$ (mg/l)	$q_e$ (mg/g)	$K_d$ (l/g)	Improvement (%) in $q_e$	Improvement (%) in $K_d$
10	$0.708 \pm 0.013$	0.520	0.095	0.182	3.26	51.67
20	$1.001 \pm 0.010$	0.736	0.193	0.262	3.21	77.03
30	$0.801 \pm 0.005$	0.589	0.294	0.500	1.03	51.98
40	$0.651 \pm 0.032$	0.478	0.395	0.827	0.25	30.28
50	$0.615 \pm 0.017$	0.451	0.495	1.098	0.41	53.37

Table 5: The adsorption, distribution coefficient, and percent improvement of imidacloprid in cow dung amended soil

$C_0$ (mg/l)	Absorbance	$C_e$ (mg/l)	$q_e$ (mg/g)	$K_d$ (l/g)	Improvement (%) in $q_e$	Improvement (%) in $K_d$
--------------	------------	--------------	--------------	-------------	-----------------------------	-----------------------------

10	0.852± 0.005	0.626	0.094	0.150	2.17	25.00
20	1.309± 0.059	0.964	0.190	0.197	1.60	33.11
30	0.979± 0.005	0.720	0.293	0.407	0.69	23.71
40	0.701± 0.008	0.515	0.395	0.767	0.25	20.79
50	0.756± 0.005	0.555	0.494	0.890	0.20	24.30

Table 6: Correlation coefficients (r) for soil parameters and adsorption capacities of imidacloprid

Parameter	CEC	EC	OC	Ph	q <sub>e</sub>	K <sub>d</sub>
CEC	1.00	-0.85	0.78	-0.64	0.72	0.69
EC	-0.85	1.00	-0.89	0.82	-0.77	-0.75
OC	0.78	-0.89	1.00	-0.70	0.81	0.79
pH	-0.64	0.82	-0.70	1.00	-0.62	-0.60
q <sub>e</sub>	0.72	-0.77	0.81	-0.62	1.00	0.96
K <sub>d</sub>	0.69	-0.75	0.79	-0.60	0.96	1.00

CEC: Cation exchange capacity; Electrical conductivity; Organic carbon; q<sub>e</sub> = adsorbed amount of imidacloprid; K<sub>d</sub> = distribution coefficient.

