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THE ROLE OF LIMING IN COPPER ADSORPTION OF ACIDIC SOILS

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Abstract: Investigate the impact of varying rates of liming on the availability and sorption properties of copper in a range of acid soils with differing physico-chemical futures. Soil samples with varying acidity levels were collected from different locations in the acidic Black Sea Region of Türkiye. Out of the nine soil samples collected, four were obtained from regions where hazelnuts are grown, while the other five were obtained from areas dedicated to tea growth. The sorption properties of soils limed at 0%, 50%, and 100% of lime requirement and incubated for 12 months, then the Langmuir and Freundlich adsorption isotherms were determined by batch sorption technique. The results showed that increasing the soil pH resulted in an increase in Cu adsorption. Experimental results of Cu adsorption were explained with high coefficients of determination (93.44-98.98%) of the Langmuir model. In the three experimental groups with full, half, and no lime application, pH increased significantly to 3.95, 4.46, and 5.89, respectively, while the maximum adsorption obtained from Langmuir adsorption curves, Qmax1 1553, Qmax2 2205, and Qmax3 3902 mg kg^{-1}, respectively. While the maximum adsorption in the tea plantation areas varied between 1491 and 1514 mg kg^{-1}, the maximum adsorption in hazelnut cultivation areas varied between 777 and 3333 mg kg^{-1}. These findings suggest that liming or other methods to increase soil pH could be effective soil management in reducing Cu mobility in acidic soils.

Additional keywords: Batch adsorption technique; pH; Isotherms; Langmuir; Freundlich.

1. INTRODUCTION

Human beings have been using copper (Cu) for different purposes since the early ages. Copper is used as a good heat transfer agent for air conditioning units, electrical wiring, kitchen utensils, household water transmission lines, jewelry, and even radiation barriers. In addition to being used in so many areas, the fact that it is used as a microelement fertilizer and component of plant protection products such as Bordeaux slurry and fungicides reveals that Cu needs to be monitored carefully to avoid its environmental consequences. Copper is mined as ore and used in different industries, processing, recycling, and improper rehabilitation of urban wastes cause an increase in its amount in soils. Its concentration in the soil solution may exceed the limit values due to natural and/or anthropogenic effects. Copper is present in the structure of rocks and is released due to weathering and disintegration processes (USGS, 2019). Increased Cu concentration can be observed in plants, and secondary effects can be evident in living organisms and humans that feed on these plants.

Copper has essential structural and functional roles in many plant metabolisms, such as protein synthesis, enzyme structure, cell wall metabolism, water transport, and pollen release (Shabbir et al., 2020). The critical Cu level for plant development is required at 1-5 mg kg^{-1} dry matter (Marschner, 2011). Plant requirement for Cu in plants is maximized in the generative growth stages (Bell & Dell, 2008).

The plant-available form of Cu in the soil is typically regulated by adsorption-desorption reactions (Sposito, 2008). Copper adsorption-desorption reactions are controlled by soil organic matter (Laurent et al., 2020), oxide-hydroxyoxides (Field et al., 2019), clays, and pH (Shaheen & Rinklebe, 2014), and other main soil components. The very strong chelating ability of soil organic matter reduces the bioavailability of Cu as well as microelements by adsorption mechanism (Bell & Dell, 2008). In soils, Cu is mainly adsorbed in the inner sphere complexes of organic matter, clays, and oxides-hydroxyoxides (Bell & Dell, 2008). Oxides and hydroxyoxides significantly influence the adsorption of microelements. Unlike Mn and Fe, Cu is not modified under redox conditions since it is usually present in soils in the 2+ oxidation state at pH<6 (Bell & Dell, 2008); this makes it mobile and readily plant-available. As a function of increasing pH, it precipitates as $Cu(OH)_2$ and/or carbonates from the aqueous solutions. Clay type, concentration, and CEC are substantially responsible for soil Cu adsorption. pH is another crucial factor in microelement adsorption, which changes both surface adsorption sites and ionic species in the soil solution. Copper adsorption also has an indirect effect, although pH does not affect its own. Its adsorption also indirectly affects organic and inorganic surfaces owing to pH-dependent charges (Nadaroğlu et al., 2014).

