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Competitive Sorption and Retention of Chromium, Copper, Lead, and Zinc in Brewery Biosolid-Amended Ferralsol (Oxisol): Selectivity, Mechanisms, and Environmental Implications

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Abstract

This study investigated the competitive sorption and desorption behaviour of potentially toxic elements (PTEs) or trace metals (chromium, copper, lead, and zinc) from brewery biosolid-amended Ferralsol (Oxisol), addressing critical gaps in understanding metal mobility and retention in tropical agricultural soils receiving industrial organic amendments. Batch equilibrium experiments were conducted using Ferralsol amended with brewery biosolid at application rates of 0, 2.5, 5.0, and 7.5 tons·ha^{-1}, with single superphosphate (SSP) at 0, 25, 50, and 75 kg·ha^{-1}. Multi-metal nitrate solutions (25 - 500 mg·L^{-1}) containing equal concentrations of Cr^{3+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} were equilibrated with sorbents for 1 day (24 hours) at pH 4.5 (buffered with 0.02 M acetic acid/sodium acetate). Metal concentrations were determined by atomic absorption spectrophotometry. Sorption and desorption data were fitted to Langmuir and Freundlich isotherms, and distribution coefficients (K_d) were calculated to establish selectivity sequences. Chromium (Cr^{3+}) exhibited the highest sorption and retention capacity across all treatment rates, with K_d values 2 - 3 orders of magnitude greater than those of other metals. The selectivity sequence for adsorption followed Cr > Zn > Pb > Cu at 100 mg·L^{-1}, shifting to Zn > Cr > Pb > Cu at 7.5 metric tons·ha^{-1} brewery biosolid application. Desorption studies revealed near-irreversible binding for chromium (retention K_d = 14.2 - 33.4 L·g^{-1}), while zinc demonstrated the greatest reversibility (retention K_d = 0.09 - 0.27 L·g^{-1}).

Langmuir and Freundlich models showed limited applicability (only 43.6% of potential isotherms fitted $r^2 > 0.75$), with Freundlich providing superior fits for most metal-sorbent combinations. The high charge-to-radius ratio of Cr^{3+} (49.2 against 16.8 - 27.4 for other metals) drives its preferential retention through inner-sphere complexation and possible surface precipitation. Brewery biosolid addition increased organic matter content (from 2.51% to 4.5%) and cation exchange capacity (from 8.7 to 17.6 $cmol{\cdot}kg^{-1}$), enhancing overall metal retention capacity. The S-type isotherms observed indicate cooperative adsorption mechanisms. These findings demonstrate that brewery biosolid-amended Ferralsol (Oxisol) effectively immobilizes chromium, reducing its bioavailability and leaching potential, while zinc remains comparatively mobile. Application rates above 5.0 $tons{\cdot}ha^{-1}$ optimize metal retention without compromising soil quality.

Keywords

Competitive Sorption, Potentially Toxic Elements (PTEs), Brewery Biosolid, Ferralsol, Distribution Coefficient, Selectivity Sequence

1. Introduction

Industrial biosolids have gained increasing attention as soil amendments for agricultural production systems in Sub-Saharan Africa, where access to mineral fertilizers is constrained by high costs and limited availability [1] [2]. Brewery biosolid, a byproduct of beer production, contains substantial organic matter (35% - 40%) and plant nutrients including nitrogen, phosphorus, potassium, calcium, and magnesium. However, these materials also accumulate potentially toxic elements (PTEs) from brewing equipment (copper kettles), processing chemicals, and wastewater treatment operations.

The environmental fate of PTEs introduced through biosolid application depends critically on sorption-desorption reactions at the soil-water interface [3] [4]. Unlike organic contaminants that undergo microbial degradation, PTEs persist in soils indefinitely, with changes limited to speciation and bioavailability transformations [5]. Understanding competitive sorption behaviour is essential because contaminated sites invariably contain multiple metals that compete for finite binding sites [6] [7]. Recent studies have demonstrated that biosolids application can significantly affect the competitive sorption and lability of metals, with strong metal- and soil-specific effects [8]. For example, at low loading rates, biosolids may increase metal lability, while at higher rates, they can act as immobilizing agents, particularly for copper (Cu) and lead (Pb).

Ferralsols (Oxisols) dominate much of tropical Africa and are characterized by low pH, high iron and aluminum oxide content, variable charge surfaces, and significant phosphorus fixation capacity [9]. These properties profoundly influence trace metals retention through mechanisms including specific adsorption on ox-

ide surfaces, ion exchange on clay minerals, and complexation with soil organic matter [10] [11]. Recent spectroscopic and batch studies have shown that chromium(III) forms predominantly monomeric complexes with natural organic matter at low pH (<5) and polynuclear complexes at higher pH, with complexation kinetics being slow (months) at pH < 4 [12]. Therefore, the dynamics of metal binding in Ferralsols require careful evaluation, especially when amended with organic materials such as brewery biosolid.

Despite the increasing use of brewery biosolid as a soil amendment in East Africa, systematic characterization of competitive PTEs or trace metals sorption-desorption behaviour in Ferralsols remains inadequate. Previous studies have predominantly examined single-metal systems or focused on temperate soils with different mineralogies [13] [14]. The simultaneous presence of multiple metals creates competition effects that cannot be predicted from individual metal isotherms, yet few investigations have addressed competitive sorption in biosolid-amended tropical soils. Additionally, recent work has highlighted that the effectiveness of biosolids and other organic amendments in immobilizing metals can be highly variable depending on amendment type, soil properties, and the specific metal(loid) of concern [15]. The use of fresh versus air-dried biosolids can also influence metal solubility and plant responses [16].

This study aimed to quantify competitive sorption and desorption of Cr^{3+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} by Ferralsol amended with brewery biosolid and P-fertilizer at variable application rates; determine the applicability of Langmuir and Freundlich isotherm models for describing multi-metal sorption behaviour, establish the selectivity sequences based on distribution coefficients for sorption and retention; and identify the primary soil and metal properties governing differential metal retention.

This research provides essential data for: i) predicting PTE mobility and bioavailability in brewery biosolid- and P-fertilizer amended Ferralsols, ii) establishing evidence-based application rates that minimize environmental risk, iii) informing regulatory frameworks for biosolid use in tropical agriculture, and iv) developing remediation strategies for metal-contaminated sites in Sub-Saharan Africa.

2. Materials and Methods

2.1. Study Site and Soil Collection

Bulk soil samples (approximately 100 kg) were collected from Makerere University Agricultural Research Institute, Kabanyolo (MUARIK), located in central Uganda (0˚28'N, 32˚37'E). The soil was classified as Ferralsol (Oxisol) (FAO-WRB system) with predominantly kaolinitic clay mineralogy, high sesquioxide content, and low native fertility. Selection criteria included absence of cultivation for ≥ 10 years, no fertilizer history, and documented low productivity—ensuring minimal background PTE interference.

Soil was collected from 0 - 20 cm depth using plastic implements to avoid metal

contamination, air-dried on clean polyethylene sheets for 7 days, then crushed using a porcelain mortar and pestle. Thereafter, it was passed through a 2 mm sieve to remove coarse fragments and homogenized. Three sub-samples were taken for laboratory analysis.

2.2. Brewery Biosolid Collection

Brewery biosolid (BSW) was obtained from Uganda Breweries Limited, Luzira, Kampala District at the treatment site. The polyethylene sampling bags used to collect the samples were pre-cleaned with analytical nitric acid (about 50 mL), and rinsed three times with de-ionised water (500 mL). The material represented anaerobically digested, dewatered sludge from wastewater treatment operations. Approximately 50 kg was collected in the cleaned polyethylene bags, sealed to prevent volatile loss, transported to the soil laboratory where non-organic materials were like stones, glass pieces, and plastic materials were removed. The remaining brewery biosolid was air-dried for 5 days at 25˚C, ground to finer particles (<2 mm) using a porcelain mortar and pestle, and stored at room temperature in sealed containers until laboratory analysis was done.

