

Dynamics of Phosphorus Sorption and Desorption in Ultisols Ameliorated with Humic Substances from Potential Ameliorants

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Abstract: Ultisols have a very high P sorption capacity, which limits the availability of P to plants. Therefore, it is necessary to understand the P sorption-desorption mechanism after humic substances (HS) amelioration to improve fertilizer efficiency and land productivity. This study has examined the complexity of phosphorus fixation and the potential of HS in modifying the surface charge of Ultisols. This study used the batch equilibrium method and the Freundlich and Langmuir isotherm model approaches. Meanwhile, the surface charge characteristics of Ultisols ameliorated with humic substances (HS) from potential ameliorants (control, HS-chicken manure, HS-black soldier fly, HS-wet decanter solid, and HS-peat) were evaluated using a completely randomized design with three replications. The HS from potential ameliorants significantly increases pH, PZC, electrical conductivity (EC), mineral and organic matter composition, CEC, and reduces potential redox (Eh), thereby increasing the soil's negative charge and buffering capacity. The HS—wet decanter solid and chicken manure were most effective, proven to remove Al-exchange to unmeasurable levels through strong complexation between Al³⁺ and carboxylate and phenolic groups. The HS—wet decanter solid and chicken manure also drastically reduce P sorption and increase desorption through ligand competition and blocking of Al/Fe reactive sites, which resulted in increased P availability up to >600 mg kg⁻¹ P₂O₅ at a concentration of 1000 mg L⁻¹ P or 2290 mg kg⁻¹ P₂O₅ or 6.37g SP-36 per liter or 6.37 kg SP-36 per hectare for an application volume of 1,000 liters per hectare.

Keywords: Amelioration; Humic substances; Fixation, Phosphorus, Ultisols

1. INTRODUCTION

Ultisols are one of the most commonly found soil orders in wet tropical regions and are highly relevant in the context of Indonesian agriculture. These soils are characterized by advanced weathering, low base saturation, and high Al and Fe oxide and hydroxide content, which causes intensive phosphorus (P) fixation and reduces its availability to plants (Johan et al., 2021). The acidic chemical conditions of Ultisols with positive surface charges on clay minerals cause P to be strongly bound in the form of Al-P or Fe-P complexes, making P fertilizer contributions

inefficient. The problem of low P availability in Ultisols is not only related to low total P content, but is more due to the high rate of P sorption, which is strong and tends to be irreversible. This high sorption rate results in very low P fertilization efficiency, with even phosphate fertilizers being sorbed by more than 80%, thereby increasing the fertilizer dose required to achieve optimal crop yields (Korzeniowska *et al.*, 2025). Dependence on high doses of P fertilizer not only increases production costs but also has the potential to cause the accumulation of P residues that are not effectively utilized.

The P sorption mechanism in Ultisols is greatly influenced by the chemical characteristics of acidic soils. Under these conditions, the positively charged clay mineral surface and the presence of active Al and Fe increase the soil's affinity for phosphate ions, resulting in the formation of strong, even covalent bonds (Ahmed *et al.*, 2024). This process causes P to not only be adsorbed electrostatically but also fixed in the form of insoluble secondary minerals. Therefore, P management strategies in Ultisols should focus not only on adding fertilizers but also on modifying the chemical properties of the soil so that sorption can be minimized. Efforts to improve Ultisols are largely directed towards the use of organic material (ameliorant) rich in humic substances (HS). The HS are known to form stable complexes with Al and Fe ions, thereby reducing the number of active sites available for P binding (Li *et al.*, 2022). The reduction in Al and Fe activity suppresses the P sorption process and increases P availability to plants. In addition to their ability to complex Al and Fe, HS also play a role in increasing the pH of acidic soils through a buffering mechanism. This increase in pH contributes to a decrease in the positive charge on the surface of clay minerals, thereby reducing the affinity of phosphate for adsorption sites and increasing the availability of P in the soil solution (Bao *et al.*, 2024). Thus, improving soil chemical conditions through the supply of HS is an important strategy for optimizing P uptake by plants.