The occurrence of calcium carbonate ($CaCO_3$) in soil exerts a significant influence on the collective levels and responsiveness of heavy metals, which can either obstruct or impede plant uptake. Xian et al., (2010) have reported that the absorption of heavy metals by plants is facilitated by soil acidity, which enhances their activity and is reduced by $CaCO_3$ content. Conversely, it has been observed that in soils possessing elevated levels of pH and carbonate minerals, heavy metals are precipitated or chemisorbed by hydroxyoxides and/or carbonates, thereby producing a buffer effect (Yohey et al., 2009). Huang et al., (2016) conducted an investigation into the immobilization of diverse heavy metals (Cd, Pb, and Cu) in contaminated soils, with a focus on the influence of phosphates and carbonates. The findings indicate that the utilization of $CaCO_3$ can considerably diminish the levels of plant availability and increase the carbonate-bound metallic elements. Furthermore, $CaCO_3$ plays a significant role as a binding agent for microaggregates and has the ability to generate humic substances in conjunction with soil organic matter. This process can result in an augmentation of the soil's surface area and negative charge, ultimately leading to an enhancement of various elements such as Cr^{3+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, among others (Kužel et al., 2010). Regrettably, the stability of the aggregates that were produced utilizing $CaCO_3$ as a binding agent was suboptimal owing to the hydrolysis phenomenon that occurs in an aqueous environment (Da Silveira et al., 2018). The calcium carbonate concentration in soil has a notable impact on the nature of heavy metals, including Cu (He et al., 2020).

When studying the adsorption of Cu in soils, factors such as soil pH (Xu et al., 2013; Wang et al., 2024a), organic matter content in soils (Wang et al., 2024b), various clay minerals (De Carsalade du Pont et al., 2024), and soils with different oxide and hydroxide contents (De Carsalade du Pont et al., 2024) are considered. Additionally, the effects of regulators like sewage sludge, sewage wastes, and farmyard manure, which can lead to an increase in organic matter (Wang et al., 2024b), are also taken into account. No good data on the Cu adsorption ability of soils under acidic conditions after liming were obtained.

The subject that makes us wonder about this study is to provide the soil science community with the answer to the question of what kind of changes will occur in the Cu adsorption of acid soils with different liming levels. Knowing how acid soils limed at different rates will contribute to heavy metal adsorption is important. This information will serve as a reference for Cu-contaminated areas in acid soils worldwide. Anthropogenic Cu pollution in soils causes yield losses and degradation. The use of agricultural lime will contribute significantly to soil remediation by increasing Cu adsorption as well as setting up new nutrient and pH balances in favor of better crop performance. Hence, this work aims to investigate the impact of various liming techniques on the adsorption of copper in acidic soils with diverse physicochemical characteristics.

2. MATERIAL AND METHODS

2.1. Soil sites and preparation

In this study, surface (0-20 cm) soil samples with varying acidity levels were taken from nine (9) different locations in the Black Sea Region of Türkiye. Values ranging from 850 mm to approximately 2500 mm have been reported for the average annual precipitation in the study area (Gürgen, 2004). Copper exhibits low mobility in soil, resulting in its predominant accumulation in the uppermost layer of soil (Araújo et al., 2019). Composite soil sampling was carried out from 0-20 cm depth because liming materials were only mixed into the surface soil layer 15 to 20 cm deep. After collection, the soil samples were dried and sieved using a 2 mm sieve for further experiments.

The methods outlined by Sparks et al., (1996) were utilized to conduct descriptive analyses on soil samples. The study involved the determination of pH and electrical conductivity (EC) of soil samples using a 1:2.5 soil: water suspension. Organic matter (OM) was measured using the modified Walkley-Black method as described. The calcium carbonate ($CaCO_3$) content was determined using a Scheibler calcimeter. Soil texture was determined using the hydrometer method. Available phosphorus (P) was measured using the $NaHCO_3$ method. The availability of plant nutrients such as K, Na, Ca, and Mg was determined using an extract of 1 M ammonium acetate.

2.2. Lime requirements

In the studies on liming the acid soils of the Black Sea Region, it was determined that Dunn and SMT methods were the most suitable methods for calcium carbonate incubation method (Özuygur et al., 1974); thus, the lime requirement of soils was determined according to Dunn method (Dunn, 1943). After determination of the soil's lime requirement, soil samples (250 g) were thoroughly mixed with analytical grade $CaCO_3$ at 0%, 50 %, and 100 % of the lime requirement. Each treatment was done in 3 replicates. Soil samples were then incubated for one year at 20 ± 2°C and irrigated with pure water at 80% of field capacity. Water loss was measured at regular intervals (2-7 days), and water was supplied. Subsequently, the incubated soils were subjected to desiccation in an oven set at 40°C, following which the processes of Cu adsorption were investigated.

2.3. Adsorption studies

Triplicates of soil samples weighing 5 g each were measured and placed into 50 mL plastic tubes. The soil samples underwent equilibration with 20 mL solutions containing varying concentrations of Cu (0, 1, 2, 3, 5, 10, 20, and 40 mg L^{-1}) that were prepared in 0.01 M $CaCl_2$. The equilibration process was carried out at a constant temperature of 24±1 °C on a reciprocal shaker at 150 rpm for a duration of 23 hours. The supernatants underwent centrifugation at 4000 rpm for a duration of 10 minutes, followed by filtration through Whatman No. 42 filter paper. The atomic absorption spectroscopy (Varian AA 240FS) was utilized to determine the Cu concentrations of the supernatants.