2.3. Analytical Methods

Soil and Brewery Biosolid Characterization

The soil sample or brewery biosolid, which was air-dried, crushed and passed through a 2 mm sieve to remove any debris or stones was used to determine the pH, organic matter, electroconductivity, cation exchange capacity, total nitrogen, available phosphorus and PTEs (cadmium, copper, zinc, chromium, lead). The pH of soil was determined in a suspension of soil: water ratio 1:2.5 w/v [17]. The suspension was stirred at regular intervals for one hour and pH was measured using a pH meter using a glass electrode of a calibrated pH meter. The pH of the brewery biosolids was determined by suspension (the suspension was prepared by taking 3.2 g of a well-mixed sample of dry biosolid in 150 mL beaker, then adding 96.8 mL of deionized water and shaking the sample for 30 min at 150 oscillations per minute as described by Doty *et al.* [18]). The soil or brewery biosolids suspensions were allowed to settle for 1 day (24 hours) and then measurement of the conductivity of the supernatant liquid was done using a conductivity meter [19].

The Walkley-Black method was used to determine the organic matter of soil and brewery biosolids [20]. A sample was passed through a 0.5 mm sieve and 0.5 g was weighed into a 500 mL Erlenmeyer flask. Potassium dichromate (10 mL) was added followed by concentrated sulphuric acid. The mixture was cooled, diluted with distilled water (150 mL) and concentrated phosphoric acid (10 mL) was added. The contents were titrated with ferrous-ammonium-sulphate (0.4 N) after adding o-phenanthroline indicator (6 drops). A blank was performed using the same procedure and organic matter content was calculated using Equation (1).

$$\%\ \text{organic matter} = 10\left(1-\frac{S}{B}\right)\times 0.67 \quad (1)$$

where S is the volume of titrant used for the soil sample, and B is the volume used for the blank.

The standard ammonium acetate method as described by Chapman [21] was used to determine cation exchange capacity (CEC). Briefly, an air-dried soil sample that was crushed and sieved to 2 mm, 1N ammonium acetate solution buffered at pH 7.0 was added. The mixture was then shaken and filtered, removing the exchangeable cations and saturating the exchange complex with NH_4^+. The sample soil was washed with a solvent (like alcohol) to remove the excess, unadsorbed ammonium acetate solution. A solution containing displacing ion like potassium chloride or sodium chloride was added. The NH_4^+ previously occupying the exchange sites was displaced into the solution. Then the displaced solution was analysed to determine the amount of NH_4^+ present. The quantity was then used to calculate the CEC value, typically expressed in $cmol^+/kg$.

Total N was determined by the Kjeldahl digestion technique of both soil and brewery biosolid samples [17] [22]. A soil or brewery biosolids sample of 0.3 g was taken into digestion tubes. This was followed by concentrated sulphuric acid (5 mL) and mixed catalyst. The mixture was digested at 35˚C for two hours, cooled and transferred into 50 mL volumetric flask. The solution was made up to the mark with distilled water and homogenised. A 10 mL aliquot was taken for distillation in the Markham still apparatus. The distillate containing ammonia was trapped in boric acid (1%, 5 mL) containing the indicator and this was titrated against hydrochloric acid (0.007 M). Hence, the amount of nitrogen was obtained.

Plant available phosphorus in soil sample was estimated using the Bray I extraction procedure [17]. For total phosphorus in the brewery biosolids samples, the procedure involved treating the standards and the samples with p-nitrophenol (0.5%, 0.2 mL) indicator solution, making the mixture with ammonia solution (6 N). This was followed by addition of nitric acid (1 N) and then ammonium molybdate/ammonium vanadate mixed reagent (5 mL). The solution was diluted with distilled water (50 mL) and kept for about 30 minutes. Absorption of the solution was also read from a colorimeter at 400 nm wavelength and amount of phosphorus obtained from a calibration curve.

The soil or brewery biosolids samples were prepared and analysed for PTEs (cadmium, copper, zinc, chromium, lead) as described by [23]. Dry samples (0.2 g) in Teflon crucibles were digested with a mixture of nitric acid (65%), perchloric acid (100%) and hydrofluoric acid (40%). The mixture was evaporated at 160˚C. The residue was then dissolved in hydrochloric acid (1 M, 20 mL). A clear solution was carefully taken for determination of the different elements by the atomic absorption spectrophotometer (AAS, SavantaAA 2009 model manufactured in Austria by GBC Scientific Equipment).

2.4. Experimental Design

2.4.1. Treatment Structure

Treatment factors included brewery biosolid application rates of 0, 2.5, 5.0, and 7.5 metric tons·ha^{-1} on dry weight basis and those for phosphorus fertilizer (SSP)

were 0, 25, 50, and 75 kg·P·ha^{-1}. The experiment was carried out in polyethylene test bottles with treatments arranged in a completely randomized design in a factorial arrangement with three replications employed. For sorption and desorption experiments, 3.0 g of soil-brewery biosolid-P fertilizer mixture was used per experimental unit, scaled proportionally from field-equivalent rates assuming 2×10^6 kg·soil·ha^{-1} to 15 cm depth. Different PTEs (Cr, Zn, Pb and Cu), each of concentrations of 25, 50, 100, 200, 400 and 500 mg·L^{-1}, were used and these were added to the respective treatment combinations. These were got from stock solutions of Cr, Zn, Cu and Pb nitrates. These concentrations covered the concentration range in the brewery biosolids samples.

2.4.2. Maintaining the Integrity of the Specifications

Sorption experiment for the soil-brewery-phosphorous mixtures was done using the batch technique [6]. Multi-metal stock solutions containing Cr^{3+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} (as nitrates) were prepared at equal concentrations of 25, 50, 100, 200, 400, and 500 mg·L^{-1}. Working solutions were buffered at pH 4.5 using 0.02 M acetic acid/sodium acetate to simulate acidic conditions typical of Ferralsol (Oxisol) and to enable comparison with previous studies [6]. A weight of 3.0 g of sorbent (soil, biosolid, or soil-biosolid mixture) is added to 100 mL polyethylene centrifuge tubes. This was followed by adding 50 mL sorption solution containing the multi-metal mixture. Then, 3 drops of toluene were added to suppress microbial activity. The resulting solution mixture was equilibrated by using a horizontal shaking (end-over-end) at 150 rpm for 1 day (24 hours) at 25˚C to mimic environmentally relevant conditions. After equilibration, the mixture was centrifuged at 1500 rpm for 5 minutes. The resulting supernatant was filtered through Whatman No. 42 filter paper. The PTE concentration in the filtrate at equilibrium was analysed by flame atomic absorption spectrophotometry (AAS, SavantaAA 2009, GBC Scientific Equipment). The sorbed PTE concentration was calculated by difference from initial concentration using the mass balance Equation (2).

2.4.3. Desorption Experiments

Following sorption experiments, centrifuged pellets were dried at 45˚C for 48 hours. These were reweighed to determine mass loss. Then they were resuspended in 50 mL desorption solution (0.02 M acetic acid/sodium acetate, pH 4.5). These were equilibrated for 1day (24 hours) at 25˚C with horizontal shaking, centrifuged and filtered as in the sorption experiment. Analysis of the supernatant to determine the desorbed PTE concentrations was also done using flame atomic absorption spectrophotometry (AAS, SavantaAA 2009, GBC Scientific Equipment). The retained PTE concentrations were obtained as a difference between the sorbed and desorbed concentrations.

