T.C.
ISPARTA UNIVERSITY OF APPLIED SCIENCES
THE INSTITUTE OF GRADUATE EDUCATION

MASTER'S THESIS
DEPARTMENT OF SOIL SCIENCE AND PLANT NUTRITION

EFFECT OF LOW MOLECULAR WEIGHT ORGANIC ACIDS ON PHOSPHORUS (P) ADSORPTION IN ACIDIC SOILS LIMED AT DIFFERING LEVELS

Nurul Azizah ZAHRAENI

Supervisor
Prof. Dr. Veli UYGUR

ISPARTA - 2023

COMMITMENT

In this thesis study, which I prepared in accordance with the thesis writing rules of Isparta University of Applied Sciences, The Institute of Graduate Education without resorting to any means or assistance that would be contrary to scientific morals and traditions;

I hereby declare that I have obtained all the data, information, and documents presented in the thesis within the framework of academic and ethical rules, that I have presented all the information, documents, evaluations, and results in accordance with scientific ethics and morals, that I have cited all the works I have used in the thesis by giving appropriate references, that I have not made any changes in the data used and the results obtained, and that the work I have presented in this thesis is original. I also declare that, if a case contrary to my declaration is detected in my work at any time, I hereby express my consent to all the ethical and legal consequences that are involved.

15/08/2023

Nurul Azizah ZAHRAENI

…….

TABLE OF CONTENTS

Page

ÖZET

Yüksek Lisans Tezi

FARKLI SEVİYELERDE KİREÇLENMİŞ ASİT TOPRAKLARDA DÜŞÜK MOLEKÜL AĞIRLIKLI ORGANİK ASİTLERİN FOSFOR (P) ADSORPSİYONUNA ETKİSİ

Nurul Azizah ZAHRAENI

Isparta Uygulamalı Bilimler Üniversitesi
Lisansüstü Eğitim Enstitüsü
Toprak Bilimi ve Bitki Besleme Anabilim Dalı

Danışman: Prof. Dr. Veli UYGUR

Asit topraklarda fosor yarayışlılığının oluşan Al ve Fe fosfatlar nedeniyle düşük olması önemli problemeleden birisidir. Bu toprakların verimliliğinin arttırılabilmesi için zaman zaman kireçleme yapılmaktadır. Diğer taraftan değişen pH topraktaki var olan organik maddenin ayrışma dinamiği üzerinde önemli değişimlere neden olmaktadır ki bu da P ile adsorpsiyon rekabetine giren gerek düşük molekül ağırlıklı gerekse humik ve fulvik asitlerin topraktaki etkin konsantrasyonlarının değişimine neden olmaktadır. Bu bağlamda mevcut çalışmanın amacı farklı seviyelerde kireçlenmiş ve halen 15 aydır inkübe edilmiş asit topraklarda sitrik, oksalik ve malik asitlerin Doğu Karadeniz bölgesinden çay ve fındık yetiştiriciliği yapılan 11 asit toprakta P adsorpsiyonunu nasıl etkilediği araştırılmak istenilmektedir. Elde edilen verilerden Bolster ve Hornberger (2007) spreat sheet programında toprakların Langmuir ve Freundlich adsorpsiyon parametreleri tahmin edilmektedir. Ayrıca kireçleme seviyeleri ve organik asitlerin Freudlich ve Langmuir izotermlerinin P adsorpsiyon parametreleri üzerindeki etkileri ANOVA analizi ile incelenecek ve ortalamalar arasındaki farklılıklar Duncan testi ($p<0.05$) ile karşılaştırılmaktadır. Fosfor adsorpsiyonunun azaltılmasında en etkili asit organiğin sitrik asit olduğunu göstermiştir. Ardından oksalik asit, malik asit ve $CaCl_2$ gelmektedir. Sitrik asit, üç karboksil grubuna (-COOH) sahip bir organik asittir ve bu özelliği sayesinde toprağın yüzeyinde adsorbe olmuş fosforla daha fazla kompleks oluşturabilir. Kireçleme %100, fosfor adsorpsiyonunun önemli ölçüde azalmasına neden olmuştur. Sonuçlar, düşük molekül ağırlıklı organik asitlerin ve kireçleme uygulamasının fosfor adsorpsiyonunu etkilediğini göstermiştir.

Anahtar Kelimeler: Fosfor adsorpsiyonu, Kireçleme, Organik asit

2023, 115 sayfa

ABSTRACT

Master's Thesis

EFFECT OF LOW MOLECULAR WEIGHT ORGANIC ACIDS ON PHOSPHORUS (P) ADSORPTION IN ACIDIC SOILS LIMED AT DIFFERING LEVELS

Nurul Azizah ZAHRAENI

Isparta University of Applied Sciences
The Institute of Graduate Education
Department of Soil Science and Plant Nutrition

Supervisor: Prof. Dr. Veli UYGUR

Low phosphorus availability in acidic soils due to the formation of aluminum and iron phosphates was a significant concern for agricultural productivity. Liming is often applied to improve soil fertility. However, altering pH could also affect the dynamics of existing organic matter in the soil, leading to changes in the effective concentrations of competing low molecular weight acids involved in phosphorus adsorption. The study aims to investigate the effects of citric, oxalic and malic acids in acid soils from tea and hazelnut cultivation regions of the Eastern Black Sea, which had been limed at different levels and incubated for 15 months, on phosphorus adsorption in 11 acid soils. The obtained data were used to estimate the Langmuir and Freundlich adsorption parameters of soils using the spreadsheet program developed by Bolster and Hornberger (2007). Furthermore, the effects of liming levels and organic acids on the phosphorus adsorption parameters of Freundlich and Langmuir isotherms were analyzed using ANOVA, and differences between means were compared by the Duncan test ($p<0.05$). The results demonstrated that citric acid was the most effective organic acid in reducing phosphorus adsorption, followed by oxalic acid, malic acid, and $CaCl_2$. With its three carboxyl groups (-COOH), citric acid could form more complexes with adsorbed phosphorus on the soil surface. Additionally, 100% liming was found to substantially decrease phosphorus adsorption. The results indicated the significant influence of low molecular weight organic acids and liming application on soil adsorption.

Key Words: Phosphorus adsorption, Liming, Organic acid

2023, 115 pages

GENİŞLETİLMİŞ ÖZET

Asit topraklarda fosfor yarayışlılığının düşük olmasının önemli nedenlerinden biri ilave edilen gübrelerin Al ve Fe fosfatları oluşturmasıdır. Bu tür toprakların verimliliğini artırmak için zaman zaman kireçleme uygulamaları yapılması gerekmektedir. Bununla birlikte, pH seviyelerinin değişmesi, topraktaki mevcut organik maddenin reaksiyon dinamikleri üzerinde önemli değişikliklere neden olmaktadır. Bu durum, düşük molekül ağırlıklı, humik ve fulvik asitlerin etkin konsantrasyonlarının değişmesine ve fosforla adsorpsiyon rekabetine girmesine yol açmaktadır. Diğer taraftan kireçleme sonrası pH'nın zaman içerisinde yavaş yavaş düşmesi çözünürlük ve adsorpsiyon olaylarını önemli ölçüde etkilemektedir.

Fosfor, pH değişimine karşı duyarlılığı en yüksek elementlerden biridir ve değişen koşullarda toprak bileşenleri ile olan reaksiyonları farklılıklar göstermektedir. Bu durum, bitkiye yararlı olan fosfor fraksiyonunun zaman içinde azalmasına veya artmasına neden olmaktadır. Azalma bitki yetiştiriciliği için olumsuz sonuçlar doğururken, artış ise çevresel risklere yol açabilmektedir. Düşük molekül ağırlıklı ve humik ile fulvik asitler, fosforla adsorpsiyon rekabetine girerek topraktaki etkin konsantrasyonlarını değiştirebilmektedir.

Bu araştırma, kireçlemenin %0, %50, %75 ve %100'üne göre değişen fosfor adsorpsiyonunu ve 15 ay süreyle inkübe edilmiş olan toprakların organik asitlerle uygulanmasının nasıl değiştiğini değerlendirmektedir. Bu çalışmanın amacı, Türkiye'nin Karadeniz Bölgesi'ndeki asit topraklarda farklı kireçleme dozlarının ve düşük molekül ağırlıklı organik asitlerin fosfor adsorpsiyonu üzerindeki etkisini Freudlich ve Langmuir izoterm modelleri kullanarak belirlemektedir. Bu çalışma, farklı asit toprakların yönetimi ve tarımsal uygulamalar için önemli bilgiler sağlamaktadır.

Bu çalışmada, Doğu Karadeniz bölgesinde farklı asitlik seviyelerine sahip çay ve fındık yetiştiriciliği yapılan 11 toprak örneği alınmıştır. Toprakların fiziksel ve kimyasal özellikleri belirlenmiş ve kireçleme inkübasyonu gerçekleştirilmiştir. Bu topraklara sitrik, oksalik ve malik asit gibi düşük molekül ağırlıklı organik asitler ilave edilerek, batch sorpsiyon tekniği ile adsorpsiyon özellikleri Langmuir ve Freundlich

izoterm modelleriyle incelenmiştir. Kireçleme ve organik asitlerin P adsorpsiyon parametreleri üzerindeki etkileri, tesadüf parselleri deneme deseninde faktöriyel düzende (11 toprak örneği x 4 kireçleme seviyesi x 4 organik asit) yapılan ANOVA analizi ile test edilmiştir. Uygulamaların ana etkileri, $p<0.05$ düzeyinde Duncan çoklu karşılaştırma testi ile ayrıştırılmıştır.

Elde edilen sonuçlar, sitrik asitin fosfor adsorpsiyonunu azaltmada en etkili asit olduğunu göstermiştir. Ardından oksalik asit, malik asit ve $CaCl_2$ gelmektedir. Sitrik asit, üç karboksil grubuna (-COOH) sahip bir organik asittir ve bu özelliği sayesinde toprak yüzeyinde adsorbe olmuş fosforu yerinden çıkartabilmekte ya da ilave edilen fosforla adsorpsiyon yüzeyleri için rekabete girmektedir. Ayrıca, oksalik asit ve malik asit iki karboksil grubuna (-COOH) sahip bir organik asittir. Karşılaştırıldığında, sitrik asit (üç karboksil grubu) oksalik asitten (iki karboksil grubu) topraktan fosfor salınımı ve/veya adsorpsiyonu engellemede daha etkin olduğu tespit edilmiştir. Sitrik asitte daha fazla karboksil grubunun bulunmasından kaynaklandığı için toprak yüzeyine bağlanma eğiliminin fosfordan yüksek olmasını beraberinde getirmiştir.

$CaCl_2$, organik asitlerden farklı olarak inorganik bir bileşiktir, fosfor adsorpsiyon çalışmalarında iyonik gücün sabitlenmesi için kullanılan bir çözeltidir. Dolayısıyla bu çözelti ortama yüksek miktarlarda Ca sağladığı için genelde apatit ve benzeri katı fazların oluşumunu sağlayacak Ca sağlayabilmektedir. Nötral pH'da olmasından kaynaklı göreceli olarak toprak pH sını arttırıcı etkisi nedeniyle de asit topraklarda Fe ve Al fosfatların çözünürlüğünü arttırabilmektedir. Ancak yüzeylerdeki asit iyonlarının çözelti fazına geçmesiyle aktif asitliğin artmasına da neden olmaktadır. Dolayısıyla herhangi bir toprakta etkisi bu etkilerin net sonucuna bağlıdır.

Artan kireçleme oranının fosfor adsorpsiyonunu önemli ölçüde azalttığı belirlenmiştir. Toprakların düşük pH değerleri, fosforun Al/Fe ile birleşerek çözünmez hale gelmesine neden olmuştur. Sonuçlar, düşük molekül ağırlıklı organik asitlerin ve kireçleme uygulamasının fosfor adsorpsiyonunu etkilediğini açıkça göstermiştir.