2.4. Data analysis

The amount of adsorbed Cu was calculated based on the following equation;

$$q = \frac{(Co-Ce)*V}{W} \qquad (1)$$

where, q is the amount of adsorbed Cu (mg kg^{-1}), *Co* is the initial concentration of Cu (mg L^{-1}), *Ce* is the equilibrium concentration of Cu (mg L^{-1}), V is the solution volume (mL), and *W* is the dry weight of the soil used in the experiment (g).

Langmuir adsorption isotherm;

$$q = \frac{Q_{max}K_L Ce}{1+K_L Ce} \qquad (2)$$

Qmax: maximum adsorption
K_L: binding energy
Ce: equilibrium concentration

Freundlich adsorption isotherm;

$$q = K_F * C_e^{1/n} \qquad (3)$$

KF: adsorption capacity constant
n: density constant
Ce: equilibrium concentration

The maximum adsorption is denoted by *Qmax* and measured in mg·kg^{-1}. The constant K_L is related to the adsorption energy and measured in L·Kg^{-1}. The constant K_F is related to the adsorption strength and measured in mg·kg^{-1}. The heterogeneity of the adsorbent is represented by the variable *n*. The sorption parameters of the isotherms were calculated with the help of the CHB SSSAJ 71 spreadsheets ver. 1.6 (Bolster & Hornberger, 2007).

To evaluate the adsorption isotherms, the equations with the highest coefficient of determination coefficient (R^2) were selected as the best equation for predicting the adsorption isotherms of Cu in the soil. Analysis of variance (ANOVA) tests were used to compare the effects of the lime rate and adsorption of Cu in the soils; the Duncan post-hoc test was used at $p \leq 0.05$. The statistical evaluation was performed using the R Studio 4.4.0 software (R Core Team, 2024).

3. RESULTS

The properties of experimental soils are given in Table 1. The pH values of the soil-solution suspensions (1:2.5) exhibited a range of acidity, with values ranging from highly acidic to mildly acidic, spanning from 3.81 to 5.12. The soils exhibit virtually no lime content owing to their acidic nature. Within this particular context, the soil samples exhibit a negligible presence of lime (<0.05%), with the exception of certain data points that may be attributed to analytical measurement errors. The soil does not exhibit any salinity issues. The study determined that the soils' organic carbon content (OC) exhibited a range of values, with the highest recorded at 4.27% and the lowest at 0.91%.

The investigation revealed that the concentrations of Cu in the soil samples ranged from 63 to 629 mg kg^{-1}. The study area is characterized by the prevalence of podzolic and acid soils, with reported typical total Cu levels ranging from 5-30 mg kg^{-1} and 7-70 mg kg^{-1}. With the exception of one soil sample, the total Cu levels observed in the study soils exceed the aforementioned average. This suggests the presence of a Cu issue within the soil, which has resulted in varying degrees of contamination, mainly the use of phosphate fertilizers over 45 years, which can contain as high as 629 mg kg^{-1} total Cu. The adsorption efficiency of Cu^{2+} onto various rates of lime-incubated soils exhibited an upward trend with the rise in initial Cu^{2+} concentrations (Table 2). The phenomenon of heightened adsorption is universally observed across all soils upon an elevation in pH levels. Copper exhibits the highest degree of adsorption with an increase in pH, owing to the dissociation of functional groups of organic particles that occurs as pH levels rise.

Table 1. Some physical and chemical properties of soil

	pH	EC	OC	$CaCO_3$	Clay	Silt	Sand	Ca
	(1:2.5)	(µS m^{-1})	(%)	(%)	(%)	(%)	(%)	(cmol kg^{-1})
1	3.81	216.3	4.27	0.031	67.7	19.6	12.7	0.78
2	4.21	167.3	1.01	0.038	37.4	34.2	28.4	9.6
3	4.02	124	2.42	0.002	45.7	26.9	27.4	0.98
4	3.84	235	2.45	0.025	37.4	26	36.6	1.46
5	5.12	43.3	0.91	0.009	46.1	25.7	28.2	19.58
6	4.11	48.7	3.92	0.02	42.3	21	36.7	0.71
7	4.29	52.7	1.69	0.002	40	26.4	33.6	1.72
8	4.76	63.3	1.51	0.022	38	24.4	37.6	5.97
9	4.08	157.7	3.05	0.025	27.9	22.9	49.2	4.35
	Mg	K	Na	DTPA-Cu	Total-Cu	N	E	Plantation
	(cmol kg^{-1})	(cmol kg^{-1})	(cmol kg^{-1})	(mg kg^{-1})	(mg kg^{-1})			
1	0.09	0.62	0.12	0.64	474	$40^0$50'15''	$40^0$15'41''	Tea
2	1.11	2.88	0.11	3.75	629	$40^0$28'51''	$40^0$16'58''	Tea
3	0.16	0.85	0.12	0.33	506	$41^0$02'58''	$40^0$40'07''	Tea
4	0.15	0.68	0.12	2.11	171	$41^0$01'46''	$40^0$37'05''	Tea
5	2.48	0.71	0.28	0.76	336	$41^0$01'06''	$37^0$28'46''	Hazelnut
6	0.07	0.27	0.12	2.71	505	$40^0$53'36''	$37^0$46'50''	Hazelnut
7	0.1	0.26	0.16	5.48	310	$40^0$53'24''	$37^0$37'26''	Hazelnut
8	0.31	0.31	0.15	8.78	314	$40^0$59'56''	$37^0$52'09''	Hazelnut
9	0.42	0.17	0.2	3.1	63	$40^0$59'39''	$40^0$27'57''	Tea