The positive effects of HS are not limited to improving soil chemistry, but also have an impact on increasing cation exchange capacity (CEC), organic C, and overall soil structure. Stable humic components can increase nutrient retention and improve soil aggregation, thereby affecting P mobility and the effectiveness of P desorption into soil solution (Zhao *et al.*, 2025). These improved physical and chemical conditions increase the chances of P becoming available to plant roots. In the context of tropical soil management, various local resources such as humus extracts from organic waste have great potential as soil amelioration. One of them is black soldier fly (BSF) larvae and wet decanter solids (WDS) have special properties that distinguish them from conventional soil improvers such as peat or manure, as both are agro-industrial residues rich in easily decomposable organic matter, nitrogen, phosphorus, and bioactive compounds. The BSF residues are known to contain available nutrients, functional microorganisms, and organic fractions that can increase soil biological activity and nutrient efficiency (Gautam *et al.*, 2025; Tariq *et al.*, 2025). Meanwhile, WDS from the palm oil industry is rich in organic carbon, base cations, and colloidal fractions that play a role in increasing cation exchange capacity, soil aggregation, and water retention (Gofar *et al.*, 2022; Nurjanah *et al.*, 2025). Therefore, although unconventional, BSF and WDS are considered potential soil conditioners because they can simultaneously improve the physical, chemical, and biological properties of soil while supporting a circular economy approach and sustainable waste management. However, this potential has not been fully evaluated systematically in the context of P sorption/desorption in Ultisols. The diversity of the chemical characteristics of HS means that the response of the soil to the application of ameliorants is not always uniform. This highlights the importance of identifying the most effective type of HS soil amelioration for specific Ultisols conditions. Therefore, it is interesting to examine the complexity of phosphorus fixation and the potential of HS in modifying the surface charge of Ultisols.

2. METHOD

The research was conducted at the Laboratory of Chemistry and Soil Fertility, Faculty of Agriculture, Andalas University, Padang, from April to June 2025.

Experimental design

This study used the batch equilibrium method and the Freundlich and Langmuir isotherm model approaches. Meanwhile, the surface charge characteristics of Ultisols ameliorated with humic substances (HS) from potential ameliorants (control, HS-chicken manure, HS-black soldier fly, HS-wet decanter solid, and HS-peat) were evaluated using a completely randomized design with three replications.

Humic substances production and soil sampling

Preparation of humic substances (HS) production from chicken manure, black soldier fly residue, solid wet decanter, and peat. All materials are then dried at 70°C until they reach an air content of around 20%, while the peat is dried at a lower temperature (40°C) to maintain its humic structure. After drying, the materials are ground using a grinder and sieved with a size of 0.5 mm to obtain uniform fine particles. Next, the HS extraction process is carried out using a potential extractor of 1M NaOH technical-grade with a ratio of 1:5 w/v. Meanwhile, soil samples were obtained from the experimental field of the Faculty of Agriculture, Andalas University, Padang, West Sumatra, Indonesia. The GPS coordinates are -0.908477 S, and 100.478469 E. Soil samples were collected in a composite manner at a depth of 0 to 20 cm, with three replications and a sample weight of 1kg for each replication. Soil samples from the field were air-dried for 2 × 24 hours, then crushed and sieved with a 0.5 mm sieve. The soil samples were then weighed as much as 500 g of absolute dry equivalent, mixed with 40 tons ha⁻¹ of HS, where HS was calculated as the equivalent weight of ameliorant used per pot with a potential extractant ratio (technical-grade 1M NaOH) of 1:5 w/v, and incubated for two weeks. After incubation, the soil analysis process was carried out in the laboratory.

Phosphorus solution

Phosphorus (P) solution with concentrations of 200, 400, 600, 800, and 1000 ppm using SP-36 fertilizer, where SP-36 contains 36% P₂O₅, which is equivalent to approximately 15.7% of the P element after conversion (P = P₂O₅ × 0.436). This means that every 1g of SP-36 contains approximately 157mg of P. Based on the required concentration of the P solution per liter, the amount of SP-36 fertilizer that must be weighed can be calculated by dividing the P requirement (in mg) by the P content in the fertilizer (0.157). Preparation of solutions of 200 mg L⁻¹ (requires 1.27g SP-36 per liter), 400 mg L⁻¹ (2.55g), 600 mg L⁻¹ (3.82g), 800 mg L⁻¹ (5.10g), and 1000 mg L⁻¹ requires approximately 6.37g SP-36 per liter. The weighed SP-36 fertilizer is then dissolved in a portion of distilled water while stirring and heating lightly, and filtered if there is still sediment. After that, the solution is put into a volumetric flask and diluted to reach a volume of exactly 1 liter.

Batch adsorption/ desorption experiments

The 0.5g of adsorbent was mixed with 20 ml of P solution in a closed 25 ml glass cylindrical tube. The mixture was agitated on a rotary shaker at 250 rpm for 24 hours at laboratory temperature (25°C) at concentrations of 200, 400, 600, 800, and 1000 mg L⁻¹ P. The samples were spun at 4000 rpm for 30 minutes. Filter paper No. 41 from Whatman was used to filter the model. The pH of the filtrate solution was measured at each concentration, and the equilibrium concentration of P remaining in the solution was assessed using a UV-Vis spectrophotometer at a wavelength of 889 nm with complexation. The adsorbed P was computed using formulae 1, 2, and 3 (Herviyanti *et al.*, 2023; Prasetyo *et al.*, 2024).

$$K_d (L \text{ kg}^{-1}) = \frac{Q_e}{C_e} \times 1000 \dots \dots \dots \quad (F.3)$$

where: C_0 (mg L⁻¹) = the initial concentration, C_e (mg L⁻¹) = equilibrium concentration, R (%) = removal efficiency, Q_e (mg g⁻¹) = adsorption capacity, m (g) = mass, V (L) = the quantity solution, R (%) = adsorption efficiency and K_d (L kg⁻¹) = adsorption coefficient.