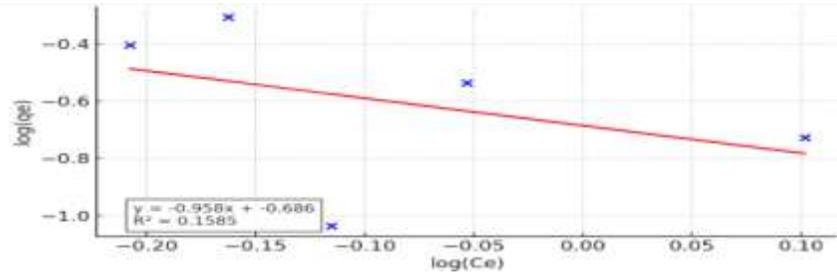


Fig. 1 Freundlich adsorption isotherm for imidacloprid in control soil

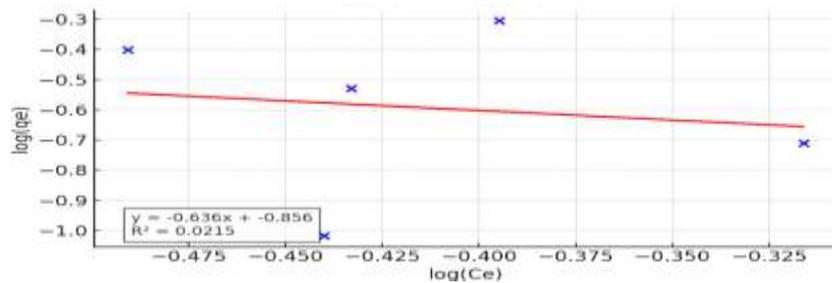


Fig. 2 Freundlich adsorption isotherm for Imidacloprid in biochar-modified soil

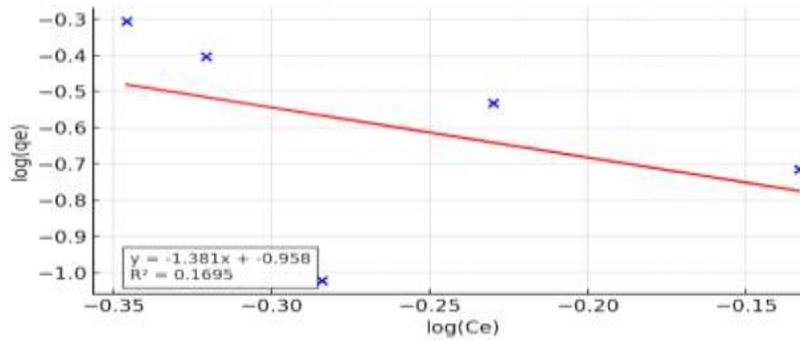


Fig. 3 Freundlich adsorption isotherm for poultry-amended soil modified soil

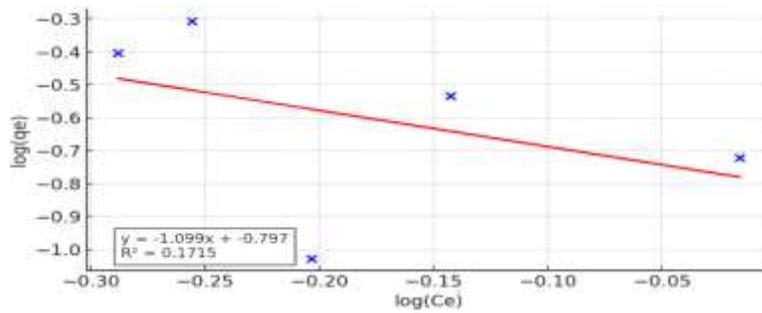


Fig. 4 Freundlich Isotherm for cow dung-modified soil

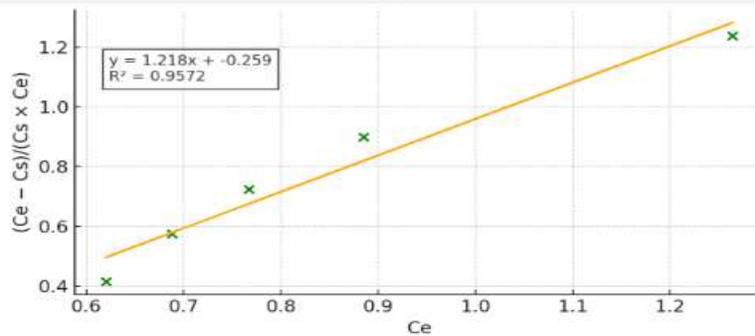