Table 2. Adsorption parameters of soils Langmuir and Freundlich isotherm models

				LANGMUIR			FREUNDLICH	
Soil	% of LR	pH	Qmax	RL	R^2	n	Kf	R^2
1	0	3.90	1724	0.02	96.17	5.73	15.99	78.99
1	50	5.84	2146	0.00	99.11	3.72	18.86	98.67
1	100	6.91	5714	0.00	99.94	2.61	26.20	86.26
2	0	4.06	1835	0.01	96.86	2.99	13.30	98.47
2	50	4.39	2971	0.02	92.26	5.33	18.27	75.79
2	100	6.47	4762	0.01	95.86	3.48	22.78	95.11
3	0	3.70	1620	0.03	89.48	6.68	15.78	67.33
3	50	4.35	2034	0.01	97.04	4.48	16.79	89.94
3	100	5.76	4869	0.01	96.98	4.52	9.37	95.91
4	0	3.70	1491	0.09	80.80	3.09	10.95	90.76
4	50	4.45	1695	0.03	98.45	2.15	12.49	92.99
4	100	5.14	3593	0.02	99.59	2.17	16.67	95.94
5	0	4.13	1852	0.01	99.35	6.39	18.03	83.35
5	50	4.98	3125	0.01	96.79	4.77	19.88	91.15
5	100	6.04	3333	0.00	99.66	4.28	21.31	99.11
6	0	4.08	1596	0.05	94.07	2.96	11.31	91.50
6	50	5.02	1786	0.01	99.32	3.29	16.11	96.43
6	100	5.20	3226	0.01	99.69	3.14	20.35	97.89
7	0	3.82	777	0.02	96.93	7.85	13.00	64.22
7	50	4.22	1538	0.01	99.10	3.98	14.78	96.82
7	100	5.17	3125	0.01	99.49	3.01	19.06	92.84
8	0	3.97	1193	0.15	89.58	2.65	9.76	98.04
8	50	3.75	1695	0.08	99.36	1.73	10.48	96.46
8	100	6.30	3226	0.04	99.70	3.85	20.57	94.94
9	0	4.27	1887	0.01	97.79	6.68	18.35	84.61
9	50	5.01	2857	0.01	96.96	5.09	20.46	96.75
9	100	6.02	3273	0.00	99.98	4.19	23.83	93.68

LR: Liming Rate

The practice of remediation for heavy metal-polluted soils has often involved the elevation of soil pH. The primary cause of this phenomenon can be ascribed to the elevation in soil pH, leading to the precipitation of metals in the form of hydroxide, carbonate, and other compounds. This, in turn, intensifies the negative charges of colloids with variable charges present in soils, including those found in clays and iron and aluminum oxides. The lime amendment exhibited the most significant impact on pH in this investigation, attributed to the elevated CaO levels present in the various amendments. The results of Duncan's posthoc test indicate a statistically significant disparity in Qmax between the treatment where the entirety of the soils' lime requirements was met and both the control group and the treatment where only half of the lime requirement was fulfilled (Table 3). This expression holds significant importance in the control of Cu. In the event of comparable Cu contamination in acidic environments, it is advisable to perform liming while taking into account the quantity of liming required to prevent both nutritional deficiencies and heavy metal pollution.

The results of Pearson's correlation analysis revealed significant correlations between Qmax1 and various soil properties, including pH, EC, OC, DTPA-Cu, and total-Cu ($P<0.05$). Additionally, Ca and Mg were found to be significantly correlated with Qmax1 ($P<0.001$), as indicated in Table 4. The statistical study demonstrated a noteworthy link between Qmax2 and pH, EC, and K ($P<0.05$), though Ca and Mg exhibited a highly significant correlation ($P<0.001$). A significant correlation was observed between Qmax3 and total-Cu as well as K, with a significance level of less than 0.05. A significant correlation ($P<0.01$) was also observed between Qmax3 and EC. The results of Pearson's correlation analysis revealed a significant correlation between soil pH and Qmax1 as well as Qmax2. The observed escalation in Qmax3 failed to establish a correlation between pH and Qmax1 as well as Qmax2. The application of lime resulted in an elevation of the solubility relationship and a direct association with electrical conductivity (EC). The table highlights a crucial finding that the correlation between Qmax2 and lime application weakens significantly at 50% LR application and becomes nearly inconsequential at Qmax3. This demonstrates that the application of lime resulted in a significant reduction in the amount of available Cu content.