Meanwhile, the desorption process was carried out after the adsorption process by extracting the remaining adsorbent residue using the Bray I method by adding 10 ml of Bray and Kurtz I extractant, which was shaken for 30 minutes. Next, the sample is filtered again, and 2 ml of the sample is pipetted, and 8 ml of phosphate dye is added, and left for 30 minutes. The solution is measured for absorbance with a UV-Vis spectrophotometer at a wavelength of 889 nm with complexation.

Data analyses

Soil analysis refers to the goal of studying the surface charge activity of Ultisols ameliorated with HS using the following pH [H₂O, KCl 1M and point of zero charge (PZC], electrical conductivity (EC), potential redox (Eh), mineral and organic matter composition, and cation exchange capacity (CEC) (Eviati et al., 2023). Linear formulas of isotherm models, Henry's equation (F.4) (Pera-titus, 2010).

where: Q_e = amount of adsorbate adsorbed per unit mass of adsorbent (mg g^{-1}), C_e = concentration of adsorbate in solution at equilibrium (mg L^{-1}), and K_H = Henry's constant (L g^{-1}).

One-parameter adsorption isotherm models (the Henry's) were utilized. The adsorption isotherm models included both linear and the batch equilibrium method was utilized to illustrate the mechanism for establishing the applicability and stability of the adsorption procedure. Data was analyzed using Microsoft Excel 2016 and SPSS 16.

3. RESULT AND DISCUSSION

Surface charge and Al-exchange on Ultisols ameliorated with humic substances from potential ameliorants.

Application of humic substance (HS)-based ameliorants resulted in significant changes in the surface charge characteristics of Ultisols, demonstrating the central role of organic-mineral interactions in modifying soil acidity, redox behavior, and charge development (**Table 1**). The pH values measured in H₂O and KCl showed substantial ameliorative effects compared to untreated soils. Native Ultisols exhibited highly acidic conditions (pH H₂O 3.70; pH KCl 3.45), consistent with high Al saturation and the dominance of permanent charges, which are characteristic of highly weathered tropical soils. The addition of humic substances, especially those derived from wet decanter solids (HS-WDS), substantially increased soil pH (pH H₂O 5.27; pH KCl 4.68), indicating effective proton consumption and complexation of exchangeable Al³⁺ by humic functional groups. This response aligns with findings that humic acid neutralizes acidity through carboxyl and phenolic groups, thereby increasing soil buffering capacity (Xu et al., 2021). The point of zero charge (PZC) followed a similar pattern, with HS-wet decanter solid significantly increasing the PZC to 4.09, while the untreated soil maintained a lower PZC (3.20). The influx of organic colloids with a higher density of acidic functional groups, which alter the variable charge surfaces of kaolinite and Fe/Al oxides (Sun et al., 2020). Higher PZC values also indicate increased

surface reactivity and the potential for increased negative charge formation at neutral pH, which has implications for nutrient retention, particularly for basic cations.

Electrical conductivity (EC) remained low at around 0.06–0.10 dS m⁻¹, confirming that the HS effect of potential ameliorants was significant in modifying the charge rather than salt accumulation (Table 1). A slight increase in EC in HS-wet decanter solid (0.08 dS m⁻¹) and HS-black soldier fly (0.07 dS m⁻¹) indicated the release of dissolved ions from mineral-rich byproducts, but was still within safe limits for plant growth. Low EC values are characteristic of organic-based ameliorated that slowly release nutrients through mineralization (Engedal *et al.*, 2025). Meanwhile, the redox potential (Eh) showed a significant difference with the HS effect of potential ameliorants, with the highest Eh recorded in the control soil (124.19 mV) and the lowest in HS-chicken manure (115.52 mV). The addition of humic substances generally decreases Eh, indicating a greater reduction microenvironment due to increased microbial activity and an increased supply of electron-donating groups from organic compounds (Tan *et al.*, 2018). Lower Eh conditions are associated with increased nutrient availability and microbial respiration, especially in tropical soil conditions with high organic matter turnover.