Fig. 5 BET adsorption isotherm for imidacloprid in control soil

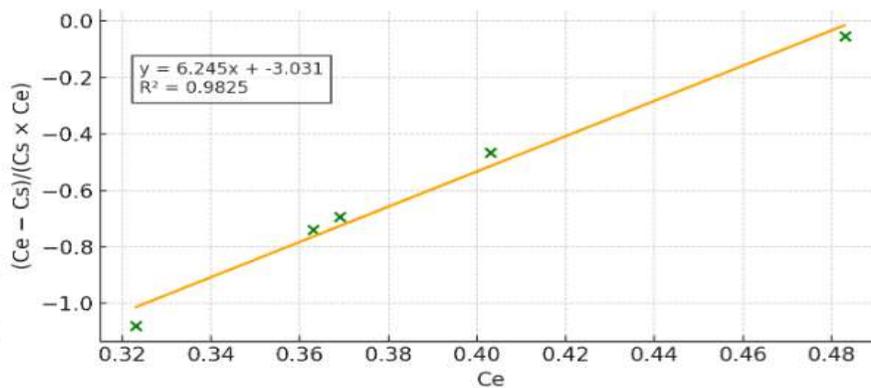


Fig. 6 BET adsorption isotherm for biochar-modified soil

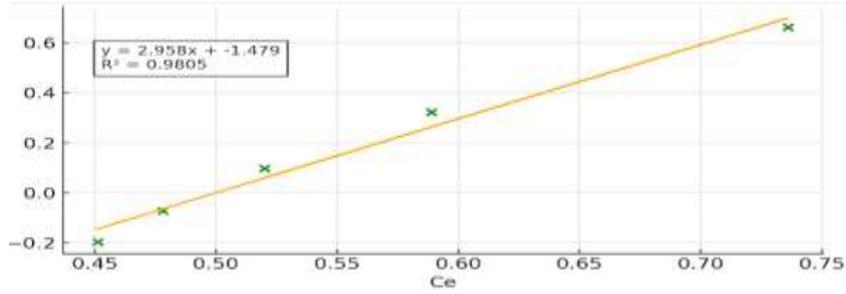


Fig.7 BET adsorption isotherm for poultry dropping-modified soil

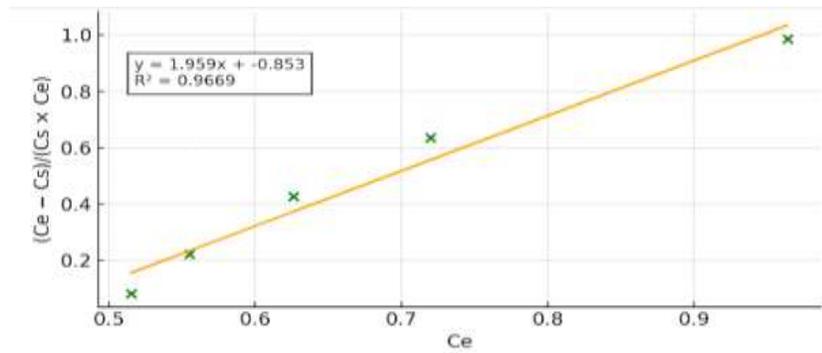


Fig. 8 BET Isotherm for cow dung-modified soil

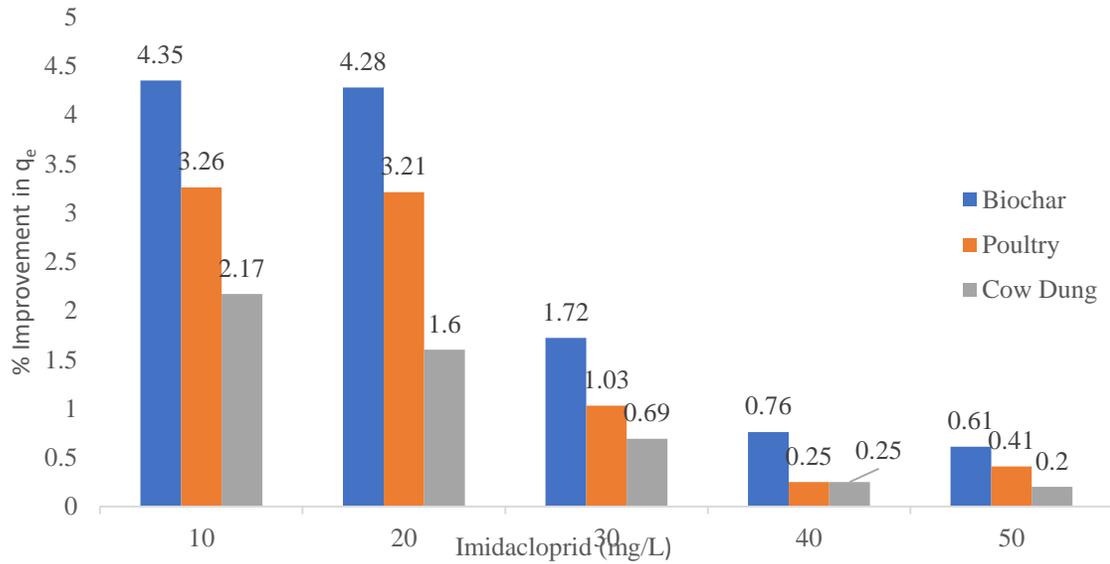


Fig. 9 Variations in improvement (%) of adsorbed concentrations of imidacloprid in the modified and unmodified soil samples