The RL parameter denotes the extent of adsorption availability and is constrained to the range of 0 to 1. On the other hand, KF represents the experimentally derived adsorption capacity, which is equivalent to of adsorption. The isotherm analysis reveals that the obtained n value is greater than 1, indicating that Cu^{2+} can be adsorbed by all types of soils. Typically, numerical values below 1 denote a robust adsorption process, whereas values exceeding 1 suggest weak retention of adsorbed Cu^{2+} ions, which may readily leach into the solution. The impact of pH on the parameters outlined in Table 2 is primarily attributed to the occurrence of functional group protonation

Table 3. The comparison of liming's main effect on the Langmuir and Freundlich isotherms' parameters by Duncan post-hoc test

% of LR	pHe	Langmuir			Freundlich		
		Qmax	RL	R^2	KF	n	R^2
0	3.95^{a}	1552.78^{a}	0.01^{a}	93.44^{a}	14.05^{a}	3.47^{a}	84.14^{a}
50	4.66^{b}	2205.19^{a}	0.02^{a}	97.59^{b}	16.45^{ab}	3.83^{ab}	92.77^{b}
100	5.89^{c}	3902.36^{b}	0.04^{a}	98.98^{b}	20.01^{b}	5.01^{b}	94.63^{b}

pHe: pH after incubation. $^{a\ ab\ b}$ duncan post-hoc analysis sorting icons.

Table 4. Correlation between soil properties and maximum adsorption

	Qmax1	Qmax2	Qmax3
pH	**0.68***	**0.61***	0.23
EC	**0.72***	**0.69***	**0.74****
OC	**0.67***	0.52	0.60
$CaCO_3$	0.54	0.43	0.45
Clay	-0.32	-0.34	0.29
Silt	-0.13	0.00	-0.04
Sand	0.40	0.36	-0.29
Ca	**0.84****	**0.93****	0.44
Mg	**0.84****	**0.92****	0.45
K	0.60	**0.69***	**0.66***
Na	0.20	0.35	-0.27
DTPA-Cu	**0.68***	0.52	0.28
Total-Cu	**0.62***	0.50	**0.69***

Qmax1 no lime applied, Qmax2 50% of lime requirement applied, Qmax3 100% of lime requirement applied. Significant at the 0.01 (**) and 0.05 (*) levels for the 2-tailed.

at lower pH levels. This phenomenon leads to the obstruction of the aforementioned groups, resulting in a reduction in the quantity of active sites available for ion adsorption.

The adsorption capacity of Cu exhibited a noticeable variation in response to the augmentation of the liming level in the soil. The addition of calcium carbonate increased the soil's pH value, thereby facilitating the precipitation reaction of exchangeable Cu^{2+} with carbonate and hydroxide in the soil. Simultaneously, the co-precipitation of calcium ions (Ca^{2+}) is also advantageous for the conversion of the exchange state into alternative forms. Moreover, the elevation in soil pH has the potential to augment the chelation potential of clay and organic matter, as well as stimulate the soil's adsorption capacity. On the contrary, the soil materials' adsorption capacity exhibited a continuous increase as the liming level increased (Figure 1). The observed phenomenon could be attributed to the correlation between the rise in pH levels and the augmentation of negative charges on the surface of soil constituents such as clay minerals, hydrated oxides, and organic matter. This, in turn, leads to an increase in the adsorption potential of heavy metals. The adsorption of heavy metals onto oxide surfaces and the stability of metal complexes with soil organic matter were observed to decrease as the pH value increased. As pH levels decrease, the concentrations of H^+ and Fe^{2+}/Fe^{3+} in soil solution also increase, leading to heightened competitive adsorption with heavy metals. This phenomenon promotes the adsorption of heavy metals by a selectivity order.

4. DISCUSSION

Soils possessing a substantial proportion of silt particles are inclined to exhibit a diminished quantity of organic matter. It is hypothesized that this outcome is attributable to the prevalence of silt as the secondary dominant fraction of texture. Typically, the safeguarding of clay minerals and organic matter against mineralization is achieved through the creation of organo-mineral structures, as posited (Usta, 1995). With an increase in the silt fraction, there is a relatively lower formation of these components, and the organic matter becomes vulnerable to both decomposition and erosion under a precipitation amounting to over 3000 mm year^{-1}.

The findings presently obtained are consistent with the notion that the adsorption capability of adsorbents is closely associated with the initial concentration of Cu ions in the reaction system, as previously observed by Tomczyk et al., (2019). The presence of carboxylic and phenolic groups generates a negative charge, thereby facilitating the attraction of metal cations that carry a positive charge (Boguta et al., 2016).