ACKNOWLEDGMENTS

I would like to express my deep gratitude to my supervisor, Prof. Dr. Veli UYGUR for his guidance and encouragement throughout the process of writing the thesis; to Arş. Gör. Enise SUKUŞU for her guidance during the laboratory during my work in the laboratory.

I want to thank the Republic of Turkey Ministry of Culture and Tourism, the Presidency for Turks Abroad, and Related Communities for their financial and moral support during my graduate education.

I also would like to thank Isparta University of Applied Sciences, Scientific Research Projects Supporting Unit (BAP). This work was supported by The Department of Scientific Research Projects in Isparta University of Applied Sciences with the project named "Effect of low molecular weıght organic acids on phosphorus (p) adsorption in acidic soils limed at differing levels" and project number 2022-YL1-0169.

I would like to express my endless love and respect to my family and my beloved friends, who did not leave me alone at every stage of my thesis.

Nurul Azizah ZAHRAENI
ISPARTA, 2023

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS AND ABBREVIATIONS

Ca	Calcium
Fe	Iron
LMWOAc	Low molecular weight organic acids
P	Phosphorus

1. INTRODUCTION

1.1. Background of Study

Soil pH may be regarded as a key soil property to control soil chemical, physical, and biological features. The soil pH is acidic depending on the overall effect of soil-forming factors, mainly in humid and hot climate environments. Increasing severity of low-pH is a serious soil degradation process that limits soil fertility and sustainable agriculture. These severe conditions are accompanied by excessive Fe and Al^{3+} ions, which form complexes with H_2O. The hydrolysis reaction of these complexes given below has the potential to produce further H^+ ions toward increasing soil degradation (Equation 1.1 and Equation 1.2):

$$Al^{3+} + 3HOH \rightarrow Al(OH)_3 + 3H^+ \quad (1.1)$$

$$Fe^{3+} + 3HOH \rightarrow Fe(OH)_3 + 3H^+ \quad (1.2)$$

pH affects the availability of macro and micro elements in the soil. The soil is responsible for providing essential nutrient elements to plants; therefore, the pH must be managed toward optimal limits to ensure maximizing the yield quantity and quality. Liming is therefore a commonly used practice to optimize soil pH in acidic soils (Hardjowigeno, 2003).

Liming is occasionally required to keep acidic soils productive and eliminate the deleterious effects of acidity on plants. Liming amends the pH of the soil, which is essential for maintaining the availability of plant nutrients within a range of tolerances. This change manifest initially a pH rise relatively short time, followed by a subsequent fall in a longer time up to 3 – 5 years. This dramatically changes the dynamics of nutrients and the balance between them in the liming sequences (Ball, 1999).

Hydrogen, Al, and Fe are present on the soil surface in acidic soils. As lime dissolves in the soil, calcium (Ca) ions are adsorbed on the colloidal surfaces in soil by displacing the acid or acid generating ions. The H ions react with CO_3, and carbon dioxide (CO_2) and water (H_2O) are produced. The neutralization reactions resulted in

a mild soil pH as requested for better crop performance. The ongoing neutralization reaction is described in Figure 1.1 (Ball, 1999).

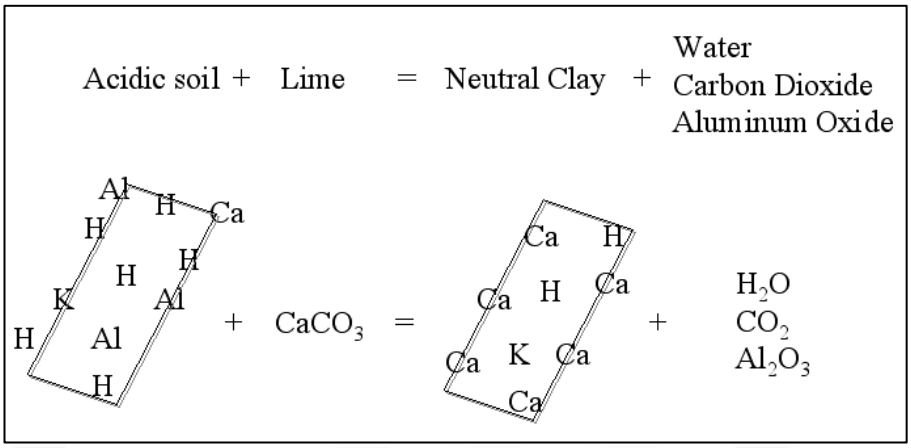

Figure 1.1. Reaction of lime or calcium carbonate with acidic soil (Ball, 1999)

Phosphorus, one of the most sensitive nutrient elements to pH changes, shows different adsorption and precipitation reactions depending on soil pH. This situation is manifested as an increase or decrease in the plant-available fraction over time, where the decrease poses risks for losing the yield and the increase poses risks for environmental pollution (Lindsay, 2001). Mojority of indigenous and fertilizer P in acidic soils precipitates Al (variscite) and Fe phosphates or is chemisorbed by soil colloidal phases, mainly oxides of Al and Fe and clay minerals (Hardjowigeno, 2003). Three types of binding mechanisms are reported for Al-P or Fe-P:

1. Precipitation with water-soluble Al^{3+} and Fe^{3+} ions (Lindsay, 2001) (Equation 1.3 and Equation 1.4):

$$Al^{3+} + H_2PO_4^- + 2H_2O \rightarrow Al(OH)_2H_2PO_4 + 2H^+ \quad (1.3)$$

$$Fe^{3+} + H_2PO_4^- + 2H_2O \rightarrow Fe(OH)_2H_2PO_4 + 2H^+ \quad (1.4)$$

2. Adsorption on Al and Fe hydroxides

3. Adsorption by clay minerals (Equation 1.5):

$$(Al\ in\ crystal\ lattice) + H_2PO_4^- + 2H_2O \rightarrow 2H^+ + Al(OH)_2H_2PO_4 \quad (1.5)$$

One of the critical problems in acidic soils is low phosphorus utilization due to the precipitation of Al and Fe phosphates. Their solubility products severely decrease by as much as 100 times for each pH unit decrease (Lindsay, 2001). To increase the availability of P, therefore the fertility in these soils, liming must be practiced in a couple of years. This situation tremendously differentiates the phosphorus dynamics to a great extent due to both the transformations of phosphorus among different soil components during the neutralization and re-acidification periods (Tuyisenge, 2021). The displaced Fe and Al precipitate as hydroxides to form high affinity sorption sites, co-precipitation of P with ions, dissolution of variscite and strengite minerals during neutralization takes place, whereas the opposite reaction can occur in the re-acidification stage. The fertilization practices make the processes even more complex. Therefore, the sorption of P in the neutralization/re-acidification cycle should be investigated to better understand P dynamics and P availability in the post-liming period (Hardjowigeno, 2003).

Organic matter is used to increase the availability of phosphorus in acidic soils. Wong et al. (2000), investigated the effect of different organic matter on soil pH. Oxisol and were incubated with pruned saplings. An increase in pH and a decrease in varying Al content were observed during the first 14 days. This trend was reported to continue slowly for the next 42 days and then slightly decreased in the last 56 days. Soil pH increased from 4.1 to 6.8 in Ultisol and 4.8 to 5.8 in Oxisol. Ch'ng et al. (2014), used organic materials such as biochar and compost from chicken litter and pineapple leaves to improve phosphorus availability. Organic amendments increased soil pH and decreased exchangeable acidity, exchangeable aluminum, and exchangeable iron. Thus, total phosphorus, available phosphorus, inorganic phosphorus fractions, and organic phosphorus increased. Wong et al. (2000), explained that acid neutralization is due to complexation of protons and Al by organic anions. Al adsorption will result in low saturation, resulting in 3 moles of protons consumed for each mole of Al dissolved. Therefore, the dissolution of Al-bearing minerals by organic anions due to Al complexation will result in proton consumption and increase in pH.

According to molecular weight, organic acids are divided into low and high molecular weight organic acids (Adeleke et al., 2017). Examples of high molecular weight organic acids are humic acid and fulvic acid, and low molecular weight organic acids

are citric, oxalic, malic, succinic, malonic, and maleic acids. Low molecular weight organic acids generally have one to three carboxylic groups, while high molecular weight organic acids have more than three carboxylic groups. They are characterized by their molecular weight in Dalton (DA). High molecular weight has several hundred to million DA and low molecular weight ranges from 46 to 100. Therefore, it is more soluble than high molecular weight organic acid (Haynes & Mokolobate, 2001; Perminova et al., 2003; Jiang et al., 2012).

Research by Neswati et al. (2018), on using humic substances to increase phosphorus availability in Oxisol soils showed that using humic substances can improve soil chemical properties. However, it was reported that plant growth was still poor up to 900 ppm, so more doses are needed to have positive effect on plants. The research conducted by Paul et al. (2021), discussed the release of phosphorus from biochar from sewage sludge using citric acid. This research shows that phosphorus can be separated from Fe bonds in biochar using low molecular weight organic acids.

Using low molecular weight organic acids in red soil in Hubei province, China, reduced P bonds with Fe and Al (Hu et al., 2002). Low molecular organic acids represent a stable soil organic matter pool (Stevenson, 1994). Laboratory studies have shown that low molecular weight organic acids can dissolve heavy metals through complexation reactions (Hu et al., 2002).

Low molecular weight organic acids act as ligands and affect metal solubility and speciation through complexation reactions in solution and ligand exchange reactions on mineral surfaces (Fox, 1995). Naturally, low molecular weight organic acids are present in soils. According to Fox & Comerford (1990), organic acids are more complex in the rhizosphere than in the subsoil. The rhizosphere contains high oxalate concentrations and some citric, acetic, and aconic acids. Since oxalate forms stable complexes with aluminum, high oxalate concentrations may affect P availability in these soils.

In this context, the present study aims to investigate how citric, oxalic, and malic acids affect P adsorption in acid soils that have been calcified at different levels and incubated for 15 months. As a result of this study, basic information will be produced

that will contribute to the decision-making process in terms of environmental protection and phosphorus management processes in calcified acid soils by increasing P availability by imitating P-active plants without extra fertilization in deficiency situations or by reducing mobility in situations where high availability occurs. Due to its use, there is a need for research on the use of low molecular weight organic acids in the release of phosphorus in acidic soils, which has a practical effect on improving soil chemical properties, especially the presence of phosphorus.

1.2. Importance of Study

To maintain fertility in acidic soils and to eliminate the adverse effects of acidic conditions on plants, liming is required from time to time. Liming changes soil pH, which plays a crucial role in the availability of plant nutrients in soils within wide limits. This change occurs in the form of rising first and then falling again. This dramatically changes the dynamics of nutrients and the balance between them at both stages. Phosphorus, one of the most sensitive elements to pH changes, shows differences in its reactions with soil components under changing conditions. This increases or decreases the plant-available fraction over time, with a decrease posing risks for plant growth and increasing environmental risks.

On the other hand, changing pH causes significant changes in the decomposition dynamics of the organic matter present in the soil, which leads to changes in the effective concentrations of both low molecular weight humic and fulvic acids in the soil, which compete with P for adsorption. It has been reported that low molecular weight organic acids significantly affect P adsorption and solubility (Bolan et al., 1994), and even some plants in P-deficient areas can eliminate the adverse effects of P deficiency by secreting low molecular weight organic acids such as citric, ascorbic, and gallic acids. In this context, the present study aimed to investigate how citric, oxalic, and malic acids affect P adsorption in acid soils calcified at different levels and incubated for 15 months. As a result of this study, basic information will be produced that will contribute to the decision-making process in terms of environmental protection and phosphorus management processes in limed acid soils by increasing P availability by imitating P-active plants without extra fertilization in deficiency situations or by reducing mobility in situations where high availability occurs.

One of the critical problems in acidic soils is low phosphorus utilization due to Al and Fe phosphates. To increase the fertility of these soils, liming is applied from time to time. This situation changes the phosphorus dynamics to a great extent due to both the transitions between the phosphorus components existing in the soil and the re-acidification of the soil at the end of a certain time. The new surfaces formed in the process of re-acidification altered the phosphorus affinity and changed the usefulness of phosphorus supplied by fertilizer as a function of the degree of liming. Therefore, phosphorus adsorption mechanisms should be analyzed to understand the phosphorus dynamics and availability after liming. Studies on this subject are minimal worldwide in light of the current literature and have yet to be conducted in Turkey.