2.4.4. Blank Experiment

The same experiments were performed with different intact sorbent samples (without adding any metal). This was the control for all the experiments conducted. That is, 3.0 g of soil mixture (soil + brewery solid waste + P-fertilizer) was suspended

in 50 mL of the background solution (0.02 M acetic acid and 0.02 M sodium acetate), followed by the steps as were done in the sorption and desorption experiments, in polyethylene test bottles. These were equilibrated by shaking for 1 day (24 hours) at room temperature (25˚C), in a horizontal shaker and later centrifuged at 1500 rpm for 5 minutes. The PTE concentrations in supernatant were determined by AAS (SavantaAA 2009 model). The quantity of each metal sorbed/desorbed by each soil mixture was calculated by difference. Each experiment was performed three times.

2.4.5. Quality Control

The calibration standards were prepared from 1000 mg·L^{-1} stock solutions (Merck, Germany). The detection limits (mg·L^{-1}) were: Cr^{3+} 0.01, Cu^{2+} 0.005, Pb^{2+} 0.02, Zn^{2+} 0.003. The recovery tests using spiked samples averaged 96% - 104%. Blanks and certified reference materials (CRM 141R, BCR) were included in each batch.

2.5. Data Analysis

2.5.1. Sorbed Metal Calculation

The amounts of the PTE (adsorbate) adsorbed by the amended soil (adsorbent) were calculated from the differences between the adsorbate quantity added to the adsorbent and the adsorbate content of the supernatant by Equation (2) [24].

$$Q_e = \frac{V\left(C_o - C_e\right)}{M} \times 0.67 \tag{2}$$

where Q_e is the amount of PTE adsorbed per unit mass, C_o and C_e are the initial and equilibrium concentration (mg·L^{-1}), M is the mass of the adsorbent (g) and V is the volume of the solution (mL^{-1}).

2.5.2. Isothermal Modelling

A variety of models have been used to describe the sorption of ions by soils as a function of their concentrations in equilibrium solutions, but the most commonly used sorption equations are the Langmuir [25] and Freundlich [26] linear equations. The linear Langmuir equation used is as described in Equation (3).

$$\frac{C_e}{Q_e} = \frac{1}{K_a Q_m} + \frac{C_e}{Q_m} \tag{3}$$

where C_e (mg·L^{-1}) is the equilibrium concentration of the species in the aqueous solution, q_e (mg·kg^{-1}) is the amount of sorbed species, b is a constant related to the bonding strength and X_m (mg·kg^{-1}) is the maximum sorption capacity.

The Freundlich sorption equation is also commonly used in its linear form as described in Equation (4).

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \tag{4}$$

where K_f and n are the Freundlich constants related to the adsorption capacity and intensity, respectively. These two equations were used to fit the data because they are common models used to study adsorption of PTEs in aqueous solutions.

The isotherms that had a $r^2 > 0.75$ were considered acceptable fit.

2.5.3. Distribution Coefficient

The sorption and retention distribution coefficients of each metal in the brewery solid waste + P-fertilizer amended soil at equilibrium were calculated using the relation described by Covelo *et al.* [6], as indicated in Equation (5).

$$K_{da} \text{ or } K_{dr} = \frac{[C_a] \text{or} [C_r]}{[C_e]} \tag{5}$$

where $[C_a]$ or $[C_r]$ is the concentration of sorbed/retained metal ions ($mg \cdot g^{-1}$) and $[C_e]$ is the equilibrium concentration of the metal ions in solution ($mg \cdot L^{-1}$) after sorption or desorption. The average distribution coefficient ($K_{d\text{-medium}}$) was used to obtain the overall selectivity sequences. It was calculated by adding either all values for sorption (K_{da}) or those for retention (K_{dr}) for a particular metal at all the concentrations considered and dividing by their number [6].

2.5.4. Statistical Analysis

Data collected were keyed into a Microsoft Excel 7.0 spreadsheet, tested for normality using the Shapiro-Wilk test and analysed using ANOVA of the Statistical Package for Social Scientists (SPSS) version 17.0. Langmuir and Freundlich equations 3 and 4 respectively were used to obtain the sorption and desorption isotherms. Standard multiple linear regression analysis was used to obtain the best fitting isotherms, and the method of least squares was used to find the Langmuir and Freundlich parameters or constants of the isotherms. All experiments were done in triplicate. The principal component analysis (PCA) was performed using the following input variables. These were the retention distribution coefficients ($K_{d\text{-medium}}$) for copper, chromium, zinc and lead, all expressed in $L \cdot g^{-1}$. These variables represent the retention capacity of each metal in the brewery biosolid-phosphorus fertilizer amended soil systems, calculated as mean K_d values across all experimental concentrations. The PCA incorporated data from brewery biosolid + P-fertilizer amended soil treatments (T1—brewery biosolid at 2.5 $tons \cdot ha^{-1}$ + P-fertilizer 25 $kg \cdot ha^{-1}$, T2—brewery biosolid at 5.0 $tons \cdot ha^{-1}$ + P-fertilizer 50 $kg \cdot ha^{-1}$, T3—brewery biosolid at 7.5 $tons \cdot ha^{-1}$ + P-fertilizer 75 $kg \cdot ha^{-1}$) and individual sorbent materials (Unamended Ferralsol and unmixed brewery biosolids). Prior to PCA, all variables were standardized to z-scores (mean = 0, standard deviation = 1) using Equation (6).

$$Z_{ij} = \frac{X_{ij} - \bar{X}_j}{s_j} \tag{6}$$

where X_{ij} = original value for sample *i* and variable *j*, $\bar{X}_j$ = mean of variable *j* across all samples, s_j = standard deviation of variable *j*.

This standardization was necessary because the metal retention variables have different units and magnitudes (Cr K_d values are 2 - 3 orders of magnitude higher than other metals). Without standardization, chromium would dominate the PCA results entirely, masking patterns in the other metals.

3. Results and Discussions

3.1. Sorbent Characteristics

The Ferralsol exhibited acidic pH (5.4), low organic matter (2.51%), and moderate CEC (8.70 cmol·kg^{-1}) (Table 1). Notably, background chromium concentration was high (131.25 mg·kg^{-1}), suggesting natural accumulation or previous contamination. Brewery biosolid contained substantially higher organic matter (35.0%), CEC (17.60 cmol·kg^{-1}), and nutrient concentrations. Zinc (346 mg·kg^{-1}) and copper (151.5 mg·kg^{-1}) were the most abundant PTEs in the biosolid.

Amendment with brewery biosolid progressively increased soil organic matter, CEC, and electrical conductivity. At 7.5 tons·ha^{-1}, organic matter increased from 2.51% to 4.5%, CEC from 8.7 to 8.15 cmol·kg^{-1}, and EC from 182 to 790 µS·cm^{-2} (Table 2). Soil pH decreased slightly from 5.8 to 5.6 with biosolid addition, attributable to organic acid production during decomposition.

The increase in organic matter and CEC upon biosolid addition provides additional binding sites for PTEs, enhancing overall retention capacity. The slight pH decrease is typical for organic amendments in acid soils and may influence metal speciation. The high native Cr content of the Ferralsol indicates that these soils naturally have a strong affinity for chromium, possibly due to parent material weathering of ultramafic rocks common in East Africa.

Table 1. Selected properties of Ferralsol and brewery biosolid used in this study.

Property	Ferralsol	Brewery Biosolid
pH (H_2O)	5.4 ± 0.2	6.0 ± 0.3
Organic Matter (%)	2.51 ± 0.11	35.0 ± 3.65
CEC (cmol·kg^{-1})	8.70 ± 0.26	17.60 ± 1.32
EC (µS·cm^{-2})	182 ± 5	10,000 ± 21
Zn (mg·kg^{-1})	1.34	346.0
Cu (mg·kg^{-1})	10.00	151.5
Cr (mg·kg^{-1})	131.25	120.0
Pb (mg·kg^{-1})	12.75	15.0
P (Bray 1, mg·kg^{-1})	2.86	14,600
N (%)	0.1	2.32

Table 2. Selected properties of Ferralsol-brewery biosolid-P fertilizer mixtures.