Azouzi et al., (2015) have reported that soil pH is a crucial factor that regulates the sorption and mobility of heavy metals in soil. Furthermore, a substantial amount of research has indicated a significant positive relation between the concentrations of bio-accessible heavy metals and the total concentrations in soil (Luo et al., 2012). The results of this study suggest that the health hazards associated with high levels of ingested heavy metals in soil are not solely determined by the inorganic amendment, specifically lime, or the overall concentration of metal in the soil. Rather, the availability and mobility of heavy metals also play a significant role (Kavelidze & Kalandadze 2023; Domnariu et al., 2022; Paltineanu et al., 2021; Paltineanu et al., 2022). The findings are in alignment with the European Community Bureau of Reference method and the report of Ren et al., (2016), which demonstrated a significant correlation between the levels of bio-accessible Cu and the levels of available metals extracted through the diffusive gradient in thin-films technique.

The study conducted by Liu et al., (2002) revealed that the soil pH was influenced by the concentrations of $CaCO_3$. According to Omekeh et al., (2015), the impact of $CaCO_3$ on soil pH can be

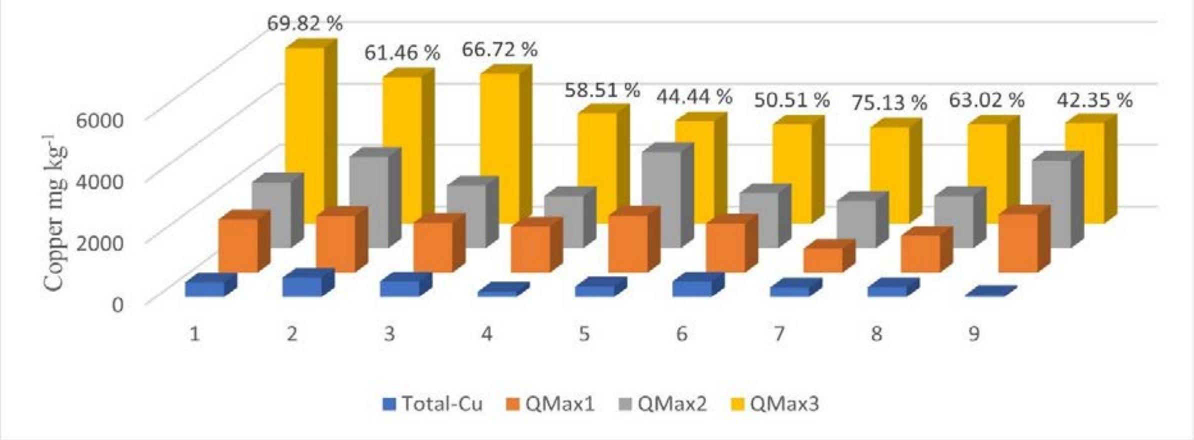

Figure 1. The predicted Cu sorption maxima for the soils treated with differing level of liming requirement

attributed to the hydrolysis of carbonate, as expressed by the chemical equation (4);

$$MCO_3 + H_2O \leftrightarrow M^{2+} + HCO^{3-} + OH^- \qquad (4)$$

These results indicate that the Langmuir model describes the Cu adsorption data in soils amended with lime better than the Freundlich model. This suggests that the adsorption process is characterized by monolayer adsorption on uniform surfaces, with no discernible interactions between the adsorbed metal ions, as reported by Golia et al., (2023). The Langmuir-Freundlich equation's parameters possess a physical significance that arises from its theoretical derivation.

This decrease in active sites is reflected in the RL and n values, respectively, and is associated with ion adsorption and surface energy heterogeneity (Kobya et al., 2005). The aforementioned observation implies a more intricate mechanism for the buildup of surface complexes that bind Cu, in contrast to the simplistic Langmuir-Freundlich previously postulated model (Marczewski & Szymula, 2002). Elevated levels of Cu concentration result in a corresponding increase in the concentration of Cu^{2+} adsorbed on the unit mass of the adsorbent. This increase is attributed to a rise in the concentration of active sites present in the solution. The aforementioned statement is supported by the studies conducted (Pellera et al., 2012). The Langmuir and Freundlich models have been employed to assess the partitioning of metal ions between the aqueous and solid phases, as well as the maximum adsorption capacities of adsorbent, as reported by Golia et al. (2023). The findings of this study indicated that lime application has the potential to act as a sorbent for the effective removal of Cu from the soil solution in acidic soil.

5. CONCLUSION

The findings indicated that employing a lime requirement of at least 50% of the minimum lime requirement can serve as a viable means of immobilizing Cu pollutants. Adsorption information was associated with Langmuir-Freundlich adsorption isotherms and demonstrated the models' effectiveness in describing the process. The aforementioned findings could hold considerable worth in forecasting the adsorption characteristics of liming in alternative research frameworks. This study presents findings regarding the management of liming as a means of acidic soil pollutant removal and soil remediation. According to the results, the lime can be used as a low-cost, eco-friendly amendment to increase the adsorption of Cu while reducing the mobility and plant availability in polluted, acidic soils.