1.3. Study Objective and Hypothesis

This research evaluates how the change in phosphorus adsorption after calcification to 0%, 50%, 75%, and 100% of the lime requirement was changed and incubated for 15 months and applied with organic acids. This study aims to determine the effect of different doses of liming and low molecular weight organic acids on phosphorus adsorption in acid soils in the Black Sea Region of Turkey using Freudlich and Langmuir isotherms. The specific objectives of this study are:

1. To evaluate the effect of liming level and low-weight organic acids on phosphorus adsorption using the Freudlich isotherm with a regression method.
2. To better understand the effect of liming level and low-weight organic acids on phosphorus adsorption using the Langmuir isotherm with a regression method.
3. To investigate the co-effects of LMWOAc and liming level on the sorption behaviour of P on acidic soils

2. LITERATURE REVIEW

Bolan et al. (1994), studied the effects of low molecular weight organic acids on phosphate adsorption by soil and the solubility and plant uptake of P from soil pre-incubated with monocalcium phosphate and North Carolina phosphate rock. Acetic, formic, lactic (monocarboxylic), malic, tartaric, oxalic (dicarboxylic), and citric (tricarboxylic) acids were used in the study. The results showed that organic acids increased the availability of P in soils mainly through decreased P adsorption and increased the solubility of P compounds. Kpomblekou-A & Tabatai (2003), used low molecular weight organic acids to aid the release of phosphorus from rock phosphate applied to the soil. Based on the results, organic acids effectively removed phosphorus from low and medium reactive phosphate rocks. Organic acids have been shown to potentially increase available phosphorus for soils applied to phosphate rock. Moradi et al. (2012), investigated applying various low molecular weight organic acids such as citric, oxalic, and malic acids to various calcareous soils. According to the results, oxalic acid was the most effective organic acid for reducing P binding in calcareous soils. Oral (2013), investigated the effect of low molecular weight organic acid on the uptake of natural phosphorus in barley plants. This study used malic acid, oxalic acid, citric acid, acetic acid, ascorbic acid, and malic acid with doses between 0 – 30 mmol kg^{-1}, with an increase of each ten mmol kg^{-1}. Oxalic acid 30 mmol kg^{-1} showed the highest phosphorus concentration among other low molecular weight organic acids. In addition, the concentration of K and N elements increased with organic acid applications and no significant change was found in Cu or Fe elements. As a result, it was determined that the phosphorus utilization efficiency increased if applied with or without phosphorus fertilizer. Zhang et al. (2020), investigated the mechanism of phosphorus and potassium release from biochar by low molecular weight organic acids. Acetic acid suppressed P release from biochar, while tartaric and citric acid were found to favor P release.

Mihoub et al. (2017), conducted a study to increase phosphorus availability to plants using P applications (0, 10, 20, 30, 50, and 100 μg P m L^{-1} as KH_2PO_4) and low molecular weight organic acids (0.001 M citric and 0.001 M oxalite acid at 1.0 mM kg^{-1}) in calcareous soils of various textures. Using organic acids provided optimum plant growth with only 0.2 mg L^{-1} P addition. Citric acid was more effective than

oxalic acid. In conclusion, organic acids can help reduce the application rate of P fertilizer by reducing its adsorption in highly P-binding soils. Wang et al. (2016a), investigated the effects of oxalic, citric, and malic acids at ten mmol kg^{-1} on P adsorption in calcareous, neutral, and acidic soils. Doses of 0, 10, 20, 20, 30, 40, and 50 mg P L^{-1} were used for phosphorus applications. The results showed that the decrease of phosphorus adsorption caused by the ligand exchange and chelation of organic acid anion (LMOWAc) with Fe and Al minerals, and low molecular weight organic acid had a negligible effect on P adsorption in acid-strength, calcareous, neutral, and acidic soils. Feng (2012), studied the effect of citric, oxalic and acetic acids on the release properties of phosphorus in a soil-leaching experiment. The results showed that at an organic acid concentration of 5 mmol L^{-1}, citric acid, acetic acid, and oxalic acid were the most effective organic acids to activate phosphorus in soils. Wang (2016b), investigated the effects of oxalic acid, citric acid, and malic acid on P adsorption in black clay soils. According to the results, oxalic acid, citric acid, and malic acid at a ratio of 10 mmol kg^{-1} decreased Freundlich parameters Kf and n, representing the P adsorption capacity and energy.

Andrade et al. (2007), studied the effect of different organic acid sources, such as acetic acid, citric acid, and humic acid, and doses of organic acids on P uptake and dry matter production of maize plants grown in oxisols. Humic acid doses in the 0 – 12 g dm^{-3} range were equivalent to organic compost addition of 0 – 80 tonnes ha^{-1}. The effectiveness of organic acids in increasing P uptake and dry matter production of maize plants was followed by humic acids, citric acid, and acetic acid, respectively. Schmitt et al. (2018), investigated the formation of organic acid Fe-P complexes in laboratory and their effect on wheat plants (T. aestivum) grown under greenhouse conditions. The concentrations of the acids were 0.1356, 0.0678 and 0.0452 M for monocarboxylic acids (acetic acid), dicarboxylic acids (malic, tartaric, malonic, oxalic, and succinic acids) and tricarboxylic acids (citric acid), respectively. The number of organic acid-Fe-P complexes formed was found to vary between 5 – 42% of the P added. However, when these complexes were added to the soil, wheat growth was lower when more complexes were added. Therefore, it was shown that complex organic acid-Fe-P had little effect on the performance of wheat plants.

Gypser (2019), characterized the kinetics and mechanism of phosphorus desorption from Fe- and Al-hydroxides. Long-term desorption experiments (56 days) were carried out with $CaCl_2$, $CaSO_4$, citric acid, and humic acid. $CaCl_2$ and $CaSO_4$ were selected as general inorganic sorbents, and citric and humic acids as organic ligands. The concentration of organic ligands was used at 2 g L^{-1}. It was observed that cumulative phosphorus desorption increased following the order of $CaCl_2$, $CaSO_4$, humic acid and citric acid. In the study of Bulmer et al. (2018), citric acid concentrations were added to each of 0, 0.5, 1, 2, 3, 4, 5, 10, 25, and 50 mM citrate concentrations. The modification of Ca levels affected P adsorption and the adsorption equilibrium of citrate, P to the soil. Accordingly, the competitive adsorption of citrate and P is the primary interaction mechanism. Gaviglio et al. (2018), studied the effects of synthetic liquid extractants containing mixed citrate and oxalate on the efficiency of mineral-bound inorganic P extraction from flow particles. This study used a 2:1 (mM ratio) oxalate/citrate mixture and citrate reagent (15, 45, or 75 mM) as the best extractants for high P extraction yields. Extraction using oxalate and citrate (2:1) resulted in higher P solubility within the first 30 min and reduced environmentally harmful Fe-bound P, indicating a potential synergy between the two low molecular weight organic acids compared to citrate and oxalate alone. Johnson & Loeppert (2006), investigated the mechanism of organic acid-induced phosphorus mobilization from different oxide minerals. According to the results, most of the phosphorus was found at pH 4. The most effective organic ligands to release phosphorus were citrate 19% of the total adsorbed P, malate 14%, tartrate 5%, oxalate 0.3 – 1.2%, malonate, and succinate.

Wang et al. (2015), determined the concentrations and release rates of inorganic and organic phosphorus in calcareous, neutral, and acidic soils using oxalic acid, citric acid, and malic acid. This study used 10 mmol kg^{-1} low molecular weight organic acids. As a result, the cumulative organic phosphorus release was ranked as oxalic acid (0.63 – 3.17 mg kg^{-1}), citric acid (0.61 – 2.82 mg kg^{-1}), and malic acid (0.52 – 1.76 mg kg^{-1}). In contrast, oxalic acid was found to be most effective for increasing inorganic phosphorus release from HCl-Pi (Ca-Pi) fractions in lime soils. Furthermore, citric acid from NaOH-Pi (Fe/Al-Pi) fractions was the most effective in neutral and acidic soils. In Mendes et al. (2020), citric, gluconic, itaconic, malic, and oxalic were applied to increase soluble phosphorus from phosphate rocks, and P

solubility with organic acids was compared with sulfuric acid, the standard reagent applied in rock phosphate solubility for fertilizer production. Oxalic and sulphuric acids solubilized 100% of the P in all rock phosphates. However, oxalic acid was reported to be more effective than sulfuric acid. Each mmol of oxalic acid released 21 mg P, while sulfuric acid solubilized 14 mg P $mmol^{-1}$.

Zhu et al. (2021), used low molecular weight organic acids to increase phosphorus availability in topsoil and subsoil at four different elevations (2800 – 3500 m). The results showed that available phosphorus concentrations were higher in rhizosphere soils than in bulk soils, and the elevation trend was unaffected. The increase in available phosphorus concentrations in rhizosphere soils was significantly associated with low molecular weight organic acids, especially citric acid. Yang et al. (2019), investigated the potential effects of low molecular weight organic acids on inorganic phosphorus activation in black soil. Both oxalic and citric acids treated with 0 – 2.5 mmol L^{-1} concentrations and pH values were carefully selected. According to the results, the total amount of activating Pi increased as oxalic and citric acid concentrations increased. At a concentration $\leq$ 1.0 mmol L^{-1}, oxalic acid showed lower ability activating Pi than citric acid. At a concentration $\geq$ 1.5 mmol L^{-1}, higher ability of oxalic acid was found. The amount of total activator-Pi decreased with increasing pH of low molecular weight organic acids.

Harrold & Tabatabai (2006), investigated the effectiveness of low molecular weight organic acids in releasing inorganic phosphorus from soils. The study showed that, in general, di- and tricarboxylic acids were most effective in releasing P from two Iowa soils, whereas monocarboxylic, phenolic, and mineral acids released similar amounts of P. Oxalic, malonic, citric, or in some cases malic and tartaric acids were found to be the most effective in releasing inorganic P from the two surface soils studied. In a study of Fu & Wan (2021), up to 0.5 g of low weight organic acid (malonic acid) was used to determine phosphorus availability in calcareous soils. The study compared phosphorus fertilizers, phosphorus fertilizers, and malonic acid as treatment and controls (without phosphorus fertilizers). The results showed that phosphorus availability increased by 12.02% using malonic acid. The correlation of inorganic phosphorus in the soil, phosphorus binding by calcium was found to be low. In this case, using malonic acid increased phosphorus availability in calcareous soil.

3. MATERIAL AND METHOD

3.1. Material

3.1.1. Soil sampling location and descriptive informations

A total of 11 composite soil samples (0 – 20 cm) with different acidity levels were taken from the Black Sea region, Türkiye. Descriptive information about the soil samples is given in Table 3.1.

Table 3.1. Information about soil samples (Tuyisenge, 2021)

Soil name	Province	District	Village/Altitude	Land use/Crop
E1	Trabzon	Of	Cumapazarı, Mevkeli/Altitude 154 metre	45 years tea garden
E2	Trabzon	Of	Segmented Mevkeli (Sectional District)/Altitude 543 metre	60 years tea garden
E3	Trabzon	Dernek Pazarı	Altitude/697 metre	50 years tea garden
E4	Rize	-	-	Tea
E5	Rize	-	-	Tea
E7	Ordu	-	Hasbal	Hazelnut
E8	Ordu	-	Soğukluk	Hazelnut
E9	Ordu	Gürgentepe	Eskiköy District	Hazelnut
E10	Ordu	-	Avlo	Hazelnut
E11	Rize	-	-	Tea
E14	Artvin	-	-	Tea

3.1.2. General characteristics of region's soils

The Black Sea region is known for its high mountains and high-sloped lands, and it was classified into three soil classes (i.e., class I, class II and class III) in terms of land use characteristics of its soils (Çolak & Memişoğlu, 2018). The soils of the Black Sea region were mainly classified as alluvial and podzolic soils. In the high and steep mountains of the northeastern Black Sea region, podzols and alisols-acrisols covered an area of 2 498 952 ha, with 3.5% of those for agriculture (Özey, 2002). Acrisols are

a common soil type in Rize, Artvin, Trabzon, and Ordu provinces in the Black Sea region (Özcan et al., 2018). According to the World Reference Base Soil Classification System, the yellowish-red podzolic soils formed widely in the eastern part of the Black Sea region were classified as Alisols-Acrisols. Due to the significant amounts of Al minerals in the parent materials, the production of Al^{+3} from mineral hydrolysis occupied more than 50 exchange sites (Atalay, 1983). Podzolic soils in the Black Sea region were formed on clayey deposits in coastal areas. Thus, they have clay-loam and clay texture. In general, brown-coloured soils with low pH and high organic matter were dominant in the Black Sea region (Atalay, 1983). The soil from the Black Sea region is known as acid soil and tea and hazelnuts are widely grown (Özkutlu et al., 2015).