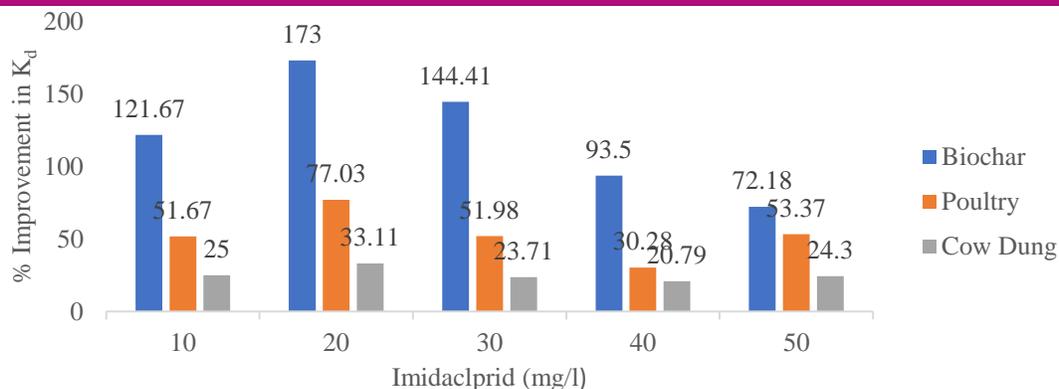


Figure 10. Variations in the improved distribution coefficient ( $K_d$ ) of imidacloprid in the modified and unmodified soil samples

## 4.0 DISCUSSION

### 4.1 Improvement in Adsorption Capacity ( $q_e$ ) and Distribution Coefficient ( $K_d$ ) Across the Amendments

The effect of organic amendments on imidacloprid adsorption was evaluated by assessing improvements in adsorption capacity ( $q_e$ ) and distribution coefficient ( $K_d$ ) relative to unamended soil (Tables 3–6). Imidacloprid's adsorption increased with concentration, with biochar showing the highest retention, followed by poultry manure, cow dung, and control soils, highlighting the role of organic amendments in enhancing pesticide retention and reducing mobility. As illustrated in Figure 9, biochar consistently showed the greatest improvement in  $q_e$  across all concentrations, with a maximum of 4.35% at 10 mg/L, decreasing to 0.61% at 50 mg/L. This trend suggests that biochar is most effective at lower concentrations where more active adsorption sites are available, with site saturation reducing effectiveness at higher concentrations [17]. Poultry manure showed moderate improvement, increasing at 4.28% at 10 mg/L and declining to 0.25% at 40 mg/L, reflecting its slightly lower adsorption capacity (4), (8). Cow dung exhibited the lowest enhancement in  $q_e$ , with a maximum of 3.26% at 10 mg/L and 0.19% at 40 mg/L, likely due to its lower surface area and fewer chemically active sites [7,10].

The distribution coefficient ( $K_d$ ) showed a more pronounced improvement across amendments (Figure 10). Biochar recorded the highest  $K_d$  enhancements, ranging from 72.18% at 50 mg/L to 173% at 20 mg/L, indicating strong retention and reduced mobility of imidacloprid. Poultry manure showed moderate  $K_d$  improvements ( $\approx 30$ –77%), reflecting enhanced adsorption due to increased organic carbon and nutrients, though partially offset by dissolved organic matter, leading to minor desorption [4,8]. Cow dung consistently had the lowest  $K_d$  improvements (20.79–33.11%), likely due to lower porosity, simpler, and potential effects of dissolved organic matter [7,10,11].

### 4.2 Isotherm Analysis of Imidacloprid Adsorption

The adsorption of imidacloprid in unamended and organically amended soils was analyzed using the Freundlich and Brunauer–Emmett–Teller (BET) isotherm models. Model performance was evaluated based on the coefficient of determination ( $R^2$ ) to assess how well each model described the experimental adsorption data across the different soil treatments.

#### 4.2.1 Freundlich model performance

The Freundlich model performed poorly for all soil treatments, as reflected by the low  $R^2$  values. In unamended soil, the model yielded an  $R^2$  of 0.158 (Figure 1), indicating weak correlation. Biochar-amended soil exhibited an  $R^2$  of 0.0215 (Figure 2), and poultry manure-amended soil had an  $R^2$  of 0.170 (Figure 3). Cow dung-amended soil showed the highest Freundlich  $R^2$  of 0.172 (Figure 4), but this still represents a poor fit. These results indicate that the Freundlich model is not suitable for predicting imidacloprid adsorption in either unamended or amended soils, likely due to the heterogeneous and complex nature of the adsorption mechanisms in these systems.