Biosolid Rate	EC (µS·cm^{-2})	OM (%)	pH	CEC (cmol·kg^{-1})
T0	182 ± 5	2.51 ± 0.11	5.8 ± 0.2	8.70 ± 0.26
T1	590 ± 10	3.9 ± 0.03	5.4 ± 0.7	5.44 ± 0.24
T2	418 ± 6	4.5 ± 0.88	5.5 ± 0.3	7.61 ± 0.18
T3	790 ± 5	4.5 ± 0.90	5.6 ± 0.5	8.15 ± 0.28

Note: T0 = Soil only; T1 = 2.5 metric tones/ha brewery biosolid + 25 kg/ha·P; T2 = 5.0 metric tones/ha brewery biosolid + 50 kg/ha·P; T3 = 7.5 metric tones/ha brewery biosolid+ 75 kg/ha·P.

3.2. Sorption Isotherms

3.2.1. General Characteristics and S-Type Curvature

Sorption isotherms for all four metals exhibited S-type curvature (Giles classification), characterized by initial convexity to the concentration axis followed by increased sorption at higher concentrations (Figures 1(a)-(c), Table 3). This pattern indicates cooperative adsorption—the presence of previously sorbed metal facilitates additional metal retention, suggesting side-by-side interactions among adsorbed species or surface precipitation at higher loadings [27] [28].

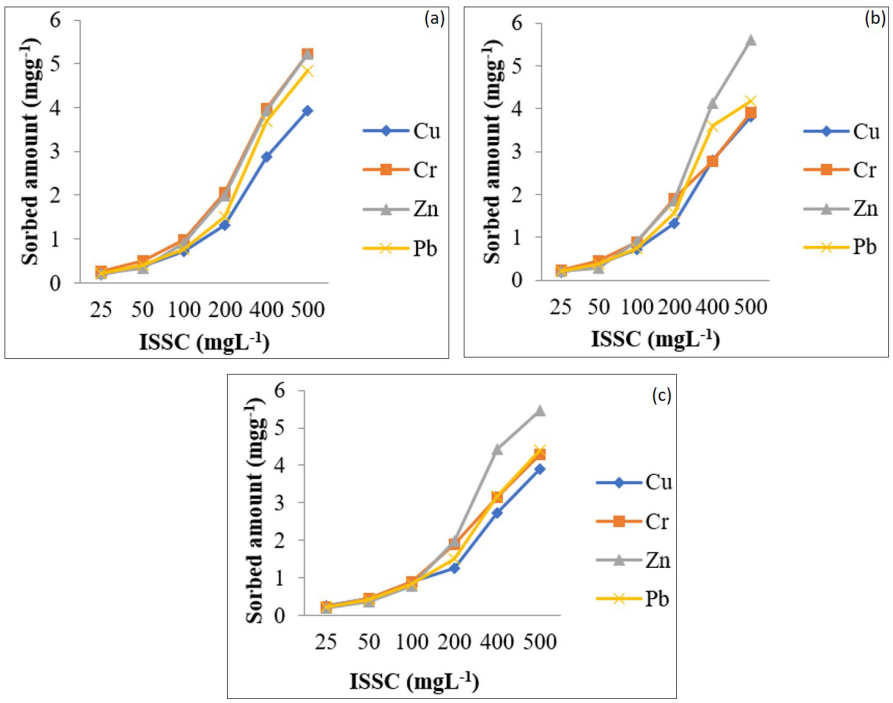

Figure 1. Amount of each metal sorbed in the sorption stage of the experiment against its ISSC for brewery biosolid and P-fertilizer (a = 2.5 metric tones·ha^{-1} + P-fertiliser 25 tones·ha^{-1}; b = 5.0 metric tones·ha^{-1} + P-fertiliser 50 kg·ha^{-1}; c = 7.5 metric tones·ha^{-1} + P-fertiliser 75 kg·ha^{-1}).

Below 100 mg·L^{-1} initial concentration, all the four metals showed similar sorption behaviour, indicating equal competitive ability for binding sites. Above 100 mg·L^{-1}, metal-specific differences emerged, with chromium demonstrating markedly higher sorption than the other metals.

The S-type isotherm implies that at low metal concentrations, binding sites are abundant and competition is minimal. As concentration increases, sorbed metals may modify the surface charge or create nucleation sites, making it easier for additional metals to bind. This cooperative effect is more pronounced for Cr^{3+} because its hydrolysis products ($CrOH^{2+}$) can form bridges between surface sites. The similarity in sorption at low concentrations suggests that all metals initially access a common pool of high-affinity sites (e.g., carboxyl groups on organic matter, edge hydroxyls on oxides). The divergence above 100 mg·L^{-1} reflects differences in their

intrinsic binding strengths and coordination chemistry.

Table 3. Sorption of lead, chromium, zinc and copper on Ferralsol amended with brewery biosolid and P-fertilizer.

	T1				T2				T3			
ISSC	Pb	Cr	Zn	Cu	Pb	Cr	Zn	Cu	Pb	Cr	Zn	Cu
25	0.202	0.202	0.202	0.202	0.200	0.200	0.200	0.200	0.228	0.228	0.228	0.228
50	0.393	0.393	0.393	0.393	0.287	0.387	0.387	0.387	0.422	0.422	0.422	0.422
100	0.758	0.998	0.910	0.758	0.750	0.750	0.750	0.750	0.820	0.820	0.820	0.820
200	1.496	1.992	1.992	1.325	1.565	1.848	3.600	1.318	1.506	1.500	1.975	1.238
400	3.698	3.939	3.698	2.863	3.600	2.772	4.129	2.772	3.185	3.185	4.436	2.722
500	4.842	5.226	5.226	3.939	4.181	4.181	5.391	3.819	4.409	4.409	5.471	3.894

Note: T1 = 2.5 metric tones·ha^{-1} brewery biosolid + 25 kg/ha·P; T2 = 5.0 metric tones·ha^{-1} brewery biosolid + 50 kg/ha·P; T3 = 7.5 metric tones·ha^{-1} brewery biosolid + 75 kg/ha·P.

3.2.2. Effect of Brewery Biosolid and P-Fertilizer Application Rate

Increasing brewery biosolid and P-fertilizer application rate enhanced sorption capacity for all metals, consistent with increased organic matter content providing additional binding sites. At T1, chromium sorption at 100 mg·L^{-1} reached 1.016 mg·g^{-1}; at T3, sorption increased to 1.939 mg·g^{-1} (**Figure 1(a)** and **Figure 1(c)**). The biosolid effect was most pronounced for chromium and least for zinc. The greater enhancement for Cr^{3+} can be explained by the biosolid's high content of oxygen-containing functional groups (carboxyl, phenolic, hydroxyl) that form strong inner-sphere complexes with hard acids like Cr^{3+}. The minimal effect on Zn suggests that Zn binds predominantly via weaker electrostatic (outer-sphere) interactions, which are less dependent on the quantity of organic matter.

3.2.3. Metal-Specific Sorption Profiles

Chromium consistently showed the highest sorption across all concentrations and application rates. At 500 mg·L^{-1}, Cr sorption ranged from 4.01 to 5.38 mg·g^{-1} depending on treatment rate. The high sorption capacity persisted even at elevated concentrations, with no clear saturation plateau. Chromium(III) has the highest charge density (49.2), low pKa (4.0), and a kinetically inert d^3 electron configuration. These properties favour specific adsorption (inner-sphere complexation) [29] and, at higher loadings, surface precipitation of $Cr(OH)_3$ or mixed Cr-Fe hydroxides. The absence of a plateau indicates multilayer formation or continued precipitation, which is consistent with the S-type isotherm and near-irreversible retention.