Ünal (1967), studied the correlation between the activities of soil enzymes and soil properties in the tea garden of Rize province. Based on this research, Rize had strongly acidic soils with a range of pH-KCl 3.47 – 4.97 and pH-H_2O 3.5 – 4.5. In addition, the pH of the surface soil was reported to be as low as 2.8 in the tea garden due to the continuous application of acid fertilizers. Based on Özkutlu et al. (2015) analysis, soil pH in a tea garden in Rize ranged from 3.49 to 5.01. Özyazıcı et al. (2013), studied red-yellow podzolic soils' basic characteristic properties and fertility conditions in the eastern black sea region. Based on the research, the soils in the eastern black sea region were classified as podzolic soils with pH ranging from 3.14 to 7.69, and 62.43% were firmly acidic below 4.5. In the other study of Özyazıcı et al. (2010), pH range of soil in a tea garden in Artvin and Rize was 2.80 – 5.97, and it was reported that 90% of the samples were as low as 4.5.

The amount of available phosphorus in soil can vary depending on various factors such as soil type, management practices, and previous fertilizer applications. Taşkın et al. (2015), analyzed the concentration of phosphorus in tea gardens in the East Black Sea Region, and the results showed that the available phosphorus ranged from 1.11 – 337.05 mg kg^{-1} with a mean of 45.49 mg kg^{-1}. Kahraman (2016), studied soil productivity in a hazelnut garden in Ordu district. The result showed that available P (Bray-Kurtz P) ranged from 0.3 mg kg^{-1} to 128 mg kg^{-1} and an average of 18.7 mg kg^{-1}. In another study, the range of available phosphorus in the Ordu district was 1.27 – 27.46 mg kg^{-1}. Bender-Özenç & Yazıcı (2022), studied soil properties under different

land uses in Trabzon, Black Sea region, and found that the amount of available phosphorus ranged from 0.96 – 138.7 mg kg^{-1}. However, intensive fertilization of tea soils after the 1960s (with 100-150 kg da^{-1} dose of 25-5-10 fertilizer) has significantly changed the phosphorus content of the soils in the last 60 years.

Sarımehmet & Müftoğlu (1993), studied the condition of organic matter in a tea garden in the eastern part of Black Sea, Türkiye. The soil samples were taken from different provinces, which were 1 182 soil samples from Rize, 186 samples from Artvin, and 309 samples from Ordu, Trabzon, and Giresun provinces. Based on the study, soil organic matter content in most areas of the eastern part of Black Sea was low. Despite low organic matter content, it was in a good range for the plant production. However, there were high soil organic matter in Ordu and Trabzon.

According to Ünal (1967), the organic matter content of soils in Rize increased until it reached a soil depth of 50 cm in the range of 1.21 – 6.33%. At a depth of 0 – 5 cm, the organic matter was up to 7%. Meanwhile, at a depth of 25 – 50 cm, the value decreased by about 0.65%. Özyazıcı et al. (2010), studied about the physical and chemical properties of tea grown soils in Rize and Artvin Provinces, based on the research organic matter at the depth of 20 cm ranging 0.66% – 14.91%. Gökçe (2019), assessed the soil properties in Hazelnut orchards on Central Black Sea Region and the result showed that organic matter on the study site ranged 1.71% – 14.5% with averange of 5.09%.

According to Ünal (1967), the lime requirement for 12 acid soil from a tea garden in Rize was 300 – 3 567 kg da^{-1}. The average lime requirement for most soils was 1 167 kg da^{-1}. There was a strong correlation between potential and actual acidity. In addition, there was a significant positive ($r = +0.910$) correlation between exchangeable basic cations and soil pH. On the other hand, there was a significant negative correlation ($r = -0.905$) between soil pH and exchangeable acid cations. The cation exchange capacity at a soil depth of 0 – 25 cm ranged from ±40 me/100 g to ±15 me/100 g. The exchangeable acidic cations at a depth of 0 – 50 cm were between 4 me/100 g – 25 me/100 g but mostly had a value of about 33 me/100 g. Acidic cations excluded about 16.6% – 85.7% of exchangeable cations, but most excluded 94.1%. Exchangeable basic cations ranged from 3.8 me/100 g to 27 me/100 g, with most soils

having a value above 10.4 me/100 g. The soil base saturation in Rize ranged between 14% – 83%. Some soils even had base saturation below 5.9%. However, most soils had a base saturation value of less than 50%. Calcium saturation was about 8.3% – 62%. In some cases, the value reached 0.3% at a soil depth of 0 – 50 cm. Based on the data above, the soil in Rize had poor replaceable calcium.

3.1.3. General characteristics of climate

At the end of 1985, the average annual temperature in Artvin, Ordu, Rize, and Trabzon provinces were 12.3 ºC, 13.9 ºC, 14.2 ºC, and 14.2 ºC. The annual average temperature of the Black Sea region varied between 6.9°C – 30.1°C. January was the coldest month and August was the hottest month in the Black Sea region. The temperature started increasing in June and was high until August. After that, it was getting down starting from September and decreased until February (Okman & Öztürk, 1987). Meanwhile, the annual average precipitation was between 250 and 2 500 mm. (Atalay, 1983). In the same year, the annual average rainfall in Artvin, Ordu, Rize, and Trabzon were 650.8 mm, 1177.1 mm, 2291.6 mm, and 803.1 mm (Okman & Öztürk, 1987). According to Atalay (1983), the highest precipitation in the Black Sea region occurred in December on 2.76 mm/day. On the other hand, the lowest amount was 1.46 mm/day in August. A study of 40 years of meteorological data reported that annual average precipitation was 2357 mm, average soil temperature at a depth of 20 cm was 15.2 ºC, average air temperature was 14.2 ºC, and average relative humidity was 78%. The relative humidity was typically between 40 and 60%. The most humid month is January, with average humidity of 74%. On the other hand, August was the driest month. However, the humidity in the Black Sea region can be categorized as high (Atalay, 1983).

3.2. Method

3.2.1. Taking soil samples and preliminary preparations

This study used 11 composite surface acid soil samples taken from the East Black Sea region: three soil samples from Trabzon, three from Rize, four from Ordu, and one from Artvin. The liming materials could be mixed into the soil layer at a depth of 15 –

20 cm (Brady & Ray, 2017). So, the composite soil sampling was taken from 0 – 20 cm depth of soil. The soil samples were air dried. Then, the samples were crashed and passed through 2 mm sieve size to get homogenous samples for soil caharacterization and incubation study.

3.2.2. Determination of chemical and physical properties of soils

Soil pH: The pH of the soil was measured by weighing 10 g of soil and adding it to water, 1 N KCl solution, and 0.01 M $CaCl_2$ solution at a ratio of 1:2.5 and then measuring each value using a calomel electrode in suspension (Thomas, 1996).

Potential (exchangeable) acidity: The exchangeable acidity consists of H^+, Al^{+3}, partially neutralized Al-OH complexes and organic acids retained on cation exchange surfaces. Exchangeable acidity was measured by transferring 2.5 g of the soil sample to a 100 mL flask after centrifuging it and adding 30 mL of 0.1 M $BaCl_2$. The final volume was finished with $BaCl_2$ after this procedure was repeated twice. In the presence of phenolphthalein, 25 mL of this solution and 0.1 M extraction solution were taken and titrated to pink color with 0.05 M NaOH. According to Equation (3.1), the amount of exchangeable acidity was calculated in cmol/kg (Hendershot et al., 2007).

$$\boldsymbol{Exchangeable\ acidity}\left(\frac{\boldsymbol{cmol}}{\boldsymbol{kg}}\right) = \frac{(\boldsymbol{Va}-\boldsymbol{Vb})\times\boldsymbol{M}(\boldsymbol{NaOH})\times\boldsymbol{100}\times\boldsymbol{V}}{\boldsymbol{g}\times\boldsymbol{Vs}} \qquad (3.1)$$

where Va: Volume of NaOH solution used in the titration of the sample (mL), Vb: Volume of NaOH solution spent for $BaCl_2$ solution (mL), M: Molarity of NaOH solution, V: Volume collected during extraction (mL), g: The amount of soil sample taken (g), Vs: Volume used in titration from extraction solution.

Electrical conductivity: The soil's electrical conductivity (EC) was measured by weighing 10 g of soil, mixing it with water at a ratio of 1:2.5, separating the slurry from the suspension, and then measuring the suspension with an EC meter (Thomas, 1996).

Organic matter and carbon content: To measure the soil's organic matter and carbon content, 0.5 g of air-dried, 0.5 mm sieved soil was added to 10 mL of a 1 N potassium dichromate solution in an erlenmeyer flask and 20 mL of concentrated H_2SO_4. $FeSO_4.7H_2O$ solution was employed following dichromate oxidation, and the concentration was determined by titration (i.e., a modified Walkley-Black method) (Nelson & Sommers, 1996).

Lime content: Hydrochloric acid and iron chloride were combined with 6 g of finely ground soil to dissolve the carbonates in the soil. The volume of CO_2 released was read from the calcimeter, and the amount of lime at standard pressure and temperature was calculated by Boyle-Mariotto's formula (Goh et al., 1993).

Lime requirement: Dunn and SMT methods were the most suitable for calcium carbonate incubation. For ease of application, the lime requirement of soils was determined by the Dunn method (Dunn, 1943).

Field capacity: Field capacity was assessed using a pressurized plate set (Klute, 1986).

Soil texture: Soil texture was determined by the hydrometer method (Gee & Bauder, 1989; Sheldrick & Wang, 1993).

Cation Exchange Capacity (CEC): CEC-base cations (Ca, Mg, K & Na) were determined by $BaCl_2$ method (Hendershot et al., 2007).

Available phosphorus: 1 g of soil was mixed with 7 mL NH_4-HCl solution to determine available phosphorus using the Bray-Kurtz method with a spectrophotometer (Kuo, 1996).

Extractable cations (Mg, Ca, K & Na): Soil exchangeable + soluble bases were extracted with 1M neutral NH_4OAc solution. Na, K, Ca, and Mg in the solution were determined by atomic absorption spectrometry (Summer & Miller, 1996).

DTPA-extractable Fe, Zn, Cu, and Mn: DTPA-extractable Zn, Fe, Cu, and Mn were determined by AAS (Lindsay & Norwell, 1978).

Total P, Fe, Al, Mn, Ca and Mg: Total P, Fe, Al, Mn, Ca and Mg in soil were determined by burning the sample with HNO_3 + $HClO_4$ mixture using AAS. According to the method of Murphy & Riley (1962), total P concentration was determined at a wavelength of 880 nm in a spectrophotometer by colouring with ascorbic acid.

3.2.3. The liming incubation

After determining the lime requirement of the soils, analytical $CaCO_3$ was added to the soils at 0% (control), 50%, 75%, and 100% of the lime requirement on 150 g of soil. Soil samples were incubated 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 to the samples. After, the soil samples were air dried or dried in an oven at 40°C and homogenized in a porcelain mortar to adsorption study.