#### 4.2.2 BET model performance

The BET model provided consistently strong correlations across all soils, demonstrating its suitability for describing multilayer adsorption. In unamended soil,  $R^2$  was 0.957 (Figure 5), indicating that multilayer adsorption is the dominant mechanism. Biochar-amended soil showed the highest BET fit, with  $R^2 = 0.983$  (Figure 6), consistent with biochar's high surface area and porosity, which promote multilayer adsorption. Poultry manure-amended soil also exhibited a strong correlation ( $R^2 = 0.981$ ; Figure 7), whereas cow dung-amended soil showed  $R^2 = 0.967$  (Figure 8).

The BET model reliably captured the adsorption behaviour of imidacloprid across all soil treatments. The findings suggest that multilayer adsorption predominates in both unamended and organically amended soils, with biochar showing the greatest adsorption potential due to its structural properties. The superior fit of the BET model reflects the availability of diverse sorption sites and the ability of organic amendments to enhance multilayer adsorption through surface aggregation and pore-filling mechanisms [16, 17].

### Correlation Analysis

The correlation analysis presented in Table 6 revealed strong links between soil properties (Table 1) and imidacloprid adsorption in the control and amended soils. This is supported by the adsorption patterns displayed in Tables 2-7. CEC and organic carbon showed strong positive correlations with both  $q_e$  and  $K_d$ , confirming that soils with more exchange sites and higher organic matter retained greater amounts of imidacloprid. These findings align with studies showing that amendments such as biochar and poultry manure increase CEC and OC, thereby improving agrochemical sorption [1,6,2]. In contrast, EC and pH exhibited negative correlations with  $q_e$  and  $K_d$ , indicating that higher soluble salt levels and increased alkalinity reduced adsorption efficiency. This pattern is consistent with evidence that ion competition under high EC suppresses pesticide retention [12,1], while pH effects are often moderated by gains in organic matter from amendments [4,5,6]. The strong association between  $q_e$  and  $K_d$  reinforces that the soils with higher adsorption capacity also limit imidacloprid mobility. summarily, the results confirm that CEC and OC are the primary drivers of enhanced sorption in amended soils, whereas elevated EC and pH act as secondary constraints.

### CONCLUSION

This study shows that organic amendments, biochar, poultry manure, and cow dung enhanced imidacloprid adsorption, with amended soils displaying higher  $q_e$ , larger  $K_d$  values, and greater sorption efficiency than the unamended control (Tables 2–7). Biochar produced the greatest improvement, consistent with its high surface area and organic carbon content. Isotherm modelling (Figures 1–6) revealed poor fits for the Freundlich model but strong  $R^2$  values for the BET model, confirming that multilayer adsorption dominates across treatments. Correlation analysis further identified CEC and organic carbon as the main drivers of increased adsorption, whereas higher EC and pH reduced sorption effectiveness. The findings demonstrate that organic amendments enhance imidacloprid retention by increasing the exchange sites and organic matter, thereby limiting its mobility and associated environmental risks.