Copper showed moderate sorption capacity, increasing from 0.196 mg·g^{-1} at 25 mg·L^{-1} to 4.05 mg·g^{-1} at 500 mg·L^{-1}. Above 200 mg·L^{-1}, copper sorption showed greater variability and tended to plateau at higher biosolid rates. Copper(II) has high affinity for organic matter through chelation with carboxyl and phenolic groups. The plateau at high loadings suggests saturation of specific high-affinity sites. Recent work has shown that removal of soil organic matter can decrease Cu^{2+} sorp-

tion by up to 80% and increase desorption rates [30], confirming that organic matter is the primary control on Cu retention.

Zinc behaved in a similar way to copper at low concentrations (0.214 $mg \cdot g^{-1}$ at 25 $mg \cdot L^{-1}$) but demonstrated increasing sorption at higher metal loadings (5.63 $mg \cdot g^{-1}$ at 500 $mg \cdot L^{-1}$). Zinc showed the most linear sorption response with increasing concentration. Zinc(II) behaves as a borderline Lewis acid and tends to form outer-sphere complexes, retaining its hydration shell [31]. Its sorption is more reversible and less dependent on specific organic sites. The linear increase suggests that Zn continues to occupy weaker exchange sites even at high concentrations, consistent with its higher mobility.

Lead showed intermediate sorption behaviour (0.208 - 5.59 $mg \cdot g^{-1}$). Lead sorption was more sensitive to pH effects than other metals due to its lower hydrolysis constant (pKa = 7.7). Lead(II) is a soft acid that strongly bonds to soft bases like thiol groups, which are present in biosolid-derived organic matter. Recent work has shown that dissolved organic matter (DOM) fractionation on iron oxides can significantly affect Pb complexation. For instance, fractionation of straw-derived DOM on ferrihydrite alters the binding affinity and sites for Pb(II), with nitrogen-containing molecules playing an unrecognized role [32]. At pH 4.5, Pb^{2+} predominates, but small amounts of $PbOH^{+}$ form, enhancing adsorption on oxide surfaces. The high phosphorus content of brewery biosolid (14,600 $mg \cdot kg^{-1}$) may also promote Pb immobilization via Pb-phosphate precipitation.

3.3. Desorption and Retention

Desorption experiments revealed substantial differences in metal retention strength (**Figure 2(a)-(c)**, **Table 4**). The small amounts desorbed relative to sorbed amounts indicate predominantly irreversible binding mechanisms, particularly for chromium.

Chromium showed a remarkably high retention with desorbed fractions typically <0.1% of sorbed amounts. The retention K_d values ranged from 14.2 - 33.4 $L \cdot g^{-1}$, 2 - 3 orders of magnitude higher than the other metals. This near-irreversible binding suggests inner-sphere complexation as the dominant retention mechanism. Lead showed a moderate retention with 5% - 15% desorption depending on initial concentration. The lead retention increased with biosolid application rate, attributed to additional organic matter binding sites. Copper retention was intermediate between lead and zinc, with 10% - 20% desorption. Copper's high affinity for organic matter (through complexation with carboxyl and phenolic groups) contributed to its retention. Zinc was less retained compared to the other metals. It was the most reversible (30% - 50% desorption), indicating prevalent outer-sphere complexation and cation exchange mechanisms. Zinc retention K_d values (0.09 - 0.27 $L \cdot g^{-1}$) were lowest among the studied metals.

The near-irreversible retention of Cr^{3+} is consistent with its tendency to form polynuclear hydroxo bridges and surface precipitates. The high desorption of Zn confirms that it is held mainly by electrostatic forces that can be overcome by the

acetic acid/sodium acetate buffer used in desorption. Lead (Pb) and Cu occupied an intermediate position, with Pb retention being enhanced by phosphate precipitation and Cu by organic complexation.

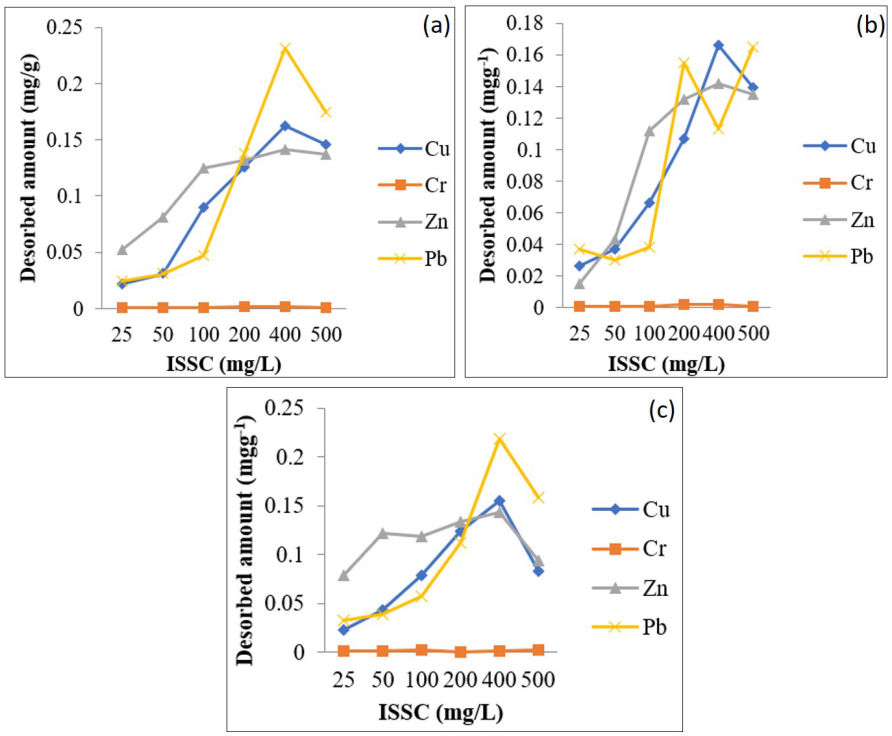

Figure 2. Amount of each metal desorbed in the desorption stage of the experiment against its initial concentration in the sorption solution (ISSC) for brewery biosolid and P-fertilizer (a = 2.5 metric tones·ha^{-1} + P-fertiliser 25 tones·ha^{-1}; b = 5.0 metric tones·ha^{-1} + P-fertiliser 50 kg·ha^{-1}; c = 7.5 metric tones·ha^{-1} + P-fertiliser 75 kg·ha^{-1}).

Table 4. Desorption of lead, chromium, zinc and copper on Ferralsol amended with brewery biosolid and P-fertilizer.

	T1				T2				T3			
ISSC	Pb	Cr	Zn	Cu	Pb	Cr	Zn	Cu	Pb	Cr	Zn	Cu
25	0.024	0.001	0.052	0.024	0.037	0.001	0.015	0.026	0.033	0.001	0.079	0.023
50	0.031	0.001	0.081	0.031	0.030	0.001	0.066	0.030	0.039	0.001	0.122	0.079
100	0.047	0.001	0.125	0.090	0.038	0.001	0.112	0.066	0.057	0.002	0.119	0.079
200	0.138	0.001	0.138	0.126	0.155	0.002	0.132	0.107	0.112	0.000	0.113	0.112
400	0.231	0.001	0.141	0.162	0.113	0.002	0.142	0.166	0218	0.001	0.143	0.155
500	0.750	0.001	0.137	0.146	0.165	0.001	0.135	0135	0.158	0.002	0.094	0.083

Note: T1 = 2.5 metric tones·ha^{-1} brewery biosolid + 25 kg/ha·P; T2 = 5.0 metric tones·ha^{-1} brewery biosolid + 50 kg/ha·P; T3 = 7.5 metric tones·ha^{-1} brewery biosolid+ 75 kg/ha·P.