Table 1. Surface charge characteristics of Ultisols ameliorated with humic substances from potential ameliorants

| Ameliorant | pH (1:1) | | | EC dS m ⁻¹ | Eh mV | Composition | | CEC cmol(+) kg ⁻¹ |
|------------------------------|------------------|-----------|--------|--------------------------|----------|-------------|---------|---------------------------------|
| | H ₂ O | KCl 1M | PZC | | | Mineral | OM | |
| | unit | | | | | % | | |
| Soil/ Control | 3.70 d | 3.45 b | 3.20 b | 0.06 c | 124.19 a | 70.85 a | 29.15 c | 8.50 c |
| Soil + HS-Chicken Manure | 4.84 b | 3.55 b | 2.26 c | 0.06 c | 115.52 c | 68.65 b | 31.35 b | 16.50 b |
| Soil + HS-Black Soldier Fly | 4.44 c | 3.46 b | 2.47 c | 0.07 b | 113.87 c | 68.85 b | 31.15 b | 21.00 b |
| Soil + HS-Wet Decanter Solid | 5.27 a | 4.68 a | 4.09 a | 0.08 a | 118.71 b | 67.65 c | 32.35 a | 30.50 a |
| Soil + HS-Peat | 3.81 d | 3.48 b | 3.15 b | 0.07 b | 116.08 c | 67.25 c | 32.75 a | 19.17 b |
| CV (%) - Duncan's | | | | | | | | |
| Test | 2.28** | 1.77** | 7.05** | 3.76** | 1.25** | 0.36** | 0.80** | 13.16** |
| SE | 0.08 | 0.05 | 0.18 | 0.002 | 1.20 | 0.20 | 0.20 | 2.06 |

Note: HS = humic substances, PZC = point of zero charge [(2*pH KCl) – pH H₂O], EC = electrical conductivity, Eh = potential redox, OM = organic matter, CEC = cation exchange capacity, CV = coefficient of variation, SE = standard error, and n = 15 samples.

Soil mineral composition fluctuated after amelioration with HS of potential ameliorants (Table 1), with HS-chicken manure (68.65%) and HS-black soldier fly (68.87%) showing the best performance. The contribution of mineral-rich organic sources capable of supplying Ca, Mg, Fe, and microelements interacts with humic molecules, forming organo-mineral complexes known to stabilize soil structure (Piccolo & Drosos, 2025). Organic matter was substantially higher in all HS effects of potential ameliorants compared to the control (29.15%). The HS-Peat effect showed the highest value at 32.75%, consistent with the inherent recalcitrant carbon fraction of the peat material. Increasing OM is crucial for Ultisols rehabilitation because it promotes the development of negative charges through functional group dissociation, increases buffering capacity, and improves aggregation (Monteiro *et al.*, 2019).

The cation exchange capacity (CEC) showed a significant increase due to the influence of HS from potential ameliorants. The control soil showed a very low CEC of $8.50 \text{ cmol}(+) \text{ kg}^{-1}$, characteristic of Ultisols dominated by kaolinite and sesquioxides. The influence of HS significantly increased the CEC, with HS-wet decanter solid reaching the highest of $30.50 \text{ cmol}(+) \text{ kg}^{-1}$. The formation of stable and reactive humic colloids capable of producing a pH-dependent negative charge, consistent with the known ability of humic acid to increase charge density through deprotonation of O-containing functional groups (Wang *et al.*, 2025). The subsequent increase in CEC indicates effective amelioration, increasing nutrient retention, and reducing leaching losses, a major limitation in highly weathered tropical soils. Thus, HS from potential ameliorants, especially those derived from wet decanter solids, chicken manure, and black soldier fly residues, provided an improvement in the surface charge characteristics of Ultisols. This improvement occurs through synergistic mechanisms, including acidity neutralization, humic-mineral complexation, organic matter enrichment, and increased cation retention capacity.

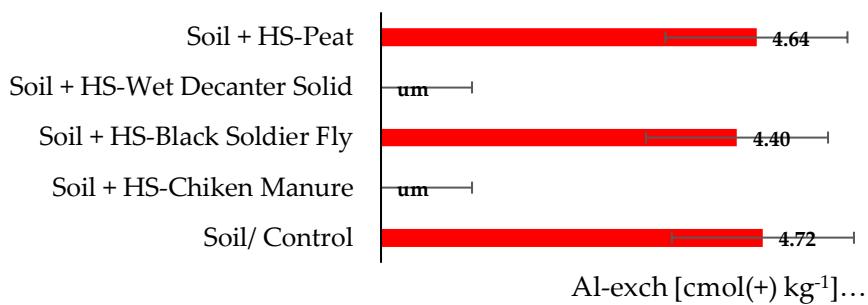


Figure 1. Al-exchangeable on Ultisols ameliorated with humic substances.