3.2.4. Determination of phosphorus adsorption

Fine soil samples (dried and shrieved) were used in phosphorus adsorption analysis. Soil samples were weighted 1 g for each sample. Then 20 mL of 0.01 M $CaCl_2$ containing 0, 5, 10, 20, 30, 40 and 60 mg L^{-1} P was added to each sample. This study used low molecular weight organic acids (oxalic, citric, and malic acid) as treatment. Next step, the organic acids were added to the phosphorus solution at a rate of 10 mmol kg^{-1} in 0.01 M $CaCl_2$ background solution. After the soil samples reached an equilibrium at a constant temperature of 20±2°C for 24 hour, the soil solution was separated by centrifulation at 3000 rpm for 10 minutes. The extracts were then filtered through Whatman No. 42 filter paper in the last step. The extracts were subjected to analysis of pH and phosphorus concentration. The soil pH was analyzed with a pH meter and the phosphorus concentration was analyzed using a spectrophotometer at 880 nm wavelength with the modified ascorbic acid method (Murphy & Riley, 1962).

According to Equation (3.2), the adsorbed numbers of phosphorus were calculated from the difference between the initial concentration and the equilibrium concentration;

$$Qe = \frac{(Ci - Ce) \times V}{W} \quad (3.2)$$

where Qe is the amount of adsorbed (mg kg^{-1}), Ci is the initial concentration of P (mg L^{-1}), Ce is the equilibrium concentration of P (mg L^{-1}), V is the volume of solution (L), and W is the weight of soil sample (g).

3.2.5. Evaluation of adsorption data

The suitability of the obtained data to Langmuir and Freundlich adsorption models was tested by regression analysis. The adsorption Langmuir models used in the research are given by Equation (3.3) below:

$$\frac{Ce}{Q} = \frac{Ce}{q} + \frac{1}{b \times Qmax} \quad (3.3)$$

where Ce is equilibrium concentration (mg L^{-1}), Q is the number of ions adsorbed by the soil (mg L^{-1}), b and q are coefficients related to binding energy and maximum adsorption, $\frac{Ce}{q}$ is maximum adsorption (Qmax).

Based on the Equation (3.4), the Freundlich isotherm given as Qe = Kf.Ce can be converted to linear on a log basis as follows:

$$\log(Qe) = \log Kf + n \log Ce \quad (3.4)$$

where Qe is the number of ions adsorbed by soil (mg L^{-1}), Ce is the equilibrium concentration (mg L^{-1}), Kf and n are the coefficients.

The modified CHB SSSAJ spreadsheet program was used for predicting the adsorption isotherm parameters (Bolster & Hornberger, 2007).

3.2.6. Evaluation of results and statistical analysis

The data without a normal distribution (skewness value > 2*standard error of skewness) were approximated to the normal distribution as a result of the primary descriptive statistical analyses performed on the descriptive properties of the soils and adsorption parameters (Berkman & Reise, 2012). After that, the conventional correlation relationships between soil properties and adsorption parameters were investigated. In addition, the effects of liming levels and organic acids on P adsorption parameters of Freudlich and Langmuir isotherms were tested by ANOVA analysis in completely randomised design with factorial arrangement (11 soil samples x 4 liming levels x 4 organic acids). The main effect treatments were separated by Duncan's multiple range test at $p<0.05$.

4. RESULTS AND DISCUSSIONS

4.1. Descriptive Characteristics of Soils and Their Relationships

Tables 4.1 and Table 4.2 provide some descriptive physical and chemical analyzes of the test soils. The pH of the experimental soils (1:2.5) ranged from very strongly acidic to slightly acidic and varied between 3.47 and 6.30. Different measurement techniques yielded varying results for the level of acidity but the general hierarchy was observed to be pH-H_2O > pH-$CaCl_2$ > pH-KCl. The character of perennial tea gardens was generally found to be more acidic. The average potential acidity, another measure of soil acidity, was 14.65 cmol kg^{-1} and was found to vary between 2.16 and 33.07 cmol kg^{-1}. This is an indication of how serious the acidification problem of soils is. It was determined that the potential acidity was very high, especially in soils with pH < 4. The potential acidity of the soils was found to be related to lime requirement, pH-$CaCl_2$, pH-H_2O, sand, pH-CaCl, and total Ca properties in descending order (Tuyisenge, 2021). The lime content of the soils is negligible due to strong acidity of soils. In this context, there is no lime (<0.05%) in the soils except for the figures that can be explained by the error in the analysis measurements in technical terms. There is no salinity problem in the soil. Salinity level varies between 417 – 43.3 μS m^{-1}, and the average is 146.2 μS m^{-1}. Interestingly, EC showed a significant relationship with the concentration of soluble P, indicating that soluble P is the dominant ion in these soils or the availability of mildly acidic soils which have higher EC and P availability.

The average organic carbon content of the soils was 2.71% and the maximum and minimum values were 5.78% and 0.91%, respectively. There is a tendency for low organic matter in soils with high silt content. This is thought to result from silt being the secondary dominant texture fraction. Clay minerals and organic matter are generally protected against mineralization by forming organomineral compounds (Usta, 1995). As the silt fraction increases, these components are formed in relatively lower amounts, and organic matter becomes susceptible to weathering and/or washing. Among the water retention characteristics of the soils, field capacity varied between 0.478 – 0.235 g g^{-1} with an average of 0.360 g g^{-1}; wilting point varied between 0.382 – 0.108 g g^{-1} with an average of 0.25 g g^{-1}. These properties were correlated with total Mg, Fe, Cu, and Na contents. Mg, Fe, and Na are the elements that indicate the degree

of decomposition (Usta, 1995). Increasing amounts of Mg and Na indicate that decomposition is relatively low, while Fe indicates that decomposition is advanced. In both cases there is an increase in water retention properties. The relationship with copper is thought to be more indirect. Because in cases where Fe is high, Cu, both originating from the parent material and subsequently added by agricultural activities, is usually strongly retained by Fe oxides (Uygur et al., 2017a; Tuyisenge, 2021).

Among the textural fractions of the soils, clay varies between 67.7% and 27.9% with an average of 40.7%; silt varies between 34.2% and 21.0% with an average of 25.1%; and sand varies between 49.2% and 12.7% with an average of 34.2%. Soils are located in different clay and loam texture classes. The main reason for this difference is that soil-forming factors vary for each sampling point. The sand fraction was highly correlated with PA and clay. Moreover, the clay fraction was highly correlated with useful phosphorus. While the relationships other than clay-available phosphorus are due to the systematics in the analysis process, this relationship indicates that the available phosphorus in the soil is mostly retained on the clay surfaces. This is because P availability in acidic soils is generally limited to a great extent by the formation of Al-P and Fe-P solid phases (Lindsay, 2001; Uygur & Karabatak, 2009). It was determined that the available P concentrations of the soils varied between 2.11 and 196.8 mg kg^{-1} with an average of 47.6 mg kg^{-1}. Regarding P content, E4 and E6 were classified as very low, E8 and 11 as low, E5 and E7 as sufficient, and the others as high (Kacar et al., 1987). These values show that the phosphorus content of the soils increased due to fertilization in the region. The ratio of fractions with highly availabile increases more rapidly upon fertilization practices (Uygur et al., 2017b).

Total Cu concentrations of the soils were found to vary between 63 mg kg^{-1} and 713 mg kg^{-1} with an average of 435 mg kg^{-1}. Total Cu was reported as 5 – 30 mg kg^{-1} in acid soils and 7 – 70 mg kg^{-1} in podzolic soils, which are typically expected in the study area (Kabata-Pendias, 2011), and the values in the experimental soils are much higher than this average except for one soil. This shows Cu problem in the soils which has reached different pollution levels. Cu concentration had significant positive correlations with field capacity, wilting point, Mn, Fe, Zn, and Mg. Field capacity, wilting point, and Mg are elements of clay mineralogy, while Fe and Mn indicate the accumulation of oxide fractions in soils. However, the solid relationship with Zn

indicates that these two elements may have been added to the soil from similar sources, most likely by phosphorus fertilization (Uygur et al., 2018). It was determined that the total Mn concentrations of the soils varied between 1 559 – 13 015 mg kg^{-1} with an average of 6 154 mg kg^{-1}. In podzolic soils, it was reported as 50 – 9 200 mg kg^{-1} (Kabata-Pendias, 2011), and the values in the study soils showed a concentration around the upper limit. Mn concentration has a significant positive correlation with Cu, Zn, Ca, and Mg. There was an addition from a similar source except for Mg (Tuyisenge, 2021). In this context, superphosphate fertilizers contain these components. The correlation with Mg is due to the parent material since the formation of olivine minerals is quite common in the region. Typically, olivine is present in the form of Mg and Fe silicates, but in some cases, it can also be present in Ca, Mn, or Ni. This partly explains the more robust relationship between Mg and Mn.

The total Fe concentrations of soils vary in a narrow range between 24 837 and 26 888 mg kg^{-1} with an average of 26 326 mg kg^{-1}. Fe concentration in soils varies within a range of 7 000 – 500 000 mg kg^{-1} (Lindsay, 2001). Fe concentration has significant positive correlations with field capacity, wilting point, and Zn among soil properties (Tuyisenge, 2021). The high correlation with Zn may result from Fe oxides adsorbing predominantly zinc added later (Uygur et al., 2017c). The total Ca concentrations of the soils varied between 3 050 and 13 927 mg kg^{-1} with an average of 6 220 mg kg^{-1}. Since Ca is relatively highly leached in acidic soils, Ca content decreases over time as a function of the parent material, depending on the progress of weathering. These are relatively low values compared to regular soil averages (13 700 mg kg^{-1}) (Lindsay, 2001). Total Ca was positively correlated with pH, Mn, and Mg and negatively correlated with lime requirement and potential acidity (Tuyisenge, 2021). All parameters are a function of the degree of soil weathering and the parent material composition.

The total Mg concentrations of the soils varied between 507 and 3 090 mg kg^{-1} with an average of 1 621 mg kg^{-1}. Since basic cations such as Mg are relatively more washed out in acidic soils, the amount of Mg decreases over time due to the progress of decomposition. These are relatively low values compared to regular soil averages (Lindsay, 2001). Based on results on Tuyisenge (2021)'s study, total Mg gave high positive correlation coefficients with field capacity, wilting point, Cu, Mn, and Ca.

The relationship between field capacity and wilting point is based on clay mineralogy. Because higher Mg causes a relatively higher formation of montmorillonite-type clays (Usta, 1995; Brady & Ray, 2017), this increases field capacity and wilting point. The relationships with other elements result from the parent material character and chemical composition. Because elements such as Mn and Cu, which have a relatively low tendency to wash away accumulate in the soil (Usta, 1995). Total Na concentrations of the soils vary between 1 085 and 3 904 mg kg^{-1} with an average of 1 826 mg kg^{-1}. Na, one of the most easily washed elements during soil formation, shows a decrease in Na content due to the progress of decomposition over time. Na concentrations are deficient compared to regular soil averages (Lindsay, 2001). Total Na gave high positive correlation coefficients with field capacity and wilting point. Since higher amounts of Na indicate higher amounts of 2:1 type clays, field capacity and wilting point were considered higher in soils with high Na content (Tuyisenge, 2021).