3.4. Isotherm Modelling

3.4.1. Model Applicability

Of the potential metal–sorbent–concentration combinations, only 43.6% yielded

acceptable fits ($r^2 > 0.75$) to either Langmuir or Freundlich models. The Freundlich isotherm provided superior fits for sorption data (average $r^2 = 0.94$ for fittable cases) compared to Langmuir (average $r^2 = 0.88$). Desorption data generally did not comply with Langmuir and showed limited Freundlich fits (34.6%).

The poor model performance reflects: i) competitive interactions among four metals violating the single-sorbate assumption, ii) heterogeneous sorption sites with varying binding energies, iii) possible surface precipitation at higher loadings not accommodated by adsorption models, and iv) cooperative adsorption mechanisms (S-type isotherms) inconsistent with Langmuir assumptions.

The failure of Langmuir and Freundlich models to describe most of the data highlights the need for competitive sorption models (e.g., the multi-component Langmuir, surface complexation models) that explicitly account for metal-metal competition and site heterogeneity. The better performance of Freundlich is consistent with the S-type isotherms and suggests that physical adsorption contributes alongside chemisorption. The very low number of fittable desorption isotherms underscores the irreversibility of metal binding, especially for Cr.

3.4.2. Freundlich Parameters

For chromium (the best-fitted metal), Freundlich K_f values (indicating relative adsorption capacity) ranged from 0.14 - 0.55, while n values (sorption intensity) ranged from 1.47 - 2.01 (Table 5 and Table 6). The K_f values below 1.0 indicate moderate adsorption capacity, while n > 1 suggests physical adsorption processes dominating. Copper and lead showed intermediate K_f and n values, while zinc exhibited the lowest K_f (0.01 - 0.05), indicating the weakest binding.

The high n values for Cr (>1.5) reflect cooperative adsorption and a relatively homogeneous set of high-energy sites. The low K_f for Zn is consistent with its high mobility and reversibility. The intermediate values for Cu and Pb confirm that their retention is driven by both specific (inner-sphere) and non-specific (outer-sphere) interactions.

Table 5. Freundlich sorption parameters for Cu(II), Zn(II), Pb(II) and Cr(III) when a Feralsol was amended with brewery biosolid and P-fertilizer at different rates.

Treatment	Metal	Freundlich Constant		
		K_f	n	r^2
T1	Cr	0.55	2.01	0.886
	Cu	0.03	1.09	0.980
	Zn	0.01	0,69	0.822
	Pb	0.05	1.05	0.894
T2	Cr	0.14	1.47	0.974
	Cu	0.04	1.15	0.984
	Zn	0.05	0.95	0.351
	Pb	0.04	1.07	0.969

Continued

T3	Cr	0.13	1.80	0.956
	Cu	0.10	1.52	0.971
	Zn	ns	ns	ns
	Pb	0.52	1.60	0.918

Note: K_f—relative adsorption capacity; n—related to sorption intensity; T1 = 2.5 metric tones·ha^{-1} brewery biosolid + 25 kg/ha·P; T2 = 5.0 metric tones·ha^{-1} brewery biosolid + 50 kg/ha·P; T3 = 7.5 metric tones·ha^{-1} brewery biosolid + 75 kg/ha·P. ns = not significant ($r^2 < 0.75$).

Table 6. Freundlich desorption (retention) parameters for Cu(II), Zn(II), Pb(II) and Cr(III) when a Ferralsol was amended with brewery biosolid and P-fertilizer at different rates.

Treatment	Metal	Freundlich Constant		
		K_f	n	r^2
T1	Cr	7.26×10^4	0.15	0.868
	Cu	0.69	0.64	0.978
	Zn	1.0×10^{-4}	0.22	0.772
	Pb	0.11	0.81	0.935
T2	Cr	4.38×10^3	0.35	0.783
	Cu	0.06	0.60	0.951
	Zn	0.09	0.66	0.744
	Pb	0.22	1.03	0.547
T3	Cr	0.02	−0.65	0.102
	Cu	0.08	0.69	0.956
	Zn	0.05	0.65	0.238
	Pb	0.14	0.80	0.907

Note: K_f—relative adsorption capacity; n—related to sorption intensity; T1 = 2.5 metric tones·ha^{-1} brewery biosolid + 25 kg/ha·P; T2 = 5.0 metric tones·ha^{-1} brewery biosolid + 50 kg/ha·P; T3 = 7.5 metric tones·ha^{-1} brewery biosolid + 75 kg/ha·P.

3.5. Distribution Coefficients

The sorbed and retained equilibrium concentrations were used to determine the distribution coefficients (K_d) for the metals Cr, Cu, Zn and Pb under the study conditions. The distribution coefficients showed strong metal-specific and concentration-dependent patterns (Table 7). Chromium consistently yielded the highest K_d values, while zinc showed the lowest. The extremely high K_d, for Cr indicates that once sorbed, Cr^{3+} is essentially immobile under the studied conditions. This has important environmental implications in the sense that Cr from brewery biosolid is unlikely to leach to groundwater or be taken up by crops. The increase in Cr K_d, at 200 mg·L^{-1} compared to 100 mg·L^{-1} suggests enhanced adsorption due to surface precipitation at higher loadings.

Table 7. Distribution coefficients, K_d (L·g^{-1}) calculated for each metal concentration added for different treatment rates of brewery biosolid and P-fertilizer.

Metal	Added Concentrations (mg·L^{-1})	Treatments					
		T1		T2		T3	
		Distribution coefficients, K_d (L·g^{-1})					
		K_{da}	K_{dr}	K_{da}	K_{dr}	K_{da}	K_{dr}
Cu	25	0.028	0.098	0.029	0.082	0.068	0.113
	50	0.022	0.135	0.024	0.116	0.048	0.118
	100	0.021	0.148	0.021	0.172	0.042	0.165
	200	0.016	0.169	0.016	0.168	0.014	0.131
	400	0.019	0.267	0.018	0.221	0.017	0.233
	500	0.025	0.352	0.023	0.378	0.024	0.304
Cr	25	0.101	4.691	0.118	9.369	0.095	3.750
	50	0.138	8.627	0.057	8.500	0.054	6.053
	100	0.132	15.859	0.058	20.444	0.044	14.203
	200	0.273	25.659	0.065	25.039	0.055	33.431
	400	0.076	55.122	0.033	38.500	0.025	39.840
	500	0.121	65.585	0.025	56.803	0.033	107.293
Zn	25	0.035	0.037	0.041	0.167	0.023	0.042
	50	0.016	0.038	0.012	0.070	0.020	0.027
	100	0.047	0.103	0.047	0.122	0.026	0.093
	200	0.075	0.227	0.048	0.210	0.076	0.219
	400	0.066	0.424	0.095	0.444	0.259	0.476
	500	0.106	0.591	0.322	0.644	0.193	1.040
Pb	25	0.059	0.091	0.047	0.055	0.190	0.111
	50	0.033	0.146	0.031	0.150	0.044	0.173
	100	0.029	0.251	0.028	0.603	0.039	.273
	200	0.024	0.146	0.027	0.132	0.024	0.194
	400	0.050	0.206	0.043	0.303	0.027	0.188
	500	0.063	0.257	0.031	0.354	0.039	0.389

Note: T1 = 2.5 metric tones·ha^{-1} brewery biosolid + 25 kg/ha·P; T2 = 5.0 metric tones·ha^{-1} brewery biosolid + 50 kg/ha·P; T3 = 7.5 metric tones·ha^{-1} brewery biosolid + 75 kg/ha·P. K_{da} = Distribution coefficient for adsorption; K_{dr} = Distribution coefficient for retention.

3.6. Selectivity Sequences

Sorption and retention selectivity sequences are given in Table 8. The high brewery biosolid and P-fertilizer application rates shifted selectivity toward zinc, suggesting that added organic matter preferentially complexed zinc through specific functional groups. The retention selectivity sequences (consistent across all rates) indicated that chromium retention dominates regardless of application rate or

concentration, reflecting its unique coordination chemistry.