Exchangeable aluminum is a key indicator of soil acidity in Ultisols, and its reduction is a primary target for soil amelioration. Untreated Ultisols exhibited high Al-exch of $4.72 \text{ cmol}(+) \text{ kg}^{-1}$, consistent with the highly acidic nature of highly weathered tropical soils dominated by kaolinite and aluminum/iron oxides. High Al-exch concentrations are known to inhibit root elongation, reduce nutrient uptake, and impair overall plant productivity due to Al^{3+} toxicity (Guo *et al.*, 2024). The high Al-exch in the control confirms the low soil buffering capacity and the strong reliance on ameliorants to reduce acidity. The most significant reductions occurred with HS from chicken manure and wet decanter solids, both of which successfully reduced Al-exch to unmeasurable levels. This complete elimination of exchangeable Al demonstrates the strong chelating capacity of the humic acids contained in these materials. The HS functional groups, primarily carboxylic and phenolic groups, are known to form stable complexes with Al^{3+} , effectively removing it from the exchange phase and reducing Al-induced phytotoxicity (Lamar *et al.*, 2024). Furthermore, these materials often contain higher concentrations of basic cations (e.g., Ca^{2+} , Mg^{2+}), which displace Al^{3+} from exchange sites through a mass-action exchange mechanism (M. Yang *et al.*, 2024). The HS from wet decanter solids results align with previous findings that agro-industrial organic byproducts enriched with amorphous minerals have strong ameliorative potential for acidic soils. In contrast, HS from black soldier fly waste and peat were less effective in reducing Al toxicity, with Al exchange rates remaining high at 4.40 and $4.64 \text{ cmol}(+) \text{ kg}^{-1}$, respectively. These levels are close to those of untreated soils, suggesting that HS from these sources contains insufficient reactive functional groups or lacks sufficient base cations to effectively replace Al^{3+} . Peat-based HS, while rich in stable organic carbon, often have a lower number of active carboxyl groups and limited mineral content, thus reducing their direct reactivity with exchangeable Al (Maffia *et al.*, 2025). Similarly, BSF residue may contain chitin-derived organic compounds that are less efficient at complexing Al than typical humic acids. Different types of ameliorants extracted into HS

provide distinct improvements to the neutralization and removal of exchangeable Al in Ultisols. The absence of Al exchange in soils ameliorated with HS from chicken manure and wet decanter solids showed significant amelioration results, indicating their suitability as sustainable organic compounds to rehabilitate Al-toxic Ultisol acidity (Fig. 1).

Sorption/ Desorption P on Ultisols Ameliorated with Humic Substances from Potential Ameliorants

Phosphorus (P) dynamics in Ultisols are strongly regulated by interactions between phosphate ions and variable-charge mineral surfaces dominated by Al oxides. Unameliorated Ultisols exhibit very high P uptake and low desorption, as reflected by increasing equilibrium P concentrations (C_e) with increasing added P (C_0), but with desorption values consistently remaining lower than uptake at all pH levels. This is a characteristic feature of highly weathered acidic soils, where P is fixed through ligand exchange on the surfaces of hydroxylated goethite, hematite, and gibbsite (Mendez *et al.*, 2020). The low available P (47.84–61.43 ppm P_2O_5) across the pH gradient further confirms the strong P-binding capacity typical of Ultisols with a high P retention index. The effect of HS-chicken manure reduced P uptake and increased P desorption relative to the control. At comparable C_0 values, the sorbed P concentration was consistently lower (0.22 vs. 0.39 mg L^{-1} at C_0 of 200 mg L^{-1} P), while the desorption rate increased (31.05 vs. 8.22 mg L^{-1} P at pH 6.9). These changes reflect the presence of abundant organic ligands, Ca-rich mineral fractions, and humic acids that compete with phosphate for sorption sites and block Fe/Al oxide surfaces through ligand exchange and surface coating (Li *et al.*, 2022). Available P significantly increased (236–397 ppm P_2O_5), indicating that HS-chicken manure increased P mobility and plant availability by reducing the formation of inner-sphere complexes. The HS from manure supplies complex organic acids that reduce P fixation in acidic soils (Shen *et al.*, 2023).