Table 4.1. Some physical and chemical properties of the experimental soils (Tuyisenge, 2021)

Soil	pH (1:2.5)			PA[1] (cmol kg^{-1})	EC ($\mu S\ m^{-1}$)	OC[2] (%)	$CaCO_3$ (%)	LR[3] (g kg^{-1})	Humidity characteristics (g g^{-1})		Texture			USDA soil texture class	CEC[4]-Base cations (cmol kg^{-1})
	H_2O	KCl	$CaCl_2$						FC	WP	Clay (%)	Silt (%)	Sandy (%)		
E1	3.81	3.47	3.52	29.95	216.3	4.27	0.031	22.6	0.397	0.305	67.7	19.6	12.7	Clay	5.01
E2	4.21	3.34	3.72	25.47	167.3	1.01	0.038	15.1	0.365	0.266	37.4	34.2	28.4	Clay loam	16.97
E3	5.97	5.31	5.75	4.05	417.0	5.78	0.034	6.95	0.478	0.382	32.1	23.0	44.9	Sandy clay loam	50.92
E4	4.02	3.62	3.78	33.07	124.0	2.42	0.002	20.5	0.377	0.307	45.7	26.9	27.4	Clay	4.53
E5	3.84	3.46	3.66	21.87	235.0	2.45	0.025	12.2	0.320	0.215	37.4	26.0	36.6	Clay loam	5.36
E7	5.12	4.08	4.77	8.96	43.3	0.91	0.009	4.59	0.400	0.314	46.1	25.7	28.2	Clay	33.14
E8	4.11	3.97	4.00	10.83	48.7	3.92	0.020	9.68	0.330	0.212	42.3	21.0	36.8	Clay	3.83
E9	4.29	3.89	4.03	10.56	52.7	1.69	0.002	7.70	0.326	0.207	40.0	26.4	33.6	Clay	5.53
E10	4.76	4.10	4.48	4.51	63.3	1.51	0.022	6.13	0.295	0.200	38.0	24.4	37.6	Clay loam	11.52
E11	4.08	3.18	3.83	9.79	157.7	3.05	0.025	8.88	0.235	0.108	27.9	22.9	49.2	Sandy clay loam	8.45
E14	6.30	5.14	5.72	2.16	83.3	2.81	0.052	1.74	0.384	0.249	33.8	26.0	40.2	Clay loam	18.16
Average	4.59	3.96	4.30	14.66	146.2	2.71	0.02	10.55	0.360	0.250	40.7	25.1	34.2	-	14.86

[1]Potential acid, [2]Organic carbon, [3]Liming requirement, [4]Cation exchange capacity

Table 4.2. Some chemical properties of the experimental soils (Tuyisenge, 2021)

Soil	Available P (mg kg^{-1})	Exchangeable base cations (cmol kg^{-1})				DTPA-Me[1] (mg kg^{-1})				Total element concentration (mg kg^{-1})						
		Ca	Mg	K	Na	Cu	Mn	Fe	Zn	Cu	Mn	Fe	Zn	Ca	Mg	Na
E1	28.8	0.78	0.09	0.62	0.12	0.64	12.3	166	2.07	474	1 559	26 774	784	3 567	1 083	1 404
E2	97.6	9.60	1.11	2.88	0.11	3.75	755	276	65.4	629	11 486	26 852	2 161	6 290	2 433	1 851
E3	196.8	33.12	3.68	2.55	0.17	13.9	151	236	75.1	713	13 015	26 888	1 920	13 927	3 017	1 980
E4	3.23	0.98	0.16	0.85	0.12	0.33	113	32.2	0.94	506	9 962	26 913	1 097	3 943	2 173	1 839
E5	17.2	1.46	0.15	0.68	0.12	2.11	19.5	524	5.39	171	2 696	24 837	366	4 183	507	1 789
E7	2.11	19.58	2.48	0.71	0.28	0.76	38.7	69.8	0.77	336	6 829	26 280	535	9 097	3 090	3 904
E8	13.7	0.71	0.07	0.27	0.12	2.71	7.51	201	1.26	505	3 231	26 695	807	3 050	610	2 393
E9	10.9	1.72	0.10	0.26	0.16	5.48	13.5	544	2.94	310	2 475	26 499	737	4 443	603	1 382
E10	44.8	5.97	0.31	0.31	0.15	8.78	40.1	467	8.13	314	3 492	26 200	691	4 540	557	1 085
E11	102.0	4.35	0.42	0.17	0.20	3.10	118	930	5.78	63	3 783	25 158	393	8 223	1 363	1 109
E14	6.67	11.28	1.63	0.88	0.19	18.1	80.8	103	19.1	766	9 168	26 484	1 267	7 160	2 393	1 460
Average	47.6	8.14	0.93	0.92	0.16	5.42	123	323	17.0	435	6 154	26 326	978	6 220	1 621	1 836

[1]DTPA-extractable element

4.2. Effect of The Liming Ratio and Organic Acids with Freundlich Isotherm

4.2.1. Liming effect

The P sorption data of the incubated soils were subjected to the linear form of the Freundlich adsorption isotherm model. Figure 4.1 and Figure 4.2 shows the adsorption isotherms along with model parameters of E1 and E2 soil. The determination coefficient of the regression models for E1 soil ranged from 0.936 – 0.950 and for E2 soil ranged from 0.956 – 0.967 with different liming levels, which means that the n and Kf values obtained are highly acceptable. Therefore, the experimental sorption data confirmed the Freundlich equation.

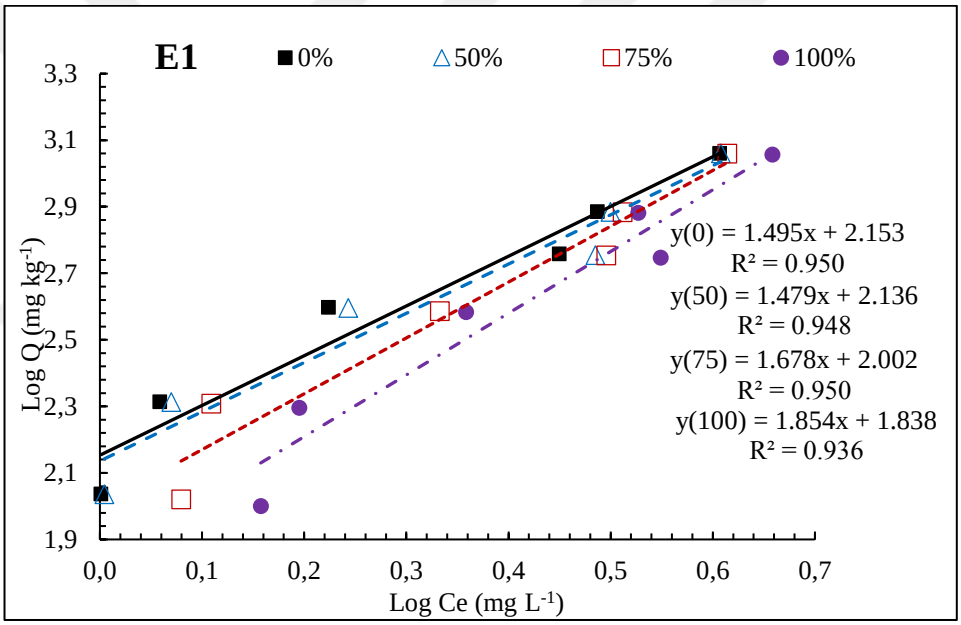

Figure 4.1. Linear Freundlich isotherms of E1 soil treated with differing lime requirements

Freundlich exponent (n) is a parameter that characterizes the affinity of surfaces to phosphorus. The range of n parameter of E1 soil was 1.495 – 1.855 and there was an decrease as a function of increasing liming levels. Meanwhile, the E2 soil has an n value greater than one, which ranged from 1.256 – 1.652. The decreases in the slope of sorption isotherms toward 3 mg L^{-1} initial concentration and the subsequent increase in the slope reflects the heterogeneity of the adsorption sites and/or mechanisms on the soil surface. Liming with different levels significantly affected the sorption parameters. This indicated that there was an increased solubility of indigenous P,

which increased in the equilibrium concentration of $CaCl_2$ background with no additional P. This also shows stronger adsorption at lower solute concentrations for the lower levels of liming practices (Zhang et al., 2014).

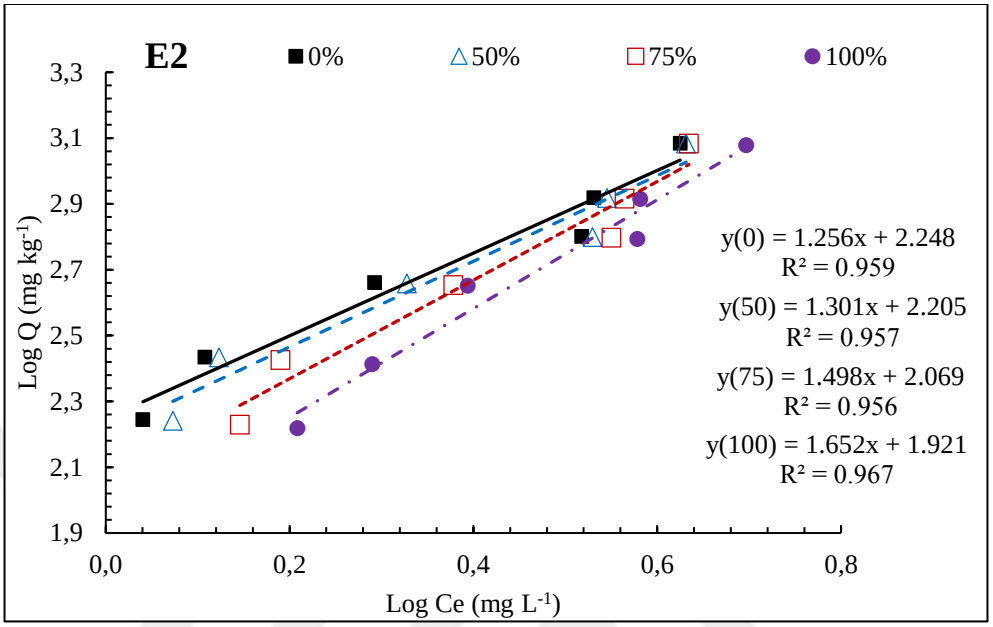

Figure 4.2. Linear Freundlich isotherms of E2 soil treated with differing lime requirements

The Freundlich constant, or Kf, was related to the adsorption capacity of the soil. A higher value of K indicates a higher adsorption capacity, implying that the adsorbent has a greater affinity for the adsorbate. In soil E1, the Kf value varied between 2.153 – 1.838 mg kg^{-1} indicating a 142 – 68.9 mg kg^{-1} P at "0" equilibrium concentration. The value of Kf ranged from 1.921 – 2.248 mg kg^{-1}. The increasing level of liming apparently decreased the log Kf value. Therefore, the soil exerted a smaller affinity to P upon liming. This behaviour enabled indigenous and/or fertilizer P in plant available fractions (Sui & Thompson, 2000; Jiao et al., 2007).

According Figure 4.3 and Figure 4.4, the E3 and E4 soil formed a linear line in the regression analysis for phosphorus adsorption using Freundlich isotherm with a constant of determination ranging from 0.935 – 0.972 for E3 and 0.932 – 0.973 for E4. These values suggested that the variables in the regression model had a fairly consistent connection, indicating that the n and Kf values met the required criteria. There was a sharp adsorption rate at low concentrations and weakened at concentrations above 4 mg L^{-1} in soil E3. This also indicates a relatively weak

interaction between the adsorbate molecules as the n value increases with the increase in the liming level and it varied between 1.049 – 1.279.