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REFERENCES

Araújo, D. F., Ponzevera, E., Briant, N., Knoery, J., Bruzac, S., Sireau, T., & Brach-Papa, C. 2019. *Copper, zinc and lead isotope signatures of sediments from a mediterranean coastal bay impacted by naval activities and urban sources,* Applied Geochemistry, 111, 104440.

Azouzi, R., Charef, A., & Hamzaoui, AH., 2015. *Assessment of effect of pH, temperature and organic matter on zinc mobility in a hydromorphic soil,* Environ. Earth Sci., 74:2967-2980.

Bell, RW., & Dell, B., 2008. *Micronutrients for sustainable food, feed, fibre and bioenergy production,* International Fertilizer Industry Association (IFA).

Boguta, P., Pieczywek, PM., & Sokołowska, Z., 2016. *A comparative study of the application of fluorescence excitation-emission matrices combined with parallel factor analysis and nonnegative matrix factorization in the analysis of Zn complexation by humic acids,* J. Sens. 16:1760.

Bolster, CH., & Hornberger, GM., 2007. *On the use of linearized Langmuir equations*, Soil Sci. Soc. Am. J., 71(6):1796-1806.

Da Silveira, MR., Ivancko, IN., Valério, MB., Reznik, LY., De Carvalho, LJ., Rodrigues, ADC., & Da Silva, ALN., 2018. *Effect of the addition of calcium carbonate on the barrier behavior of polyamide 11 used in offshore applications by electrochemical impedance analysis*, Polym. Test. 69: 410–416.

De Carsalade du Pont, V., Ben Azzouz, A., El Hadri, H., Chéry, P., & Lespes, G., 2024. *Copper Speciation in Wine Growing-Drain Waters: Mobilization, Transport, and Environmental Diffusion,* Environments, 11(1): 19.

Domnariu, H., Paltineanu, C., Marica, D., Lăcătuşu, AR., Rizea, N., Lazăr, R., Popa, GA., Vrinceanu, A., Bălăceanu, C. 2020. *Influence Of Soil-Texture on Nitrate Leaching from Small-Scale Lysimeters Toward Groundwater in Various Environments*, Carpathian Journal of Earth and Environmental Sciences, 15(2): 301-310; Doi:10.26471/cjees/2020/015/130.

Dunn, LE., 1943. *Lime requirement determination of soils by means of titration curves*, Soil Sci. Soc. Am. J., 56: 341-351.

Field, HR., Whitaker, AH., Henson, JA., & Duckworth, OW., 2019. *Sorption of copper and phosphate to diverse biogenic iron (oxyhydr)oxide deposits*, Sci. Total Environ. 697: 134111.

Golia, EE., Kantzou, OD., Chartodiplomenou, MA., Papadimou, SG., & Tsiropoulos, NG., 2023. *Study of potentially toxic metal adsorption in a polluted acid and alkaline soil: Influence of soil properties and levels of metal concentration,* Soil Syst., 7(1):16.

Gürgen, G. 2004. *Doğu Karadeniz Bölümünde Maksimum*

Yağışlar ve Taşkınlar Açısından Önemi, Gazi Üniversitesi Gazi Eğitim Fakültesi Dergisi, 24(2).

He, G., Zhang, Z., Wu, X., Cui, M., Zhang, J., & Huang, X., 2020. *Adsorption of heavy metals on soil collected from Lixisol of typical karst areas in the presence of $CaCO_3$ and soil clay and their competition behavior,* Sustainability, 12(18):7315.

Huang, G., Su, X., Rizwan, MS., Zhu, Y., & Hu, H., 2016. *Chemical immobilization of Pb, Cu, and Cd by phosphate materials and calcium carbonate in contaminated soils,* Environ. Sci. Pollut. Res., 23:16845–16856.

Kavelidze, L., Kalandadze, B. 2023. *Spatial Distribution of Heavy Metals in Soils and Waters As Exemplified By Kakheti Region (Eastern Georgia),* Carpathian Journal of Earth and Environmental Sciences August 2023, Vol. 18, No. 2, p. 289 – 298; DOI:10.26471/cjees/2023/018/259.

Kobya, M., Demirbas, E., Sentruk, E., & Ince, M., 2005. *Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone,* Bioresour. Technol., 96:1518–1521.

Kužel, S., Kolář, L., Gergel, J., Peterka, J., & Borová-Batt, J., 2010. *Influence of the degree of soil organic matter lability on the calcium carbonate equilibrium of soil water,* Soil Water Res., 5:58–68.

Laurent, C., Bravin, MN., Crouzet, O., Pelosi, C., Tillard, E., Lecomte, P., & Lamy, I., 2020. *Increased soil pH and dissolved organic matter after a decade of organic fertilizer application mitigates copper and zinc availability despite contamination,* Sci. Total Environ., 709:135927.

Liu, SQ., Zhang, SR., & Wu, J., 2002. *The relationship between soil pH and calcium carbonate content,* Soil, 34: 279–288.