The shift in sorption selectivity at high application rates (Zn becoming first) may indicate that brewery biosolid contains N- or S-containing ligands that have a particular affinity for Zn^{2+} (a borderline acid). Alternatively, it could reflect competition from dissolved organic matter that complexes Zn and enhances its apparent sorption. However, retention selectivity always placed Cr first, confirming that Cr binding is the most irreversible. Lead and copper exchange positions depend on conditions, reflecting their similar electronegativities and competition for phosphate and organic sites.

Table 8. Distribution coefficients of metals between soil and solution ($K_{d\text{-medium}}$, $L \cdot g^{-1}$) after sorption and retention, selectivity sequences when different brewery biosolid and P-fertilizer rates were used.

Brewery		Cu	Cr	Zn	Pb	Selectivity Sequence
T1	Sorption	0.0230	0.0340	0.1513	0.0297	Zn > Cr > Pb > Cu
	Retention	0.1808	22.7457	0.2700	0.1688	Cr >> Zn > Cu > Pb
T2	Sorption	0.0213	0.0453	0.1078	0.0337	Zn > Cr > Pb > Cu
	Retention	0.2135	25.4522	0.2638	0.1832	Cr >> Zn > Cu > Pb
T3	Sorption	0.0242	0.0355	0.1478	0.0412	Zn > Pb > Cr > Cu
	Retention	0.1995	23.2205	0.2692	0.2213	Cr >> Zn > Pb > Cu

Note: T1 = 2.5 metric tones·ha^{-1} brewery biosolid + 25 kg/ha·P; T2 = 5.0 metric tones·ha^{-1} brewery biosolid + 50 kg/ha·P; T3 = 7.5 metric tones·ha^{-1} brewery biosolid + 75 kg/ha·P.

3.7. Principal Component Analysis of Metal Retention Patterns

To elucidate the underlying relationships between metal retention behaviour and sorbent characteristics, principal component analysis (PCA) was performed on the $K_{d\text{-medium}}$ (retention) values for Cu, Cr, Zn, and Pb across all sorbent systems. The input variables were standardized to z-scores to eliminate scaling effects, as the K_d values for different metals differed by several orders of magnitude. Table 9 presents the component loadings for the first two principal components extracted from the retention data at different biosolid application rates.

Table 9. Principal component loadings for metal retention ($K_{d\text{-medium}}$) in brewery biosolid-amended Ferralsol systems.

Treatment	Metal	PC1	PC2
T1	Cu	**0.978**	−0.207
	Cr	**1.000**	0.030
	Zn	**−0.958**	−0.287
	Pb	−0.103	**0.995**
	Variance Explained	47.0%	25.1%
	Cumulative	47.0%	72.1%

Continued

T2	Cu	**0.720**	**−0.694**
	Cr	**−0.993**	0.122
	Zn	**0.766**	**0.643**
	Pb	0.129	**0.992**
	Variance Explained	52.7%	47.3%
	Cumulative	52.7%	100.0%
T3	Cu	**−0.999**	−0.046
	Cr	**0.991**	0.137
	Zn	0.357	**−0.934**
	Pb	0.154	**0.989**
	Variance Explained	53.3%	46.7%
	Cumulative	53.3%	100.0%

Note: T1 = 2.5 metric tones·ha^{-1} brewery biosolid + 25 kg/ha·P; T2 = 5.0 metric tones·ha^{-1} brewery biosolid + 50 kg/ha·P; T3 = 7.5 metric tones·ha^{-1} brewery biosolid + 75 kg/ha·P. Note: Loadings with absolute values > 0.7 are shown in bold.

The PCA results reveal that metal retention behaviour in brewery biosolid- and P-fertilizer amended Ferralsol is governed by two distinct processes, the relative importance of which changes with biosolid application rate.

At T1, PC1 (47.0% variance) represents general retention strength, with high positive loadings for Cu (0.978) and Cr (1.000) but a strong negative loading for Zn (−0.958). This indicates that Cu and Cr are retained together through similar mechanisms (e.g., inner-sphere complexation with organic functional groups), while Zn behaves oppositely, being the most easily desorbed metal. PC2 (25.1% variance) strongly discriminates Pb (0.995) from the other metals, suggesting that Pb retention involves unique mechanisms not shared by Cu, Cr, or Zn. The lower cumulative variance explained (72.1%) indicates that substantial metal-specific variation remains, reflecting the heterogeneous nature of retention sites at this amendment rate.

At T2, the two components explain 100% of the variance, indicating that metal retention can be fully described by two underlying processes at this application rate. PC1 (52.7% variance) separates Cr (negative loading, −0.993) from Cu (0.720) and Zn (0.766). This suggests that at moderate biosolid addition, chromium retention is increasingly dominated by surface precipitation or incorporation into neo-formed mineral phases, while Cu and Zn remain associated with exchangeable and organic-bound fractions. PC2 (47.3% variance) differentiates Pb (0.992) from Cu (−0.694), with Zn intermediate (0.643). This indicates that Pb retention is increasingly controlled by phosphate precipitation (enhanced by the brewery biosolid's high P content and the P-fertilizer amounts added), while Cu remains primarily associated with organic matter.

At T3, similar to T2, the two components explain 100% of the variance. PC1

(53.3% variance) now separates Cu (negative, −0.999) from Cr (positive, 0.991), indicating that at high biosolid loading, Cu retention decreases while Cr retention increases. This may reflect competitive displacement of Cu from organic sites by Cr^{3+}, or changes in organic matter composition (increased dissolved organic matter) that complex Cu and reduce its sorption. PC2 (46.7% variance) again discriminates Zn (negative, −0.934) from Pb (positive, 0.989), confirming that these two metals are retained through fundamentally different mechanisms regardless of biosolid rate.

3.7.1. Mechanistic Interpretation of PCA Results

The PCA loadings align with established metal retention mechanisms. Chromium (Cr^{3+}) showed positive loading on PC1 at low biosolid rates, shifting to negative at higher rates, which reflects its transition from specific adsorption to surface precipitation. The high charge density (49.2) and low pKa (4.0) of Cr^{3+} favour inner-sphere complexation and, at higher loadings, the formation of $Cr(OH)_3$ or mixed Cr-Fe precipitates. The negative loading on PC1 at T2 suggests that once precipitation dominates, Cr retention becomes independent of the general adsorption processes affecting Cu and Zn.

Zinc (Zn^{2+}) gave consistently negative or intermediate loadings. This confirms that Zn is the most mobile metal, retained primarily through weak outer-sphere (electrostatic) interactions. The negative loading on PC1 at T1 (Zn = −0.958) and the negative loading on PC2 at T3 (Zn = −0.934) indicate that Zn retention is easily overcome by the desorption solution, consistent with its high reversibility (30% - 50% desorption). At T2, Zn loads positively on both PC1 (0.766) and PC2 (0.643), suggesting that at intermediate biosolid rates, Zn begins to occupy a broader range of sites, including some specific organic sites.

Lead (Pb^{2+}) gave a strong positive loading on PC2 across all treatments and this confirms that Pb retention is controlled by mechanisms distinct from the other metals. This is consistent with lead's soft acid character and its tendency to precipitate as Pb-phosphates. The high phosphorus content of brewery biosolid (14,600 $mg{\cdot}kg^{-1}$), besides the amounts of P-fertilizer added, likely enhances Pb retention through formation of stable $Pb_3(PO_4)_2$ or Pb-hydroxyapatite phases.