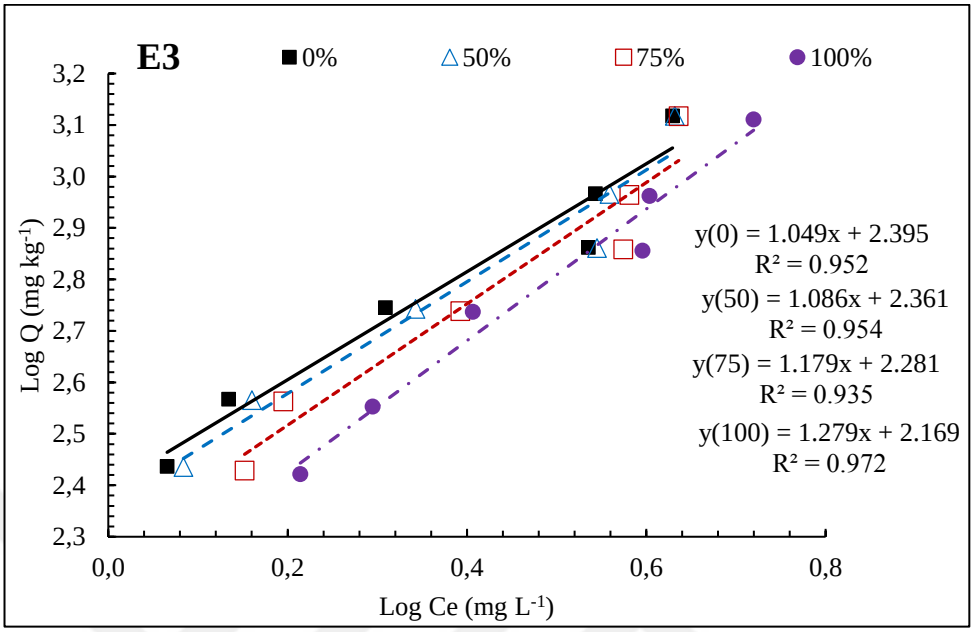

Figure 4.3. Linear Freundlich isotherms of E3 soil treated with differing lime requirements

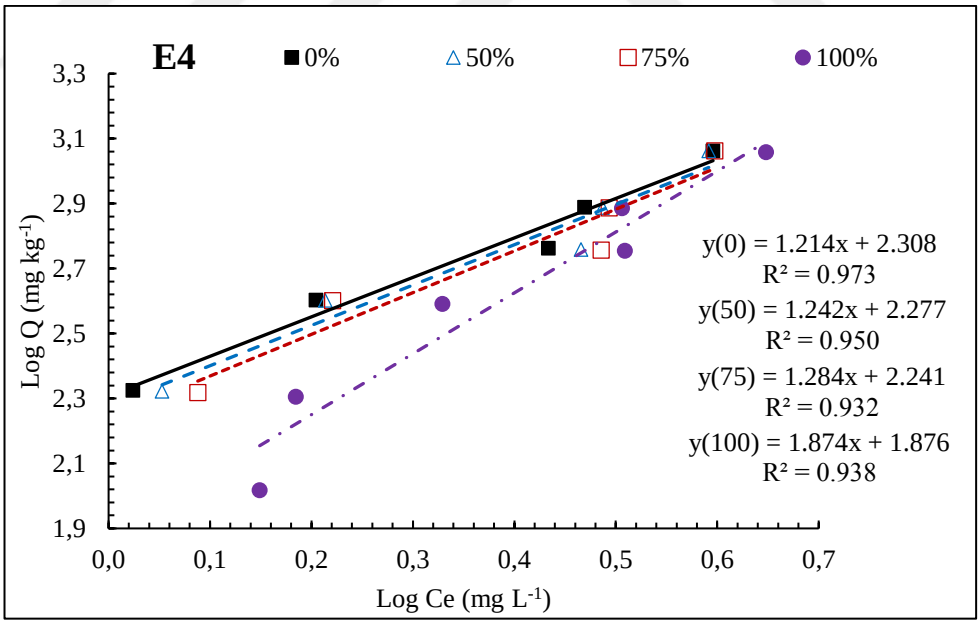

Figure 4.4. Linear Freundlich isotherms of E4 soil treated with differing lime requirements

Freundlich exponent values of E4 soil as the increase of liming ratio were 1.214, 1.241, 1.284, and 1.874. The interaction among adsorbate molecules is more robust compared to the interaction between adsorbate and adsorbent. In such situations, the adsorption of molecules starts off at a gradual pace until there is enough surface coverage, at

which point the interactions between adsorbed and unadsorbed molecules start to take precedence in the process (Myers, 1999). Precipitation of Ca phosphate minerals occurs as the soil solution becomes saturated, which is dissolved P and Ca^{2+} (Hughes et al., 2000; Penn & James, 2019). The Freundlich constant showed that the adsorption capacity of E3 and E4 soils decreases as the liming dose increases. Kf values ranged from 2.169 – 2.395 mg kg^{-1} for E3 and 2.308 – 1.875 mg kg^{-1} for E4. The Kf value at 100% liming showed the lowest value indicating that the intervention of native phosphorus in the soil led to a lower number of molecules that could be adsorbed. Liming impacts on increasing soil pH, which affects phosphorus sorption (Qayyum et al., 2015; Simonsson et al., 2018; Yang et al., 2019).

Based on Figure 4.5 and Figure 4.6, the coefficient of determination or R-squared of regression analysis of phosphorus adsorption on E5 and E7 soil with Freundlich isotherm ranged from 0.926 – 0.969 and 0.923 – 0.976. Values close to 1 means that the results of regression analysis were acceptable. The values of n in E5 and E7 ranged between 1.278 – 1.944 and 1.367 – 2.065. Freundlich exponent (n) values was greater than 1 and it increases as the increase of liming ratio. In both soils, there was a possibility of Ca-P precipitation at concentrations between 5 - 6 mg L^{-1}.

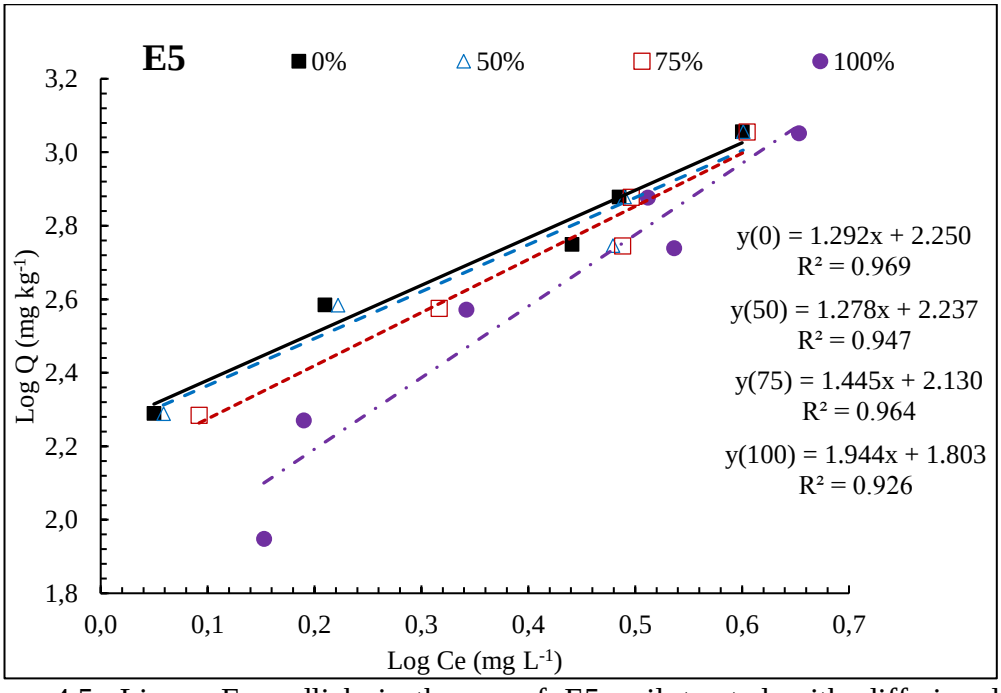

Figure 4.5. Linear Freundlich isotherms of E5 soil treated with differing lime requirements

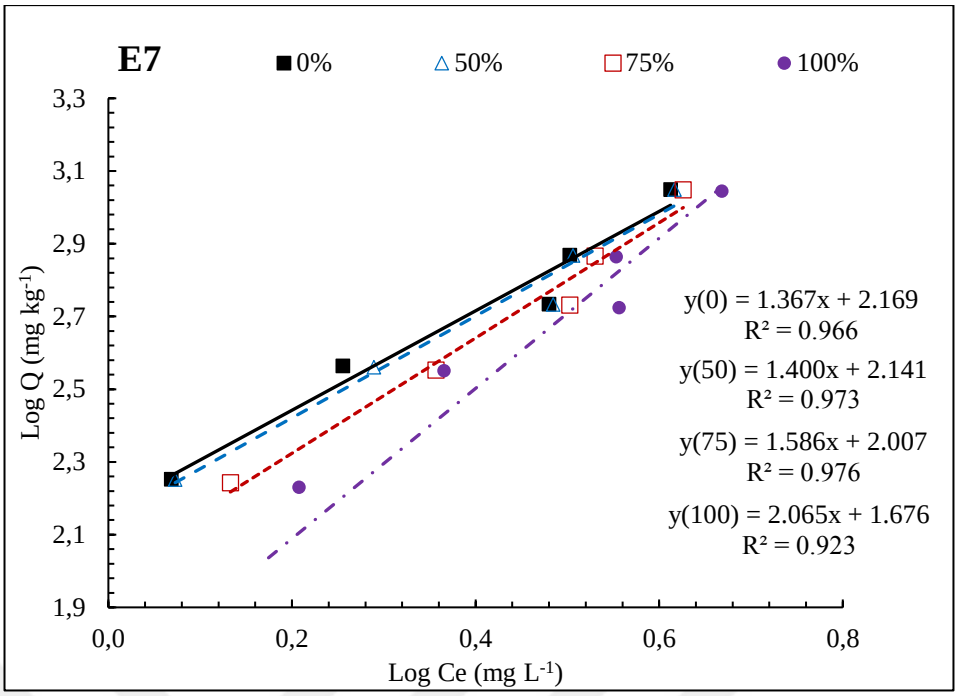

Figure 4.6. Linear Freundlich isotherms of E7 soil treated with differing lime requirements

The Kf values in E5 soil were 2.250 mg kg^{-1}, 2.237 mg kg^{-1}, 2.130 mg kg^{-1}, and 1.803 mg kg^{-1} and E7 soil were 1.676 mg kg^{-1}, 2.007 mg kg^{-1}, 2.141 mg kg^{-1}, and 2.169 mg kg^{-1}. The Kf value decreases as the liming level increases. Based on these results, there was an effect of native phosphorus from soils to the phosphorus adsorption. As the indigenous phosphorus increases, the adsorption decreases. However, liming, especially at a dose of 100%, had the lowest value of Kf, indicates that phosphorus could be more available for plants due to liming application (Qayyum et al., 2015; Simonsson et al., 2018; Yang et al., 2019).

Based on the regression analysis results shown in Figure 4.7 and Figure 4.8, the determination correlation of E8 varied between 0.935 to 0.973 and E9 ranged from 0.950 to 0.966. The phosphorus adsorption of the soils confirmed to be a linear regression curve using the Freundlich isotherm and the outcomes of the analysis were appropriate. The exponent coefficient (n) in E8 soil were 1.345, 1.365, 1.553, and 2.079 and in E9 soil were 1.332, 1.372, 1.660, and 2.246 at liming levels of 0%, 50%, 75%, and 100%, respectively. The increasing n values indicated a growing ion-ion interaction, leading to a weaker binding of phosphorus to the soil. As a result, the application of lime had a beneficial effect on enhancing the availability of phosphorus

in the soils (Shafqat & Pierzynski, 2014). In the meantime, as the liming level increases, the Kf value decreases.