Table 2. Sorption/ desorption P on Ultisols ameliorated with humic substances

| Ameliorant | pH | C_0 | Ce P – | Ce P - | Q_e | pH | Available |
|------------------------------|----------|-------|---------------|-------------|-------|--------------|-----------|
| | Solution | | Sorption | Desorption | | Adsorption | P |
| | unit | | mg L^{-1} P | mg L^{-1} | unit | ppm P_2O_5 | |
| Soil/ Control | 6.8 | 200 | 0.39 | 6.40 | 5.99 | 3.6 | 47.84 |
| | 6.9 | 400 | 0.45 | 8.22 | 11.99 | 3.63 | 61.43 |
| | 7.1 | 600 | 0.73 | 20.88 | 17.98 | 3.64 | 156.02 |
| | 7.6 | 800 | 1.02 | 78.23 | 23.97 | 4.11 | 584.64 |
| | 7.9 | 1000 | 1.07 | 79.71 | 29.97 | 4.14 | 595.71 |
| Soil + HS-Chicken Manure | 6.8 | 200 | 0.12 | 7.88 | 6.00 | 6.27 | 58.86 |
| | 6.9 | 400 | 0.22 | 31.66 | 11.99 | 6.32 | 236.62 |
| | 7.1 | 600 | 0.66 | 39.85 | 17.98 | 6.35 | 297.85 |
| | 7.6 | 800 | 0.79 | 67.12 | 23.98 | 6.39 | 501.61 |
| | 7.9 | 1000 | 1.76 | 82.57 | 29.95 | 6.49 | 617.09 |
| Soil + HS-Black Soldier Fly | 6.8 | 200 | 0.38 | 10.11 | 5.99 | 3.64 | 75.54 |
| | 6.9 | 400 | 0.47 | 15.68 | 11.99 | 3.95 | 117.21 |
| | 7.1 | 600 | 0.78 | 17.51 | 17.98 | 3.98 | 130.84 |
| | 7.6 | 800 | 0.87 | 79.26 | 23.97 | 4.09 | 592.36 |
| | 7.9 | 1000 | 1.09 | 79.67 | 29.97 | 4.55 | 595.40 |
| Soil + HS-Wet Decanter Solid | 6.8 | 200 | 0.12 | 7.65 | 6.00 | 6.19 | 57.16 |
| | 6.9 | 400 | 0.29 | 9.10 | 11.99 | 6.21 | 68.05 |
| | 7.1 | 600 | 0.54 | 13.13 | 17.98 | 6.30 | 98.16 |
| | 7.6 | 800 | 1.56 | 73.71 | 23.95 | 6.49 | 550.89 |
| | 7.9 | 1000 | 2.06 | 84.68 | 29.94 | 6.55 | 632.88 |
| Soil + HS-Peat | 6.8 | 200 | 0.33 | 9.69 | 5.99 | 3.75 | 72.39 |
| | 6.9 | 400 | 0.50 | 14.59 | 11.98 | 3.96 | 109.03 |
| | 7.1 | 600 | 0.75 | 26.93 | 17.98 | 3.99 | 201.25 |
| | 7.6 | 800 | 0.79 | 81.05 | 23.98 | 4.04 | 605.76 |
| | 7.9 | 1000 | 1.27 | 82.46 | 29.96 | 4.36 | 616.27 |

Note: P = phosphorus; C_0 = initial concentration; C_e = equilibrium concentration; Q_e = adsorption capacity; R = removal efficiency; K_d = coefficient of adsorption.