Copper (Cu^{2+}) loads with Cr on PC1 at low biosolid rates (Cu = 0.978, Cr = 1.000), but separates from Cr at higher rates (T2: Cu = 0.720, Cr = −0.993; T3: Cu = −0.999, Cr = 0.991). This transition reflects the strong affinity of Cu for organic matter through chelation with carboxyl and phenolic groups. As biosolid application increases, the added organic matter provides more specific binding sites for Cu, but also produces dissolved organic matter that can complex Cu and increase its mobility, explaining the negative loading at T3.

3.7.2. Implications for Metal Mobility and Risk Assessment

The PCA-derived groupings have important implications for metal mobility and environmental risk. Chromium has very low mobility due to inner-sphere complexation and thus, low leaching risk. The mobility of Pb is low due to phosphate

precipitation and thus it is kept in immobilized form by phosphorus. Copper mobility is moderate due to organic chelation and there is a possibility of DOM-enhanced mobility at high biosolid rates. Zinc has high mobility due to the outer-sphere or electrostatic interaction and thus, it has the greatest potential for leaching.

The consistent discrimination of Zn from other metals across all treatments confirms that zinc poses the greatest environmental risk when brewery biosolid is applied to Ferralsol. The separation of Pb on PC2 highlights the importance of phosphorus management in controlling Pb mobility, while the shifting relationship between Cu and Cr with increasing biosolid rate suggests that high application rates (>5.0 metric tones·ha^{-1}) may compromise Cu retention through dissolved organic matter complexation.

3.8. Overall Discussion of Mechanisms and Environmental Implications

The strong correlation between charge density and K_d values (r^2 = 0.87 - 0.91) supports ionic potential as the primary predictor of metal retention in variable-charge Ferralsols. The sequence Cr^{3+} (49.2) > Cu^{2+} (27.4) ≈ Zn^{2+} (27.0) > Pb^{2+} (16.8) matches observed retention except where specific organic matter affinity modifies behaviour. Previous studies have similarly reported that sorbate-specific properties such as ionic charge and ionic radius significantly affect the extent of sorption [33].

Application of HSAB theory provides additional explanatory power. Chromium(III), a hard acid, preferentially binds to hard bases (O^{2-}, OH^-, COO^-) abundant on oxide surfaces and organic carboxyl groups, forming strong ionic/covalent bonds. Copper(II), a borderline acid, binds effectively to both hard and soft bases; the N- and S-containing groups in biosolid enhance its retention. Recent work has used the HSAB principle to explain sorption selectivity of metal cations on clays [34]. Zinc(II), also a borderline acid, behaves similarly like Cu^{2+} but less covalent and its complete d^{10} shell results in more labile complexes. Lead(II), a soft acid, prefers soft bases (S^{2-}, SH^-, R_3P). These are scarce in aerobic Ferralsols, but where present (e.g., biosolid-derived thiol groups), Pb forms highly stable complexes, explaining its enhanced retention at higher biosolid rates.

At pH 4.5, only Cr^{3+} (pKa = 4.0) has appreciable hydrolysis (≈50% as $CrOH^{2+}$), explaining its enhanced sorption relative to other metals where hydrolysis is negligible (<1%). The hydrolysed metals are preferentially adsorbed due to reduced positive charge, smaller hydrated radius, and ability to form surface M-O-M linkages.

Based on $K_{d'}$ values, the mobility ranking (most to least mobile) is: Zn ($K_{d'}$ = 0.15) > Cu (0.16) > Pb (0.25) ≫ Cr (17.3). This order is consistent with recent findings that the immobilization ratio is lowest for Zn and Cd (0.208 - 0.29) and highest for Cu and Pb (0.45 - 0.55) [2].

Zinc poses the greatest leaching risk, particularly in sandy Ferralsols with low

organic matter. The high reversibility of Zn sorption (30% - 50% desorption) suggests significant potential for groundwater contamination. Chromium retention is effectively permanent under aerobic, slightly acidic conditions, aligning with studies showing that Cr(VI) removal by Oxisol can be efficient but slow, with Fe oxides playing a key role [35].

The data suggest threshold effects where application rates less than 2.5 metric tones·ha^{-1} indicate limited increase in retention capacity; soil properties dominate the desorption ability. At application rates ranging between 2.5 - 5.0 metric tones·ha^{-1}, an optimal range for enhancing retention of all metals is given, where CEC and OM increase substantially. Application rates greater than 5.0 metric tones·ha^{-1} indicate diminishing returns for Cr and Cu with possible Zn mobilization through dissolved organic matter. As noted by Zarzsevszkij *et al.* [36], organic amendments applied alone can increase metal availability in some cases, but combined treatments (e.g., with Fe-based materials or P-fertilizer) can achieve up to 99% immobilization. A precautionary limit of 5.0 metric tones·ha^{-1} per application with 3 - 5-year intervals is recommended.

The maximum permissible concentrations in crops [37] for Cu (73.3 mg·kg^{-1}), Zn (99.4 mg·kg^{-1}), and Cr (2.3 mg·kg^{-1}) provide context for phytoavailability. The low desorption of Cr^{3+} suggests plant uptake will be minimal, consistent with literature showing Cr accumulation primarily in roots with limited shoot translocation. However, the high background Cr in Ferralsol (131 mg·kg^{-1}—above many international soil quality guidelines) requires monitoring of Cr(VI) formation potential under changing redox conditions. Additionally, recent assessments have indicated that Cr and Mo uptake can remain substantial even at lower biosolid application rates, underscoring the role of dose in metal transport [2].

4. Conclusions

This study demonstrates that the competitive sorption and retention of PTEs in brewery biosolid-amended Ferralsol is a complex, metal-specific process governed by interactions between metal properties (charge density, hydrolysis behaviour, HSAB classification), sorbent characteristics (organic matter content, CEC, phosphorus availability), and competitive effects among metals.

Chromium is preferentially retained by Ferralsol amended by brewery biosolid and P-fertilizer mixtures, with K_d = 14 - 33 L·g^{-1} and desorption < 0.1%, indicating inner-sphere complexation and surface precipitation driven by high charge density (49.2), low pKa (4.0), and kinetically inert d^3 configuration. Zinc exhibits the highest mobility (K_d = 0.09 - 0.27 L·g^{-1}, 30% - 50% desorption) due to outer-sphere complexation and cation exchange, posing the greatest leaching risk. Copper and lead show intermediate retention, with Cu affinity for humic substances and Pb precipitation as phosphates enhanced at higher biosolid rates. S-type isotherms indicate cooperative adsorption, invalidating Langmuir assumptions and explaining poor model fits for multi-metal systems. Freundlich model provides superior description (r^2 = 0.89 - 0.98) but only 43.6% of isotherms were fittable, un-

derscoring the need for competitive sorption models. Selectivity sequences change with metal concentration and biosolid rate, but Cr always dominates retention, while Zn is most reversible. Charge-to-radius ratio correlates strongly with K_a (r^2 = 0.87 - 0.91), establishing ionic potential as the primary predictor of metal retention. The optimal biosolid rate of 5.0 metric tones·ha^{-1} balances enhanced retention against Zn mobilization; cumulative loading should not exceed 100 metric tones·ha^{-1} without monitoring. It would be important to monitor Zn accumulation, maintain pH > 5.5, avoid flood-prone areas, apply at 3 - 5-year intervals, and use caution where groundwater is a drinking water source. More work can be done on field validation of K_d values; Cr(III) oxidation to Cr(VI) under redox fluctuations; development of multi-metal competitive models; and plant uptake studies under realistic agronomic conditions. The PCA approach provides a robust statistical framework for elucidating the underlying retention mechanisms and offers a valuable tool for predicting metal mobility and environmental risk in biosolid-amended tropical soils. The finding that chromium is effectively immobilized while zinc remains mobile has direct implications for the safe recycling of brewery biosolid in Sub-Saharan African agriculture, supporting the use of biosolids as soil amendments while highlighting the need for careful management of zinc accumulation and long-term monitoring of metal dynamics.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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