Luo, XS., Ding, J., Xu, B., Wang, YJ., Li, HB., & Yu, S., 2012. *Incorporating bioaccessibility into human health risk assessments of heavy metals in urban park soils,* Sci. Total Environ., 424:88-96.

Marczewski, A., & Szymula, M., 2002. *Adsorption of asphaltenes from toluene on mineral surface,* Colloid Surf. A, 208:259–266.

Marschner, H., (Ed.), 2011. *Marschner's mineral nutrition of higher plants,* Academic press.

Nadaroğlu, H., Kalkan, E., & Celebi, N. 2014. *Removal of copper from aqueous solutions by using micritic limestone,* Carpathian J. Earth and Environ Sci., 9(1): 69-80.

Omekeh, AV., Friis, HA., Evje, S., & Fjelde, IA., 2015. *Model for low salinity flooding experiments: Dissolution and ion exchange,* J. Porous Media, 18:189–213

Özuygur, M., Ateşalp, M., & Börekçi, M., 1974. *Doğu Karadeniz topraklarının kireç ihtiyaçlarını tayinde uygulanacak metotlar ve kireçleme malzemeleri üzerinde bir araştırma,* TUBİTAK-TOAG Rapor No: 107.

Paltineanu, C., Domnariu, H., Marica, D., Lăcătuşu, A-R., Popa, GA., Grafu, I., Neagoe, AD., 2021. *Fertilizers` Leaching from The Root System Zone – A Potential Environmental Risk for Groundwater Pollution In Coarse And Medium-Textured Soils,* Carpathian Journal of Earth and Environmental Sciences,16(1), 139–150; Doi:10.26471/cjees/2021/016/162

Paltineanu, C., Dumitru, SI., Lăcătusu, AR., 2022. *Assessing Land Susceptibility for Possible Groundwater Pollution due to Leaching – A Case Study on România,* Carpathian Journal of Earth and Environmental Sciences, 17(1): 49-57, Doi:10.26471/cjees/2022/017/199.

Pellera, FM., Giannis, A., Kalderis, D., Anastasiadou, K., Stegmann, R., Wang, JY., & Gidarakos, E., 2012. *Adsoption of Cu(II) ions from aqueous solution on biochars prepared from agricultural byproducts,* J Environ. Manage., 96:35–42.

R Core Team. 2024. R: a language and environment for statistical computing.

Ren, LL., Wu, WC., Chen, XB., Liu, XC., Li, YB., & Song, QM., 2016. *Different effects of $CaCO_3$ and $Ca(OH)_2$ on heavy metals remediation in contaminated farmland,* Soil. Environ. Sci. Technol., 39:22–27.

Shabbir, Z., Sardar, A., Shabbir, A., Abbas, G., Shamshad, S., Khalid, S., & Shahid, M., 2020. *Copper uptake, essentiality, toxicity, detoxification and risk assessment in soil-plant environment,* Chemosphere, 259:127436.

Shaheen, SM., & Rinklebe, J., 2014. *Geochemical fractions of chromium, copper, and zinc and their vertical distribution in floodplain soil profiles along the Central Elbe River, Germany,* Geoderma, 228:142e159.

Sparks, DL., et al., (EDS) 1996. *Methods of soil analysis, part 3,* Chemical methods. 1085–1121.

Sposito, G., 2008. *The chemistry of soils.* Oxford University Press.

Tomczyk, A., Boguta, P., & Sokołowska, Z., 2019. *Biochar efficiency in copper removal from Haplic soils,* IJEST, 16(8):4899-4912.

USGS, 2019. *United States Geological Survey,* https://www.usgs.gov/centers/nmic/copper-statistics-and-information.

Usta, S., 1995. *Toprak kimyası,* Ankara Üniversitesi Ziraat Fakültesi Yayın, (1387):217.

Wang, X., Xue, J., He, M., Qi, H., & Wang, S., 2024b. *The effects of vermicompost and steel slag amendments on the physicochemical properties and bacterial community structure of acidic soil containing copper sulfide mines,* Appl. Sci., 14(3):1289.

Wang, X., Xue, J., Qi, H., Wang, S., & Wang, Y., 2024a. *Remediation of acidic soils in copper sulfide mines through combined plant amendments and their effects on soil bacterial community structure,* Water Air Soil Pollut., 235(2):141.

Xian, X., Homma, S., & Kuno, K., 2010. *Relationship between concentration of heavy metals in soil and contents of that absorbed by mulberry plant,* J. Sericult. Sci. Jpn. 57:481–488.

Xu, JM., & Sparks, DL., 2013. (Eds.), *Molecular Environmental Soil Science,* Spring, Dordrecht, pp. 193-228.

Yohey, H., Hiroki, M., Masaki, T., Hajime, T., & Takeshi, S., 2009. *Impacts of chemical amendment and plant growth on lead speciation and enzyme activities in a shooting range soil: An X-ray absorption fine structure investigation,* J. Environ. Qual., 38:1420–1427.

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