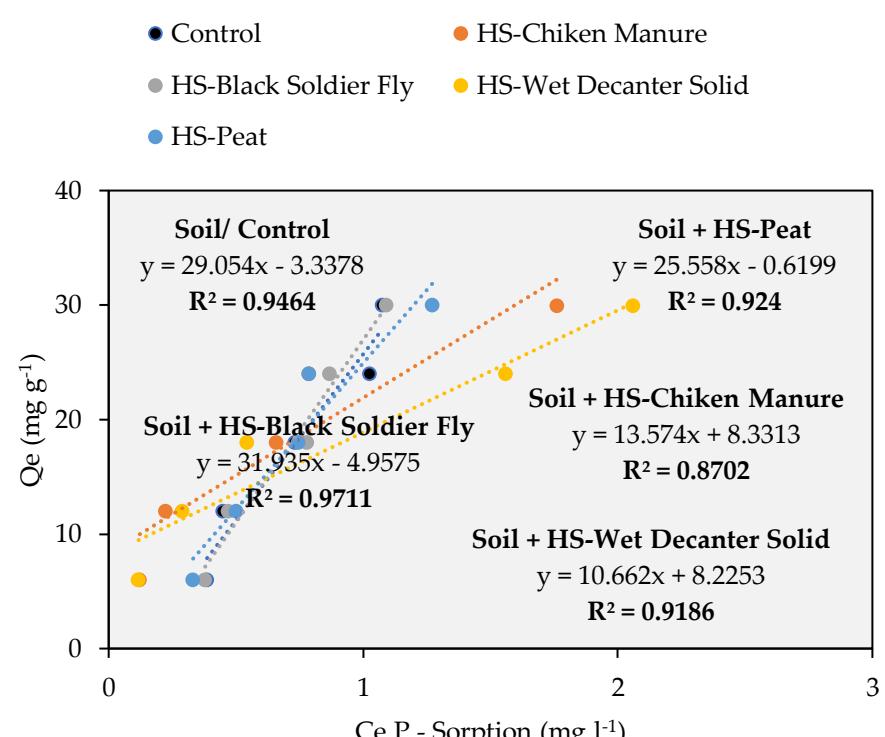
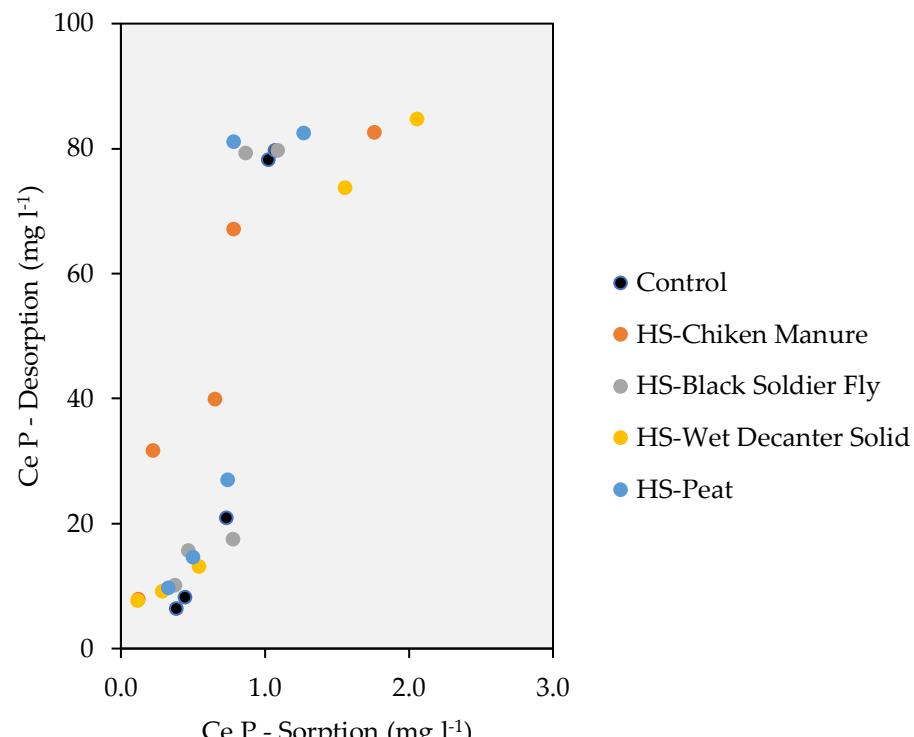
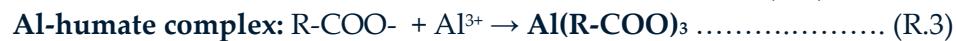
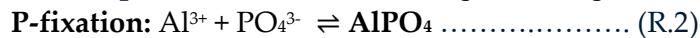


Figure 2. Distribution of sorption/desorption P (A) and the linear part of Henry's equation (B) in Ultisols ameliorated with humic substances from potential ameliorants.

The HS-black soldier fly produced an intermediate response between the control and HS-chicken manure. Sorption values were lower than the control but not as strongly suppressed as HS-chicken manure, indicating the presence of organic molecules that reduce P fixation but with a lower density of reactive functional groups. Desorption values Ce (60.47–82.80 mg L⁻¹ P) indicated a moderate release of previously adsorbed P, indicating partial surface passivation. The BSF residue contained chitin and moderately humified organic matter, which may enhance competitive surface interactions but not completely inhibit inner-sphere phosphate bonding (Xiong *et al.*, 2023).

The available P (217–300 ppm P₂O₅) reflected a moderate but significant increase relative to unameliorated Ultisols. The HS-wet decanter solids showed the strongest suppression of P sorption among all ameliorants. Sorption remained consistently low even at high C₀ levels (only 1.06 mg L⁻¹ P was sorbed at C₀ of 1000 mg L⁻¹ P), while desorption values were very high (73.71–96.80 mg L⁻¹ P). This indicates that HS-wet decanter solid effectively coated the oxide surface or replaced reactive hydroxyl groups, drastically reducing the number of available binding sites. The high organic-mineral composition of decanter solids (rich in amorphous Ca, Mg, and Fe-humic complexes) promoted the formation of outer-sphere complexes and P retention in the soil solution, rather than fixation (Gerke, 2010).