### References

1. Omara, P., Singh, H., Singh, K., Sharma, L., Otim, F., & Obia, A. (2023). Short-term effect of field application of biochar on cation exchange capacity, pH, and electrical conductivity of sandy and clay loam temperate soils. *Technology in Agronomy*, 3(1), 0-0. <https://doi.org/10.48130/tia-2023-0016>
2. Pandian, K., Subramaniyan, P., Gnasekaran, P., & Chitraputhirapillai, S. (2016). Effect of biochar amendment on soil physical, chemical and biological properties and groundnut yield in rainfed Alfisol of semi-arid tropics. *Archives of Agronomy and Soil Science*, 62(9), 1293-1310. <https://doi.org/10.1080/03650340.2016.1139086>
3. Soremi, A. O. (2019). Evaluation of adsorptive characteristics of cow dung and rice husk ash for removal of glyphosate and AMPA. *International Journal of Environmental Science and Technology*, 16, 7119–7132. <https://doi.org/10.1007/s13762-018-2120-6>
4. Agbede, T. M. (2025). *Effect of poultry manure on soil organic matter content and agrochemical retention in tropical soils*. *Journal of Soil Science and Environmental Management*, 16(2), 101–110.
5. Haliru, M., Dikko, A., Audu, M., & Aliyu, I. (2015). Effect of cow dung on soil properties and performance of sweet potato (*Ipomoea batatas* L.) in Sudan Savanna, Nigeria. *International Journal of Plant & Soil Science*, 5(4), 212-216. <https://doi.org/10.9734/ijpss/2015/14471>
6. Sun, Z., Hu, Y., Shi, L., Li, G., Pang, Z., Liu, S., Chen, Y., & Jia, B. (2022). Effects of biochar on soil chemical properties: A global meta-analysis of agricultural soil. *Plant, Soil and Environment*, 68(6), 272-289. <https://doi.org/10.17221/522/2021-pse>
7. Qiu, M., Liu, L., Ling, Q., Cai, Y., Yu, S., Wang, S., Fu, D., Hu, B., & Wang, X. (2022). Biochar for the removal of contaminants from soil and water: A review. *Biochar*, 4(1). <https://doi.org/10.1007/s42773-022-00146-1>
8. Siedt, M., Schäffer, A., Smith, K. E., Nabel, M., Roß-Nickoll, M., & Van Dongen, J. T. (2021). Comparing straw, compost, and biochar regarding their suitability as agricultural soil amendments to affect soil structure, nutrient leaching, microbial communities, and the fate of pesticides. *Science of The Total Environment*, 751, 141607. <https://doi.org/10.1016/j.scitotenv.2020.141607>
9. Onuh, M., Madukwe, D., & Ohia, G. (2010). Effects of poultry manure and cow dung on the physical and chemical properties of crude oil polluted soil. *Science World Journal*, 3(2). <https://doi.org/10.4314/swj.v3i2.51785>

10. Wang, F., Li, X., Yu, S., He, S., Cao, D., & Yao, S. (2021). Chemical factors affecting uptake and translocation of six pesticides in soil by maize (*Zea mays* L.). *Journal of Hazardous Materials*, 405, 124269. <https://doi.org/10.1016/j.jhazmat.2020.124269>
11. Hou, X., Ou, Y., Wang, X., Liu, H., Cheng, L., & Yan, L. (2024). The influence of vermicompost on atrazine microbial degradation performance and pathway in Black soil, Northeast China. *Science of The Total Environment*, 950, 175415. <https://doi.org/10.1016/j.scitotenv.2024.175415>
12. Li, X., Yan, X., Wu, T., Zhang, X., & Yu, H. (2021). Risks and phyto-uptake of micro–nano size particulates bound with potentially toxic metals in Pb-contaminated alkaline soil (NW China): The role of particle size fractions. *Chemosphere*, 266, 129508. <https://doi.org/10.1016/j.chemosphere.2020.129508>
13. Organic matter and soil amendments. (2023, February 17). University of Maryland Extension |University of Maryland Extension. <https://extension.umd.edu/resource/organic-matter-and-soil-amendments>
14. Carpio, M. J., Sánchez-Martín, M. J., Rodríguez-Cruz, M. S., & Marín-Benito, J. M. (2021). Effect of organic residues on pesticide behavior in soils: A review of laboratory research. *Environments*, 8(4), 32. <https://doi.org/10.3390/environments8040032>
15. Yu, X., Ying, G., & Kookana, R. S. (2006). Sorption and desorption behaviors of Diuron in soils amended with charcoal. *Journal of Agricultural and Food Chemistry*, 54(22), 8545-8550. <https://doi.org/10.1021/jf061354y>
16. Azra, N., Aziz, V., Ul Hasan, S., Nazir, M. S., Ali, Z., Hussain, M., & Park, Y. (2024). Investigation of the kinetics of imidacloprid adsorption onto bimetallic Cu- BTCMOF. *Journal of Industrial and Engineering Chemistry*, 140, 206–214. <https://doi.org/10.1016/j.jiec.2024.05.039>
17. Sharma, S., Bolan, S., Mukherjee, S., Petruzzelli, G., Pedron, F., Franchi, E., Fonseca, W., Wijesekara, H., Wang, L., Hou, D., Siddique, K. H., & Bolan, N. (2025). Role of organic and Biochar amendments on enhanced bioremediation of soils contaminated with persistent organic pollutants (POPs). *Current Pollution Reports*, 11(1). <https://doi.org/10.1007/s40726-025-00361-x>