Correspondingly, available P levels were the highest among all treatments (up to 550–617 ppm P₂O₅), demonstrating its superior ability to enhance P bioavailability through suppression of sorption and enhancement of desorption. The HS-peat produced a slightly different response than the control. Sorption values remained relatively high (0.30–1.27 mg L⁻¹ P), and desorption remained low compared to the other HS of potential ameliorant. Available P of 73–105 ppm P₂O₅ increased slightly but was well below those observed with HS-chicken manure or HS from wet decanter solids. Peat contains stable humic molecules dominated by aromatic carbon with fewer reactive acid groups, resulting in weaker competitive interactions with phosphate and persistent P binding to oxide surfaces (Xue *et al.*, 2024). Consequently, peat did not significantly reduce phosphate fixation, confirming that not all humic sources are equally effective in modifying P retention behavior. The effect of HS as a potential ameliorant on P sorption followed the pattern that soil + HS-wet decanter solids > soil + HS-chicken manure > soil + HS-black soldier fly > soil + HS-peat ≈ soil. Meanwhile, P desorption and available P followed the same ranking, confirming that organic matter composition and humification level determine the capacity to block or compete with Fe/Al reactive surfaces. Calcium-rich and mineral-rich ameliorants (HS-wet decanter solids and HS-chicken manure) showed the strongest P release effect through Ca-P precipitation and competition with Al/Fe oxides. Highly aromatic and recalcitrant HS (HS-peat) did not significantly increase P bioavailability.

The distribution of phosphorus (P) sorption–desorption in Ultisols ameliorated with HS of potential ameliorant showed significant differences in P retention and release capacity (**Figure 2.A**). Higher P sorption values were found in soils treated with HS-wet decanter solid and chicken manure, indicated by an increase in sorbed Ce concentration (up to >2 mg L⁻¹), while P desorption also increased, indicating that the ameliorants were able to provide active sites that bind P but still allow its release back into the soil solution. The HS rich in carboxylic and phenolic groups increases P complexation with Fe/Al oxides, thereby increasing P retention, but the binding remains reversible (Li *et al.*, 2023). In the control and HS-peat, P sorption was low (0.5–1.0 mg L⁻¹), and desorption was also lower, indicating limited active groups and organo-mineral complexation capacity for P retention in Ultisols, which naturally contain high levels of Al/Fe oxides, which bind P strongly and irreversibly. The addition of HS of a potential ameliorant can modify P sorption–desorption dynamics by increasing negative charge, forming organic-Fe/Al complexes, and increasing soil aggregate stability.

Linear analysis of Henry's equation corroborates the findings of the sorption–desorption distribution by demonstrating a strong linear relationship between adsorbed phosphorus concentration (Q_e) and equilibrium concentration (C_e), as evidenced by the high R^2 values in Ultisols ameliorated with HS from potential ameliorant (0.87–0.97) (Figure 2.B). The HS from black soldier fly showed the highest Henry's sorption constant (K_H of 31.935), reflecting the highest sorption capacity compared to other ameliorants, indicating that the bio-humate from BSF larvae has a high functional charge density and a high affinity for P. In contrast, HS-wet decanter solid had the lowest Henry's sorption constant (K_H of 10.66), indicating moderate sorption but still showed a fairly large positive intercept, indicating the contribution of organic groups in providing P-available early in the reaction. The high R^2 value indicates that P sorption in Ultisols with HS addition follows the Henry isotherm pattern well, indicating a sorption geochemistry dominated by linear surface binding in the low concentration range, as is common in high-oxidation soils (Tellinghuisen *et al.*, 2025). The chemical quality of HS, including the degree of aromaticity, the number of carboxylic/phenolic groups, and molecular size, is a key factor controlling P sorption capacity. Overall, the combination of sorption–desorption distribution and the Henry model shows that Ultisol amelioration with HS has the potential to increase P fertilization efficiency through increased retention, decreased irreversible fixation, and more controlled P release regulation.

Conclusions

Humic substances (HS) from potential ameliorants significantly increase pH, PZC, electrical conductivity (EC), mineral and organic matter composition, CEC, and reduce potential redox (Eh), thereby increasing the soil's negative charge and buffering capacity. The HS—wet decanter solid and chicken manure were most effective, proven to remove Al-exchange to unmeasurable levels through strong complexation between Al^{3+} and carboxylate and phenolic groups. The HS—wet decanter solid and chicken manure also drastically reduce P sorption and increase desorption through ligand competition and blocking of Al/Fe reactive sites, which resulted in increased P availability up to $>600\text{ mg kg}^{-1} P_2O_5$ at a concentration of $1000\text{ mg L}^{-1} P$ or $2290\text{ mg kg}^{-1} P_2O_5$ or $6.37\text{ g SP-36 per liter}$ or $6.37\text{ kg SP-36 per hectare}$ for an application volume of 1,000 liters per hectare.

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