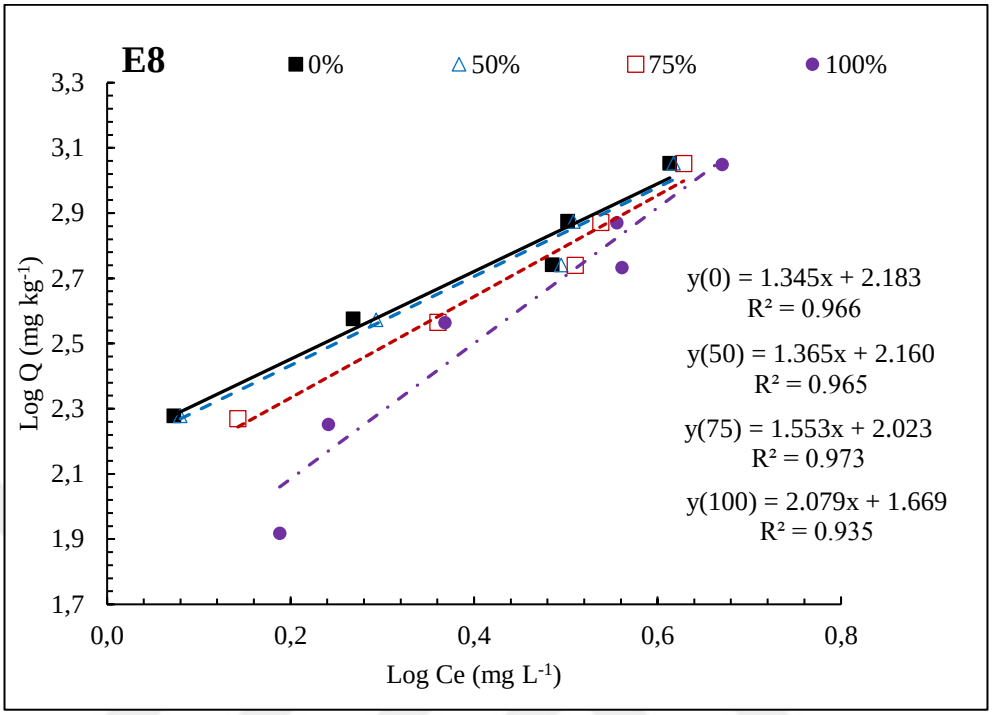

Figure 4.7. Linear Freundlich isotherms of E8 soil treated with differing lime requirements

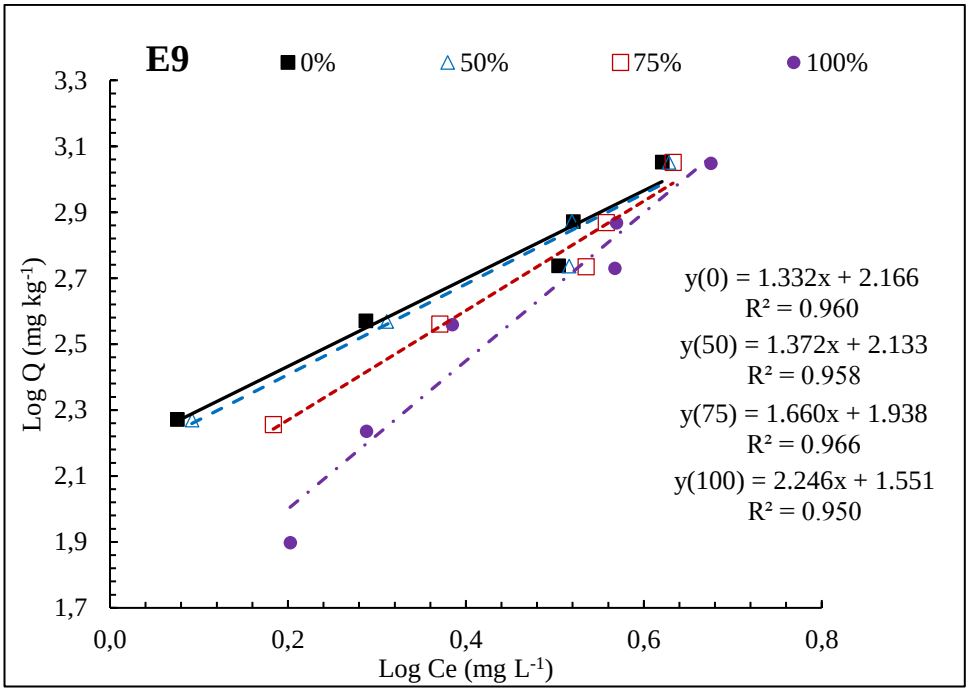

Figure 4.8. Linear Freundlich isotherms of E9 soil treated with differing lime requirements

The adsorption capacity (Kf) values in E8 soil varied between 2.183 – 1.669 mg kg^{-1} and E9 soil ranged from 1.551 – 2.166 mg kg^{-1}. According to the results, there was a reduction in the interactions between phosphorus and the soil. Consequently, with increased liming, the soil's ability to capture and hold onto phosphorus decreases, potentially resulting in increased phosphorus availability (Hughes et al., 2000). However, liming significantly impacted the phosphorus adsorption, particularly at a dosage of 100%.

The results of phosphorus adsorption on E10 and E11 soil using the Freundlich equation are shown in Figure 4.9 and Figure 4.10. According to linear regression, the n and Kf values obtained are acceptable because the R-Squared of soil E10 and E11 ranged from 0.949 – 0.970 and 0.953 – 0.967. This shows that the Freundlich isotherm can describe the adsorption of phosphorus on E10 and E11 soil adequately. The exponent coefficient (n) values of E10 ranged from 1.265 – 1.932 and E11 ranged between 1.110 – 1.669. The type of isotherm formed can be classified as a blend of type III and V isotherms, where the affinity energy of the surface sites decreases while the intermolecular bonding increases (Myers, 1999). In this case, phosphorus and calcium precipitation from liming occurred at a concentration point of 5 – 6 mg L^{-1}. Kf values varied between 2.238 to 1.771 mg kg^{-1} for E10 and 2.347 to 1.945 mg kg^{-1} for E11. As liming levels rise, the Kf value in E10 soil declines.

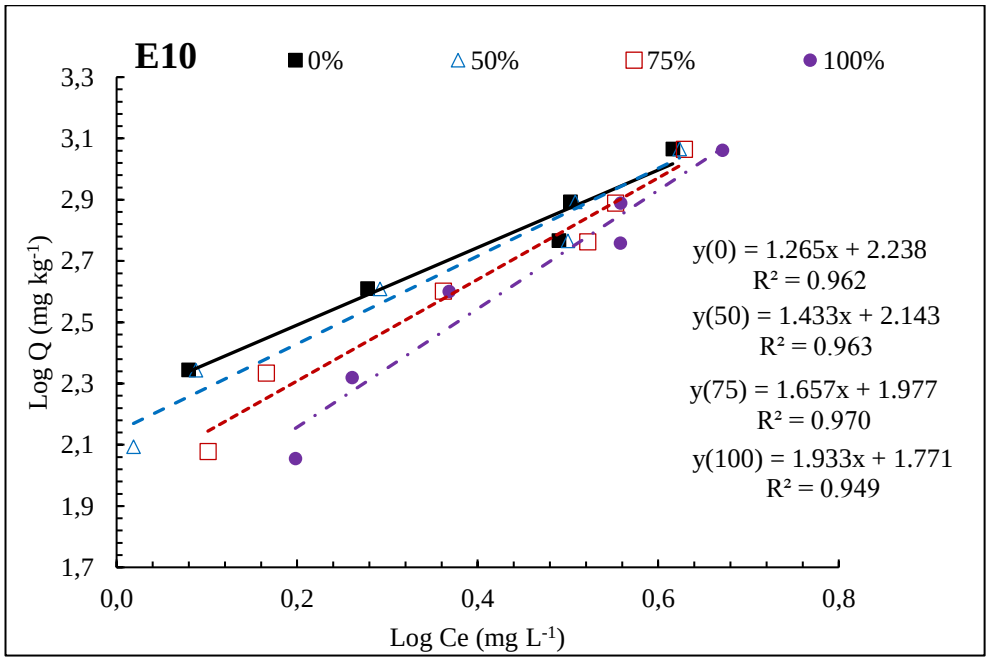

Figure 4.9. Linear Freundlich isotherms of E10 soil treated with differing lime requirements

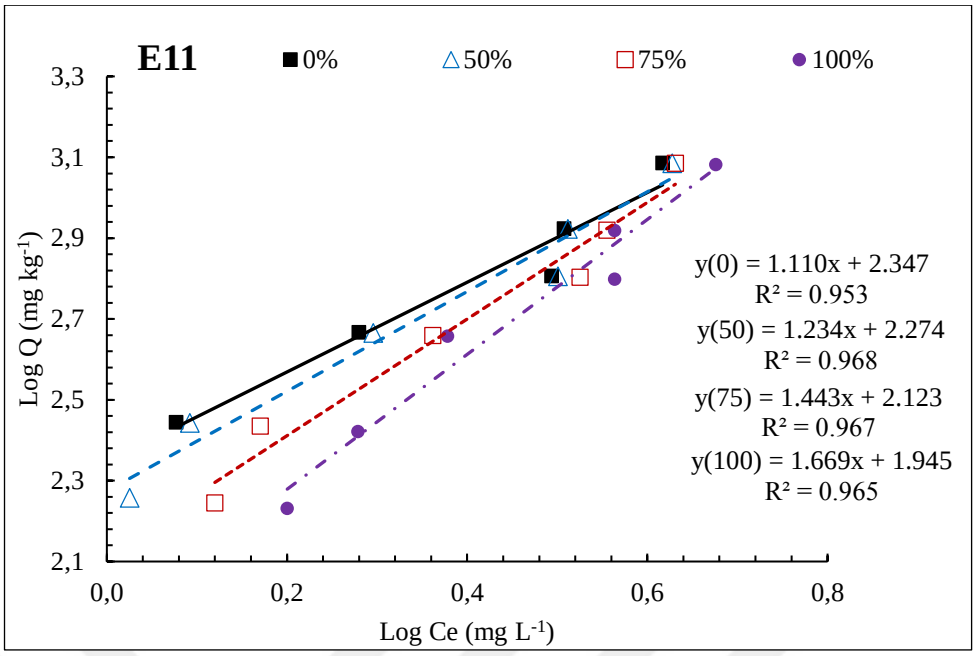

Figure 4.10. Linear Freundlich isotherms of E11 soil treated with differing lime requirements

Increased liming could increase the opportunity for phosphorus to become available in the soil. In this case, tillage with excessive P fertilizer application had been done for a long time. This impacts study's results, which made the indigenous phosphorus affects the rate of adsorption (Shafqat & Pierzynski, 2014; Qayyum et al., 2015; Simonsson et al., 2018).

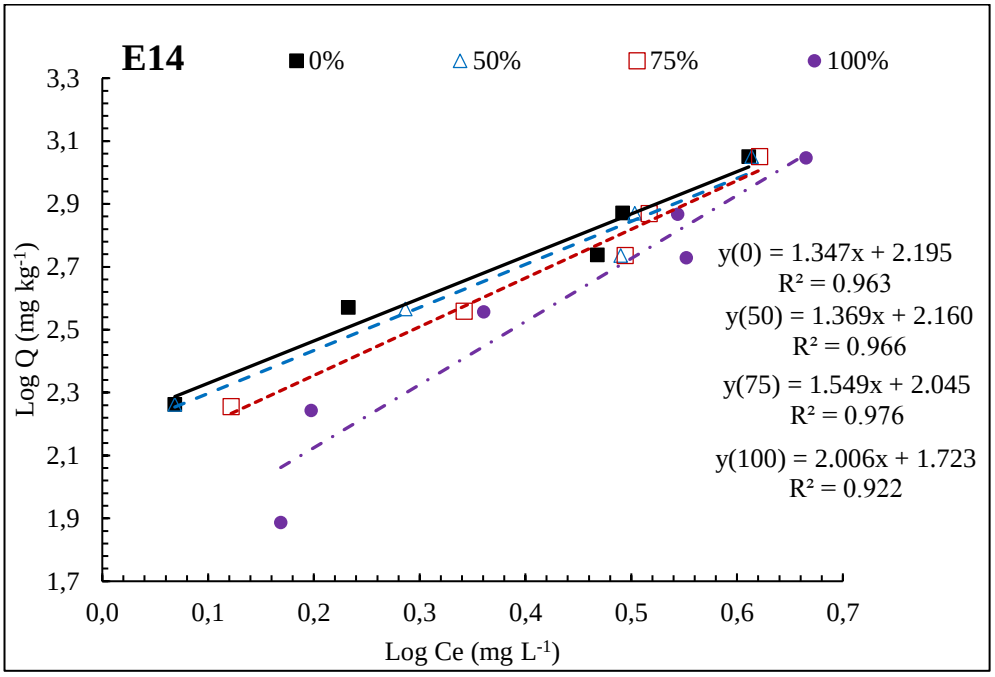

Figure 4.11. Linear Freundlich isotherms of E14 soil treated with differing lime requirements

According to Figure 4.11, the correlation (R^2) determination in E14 soil ranged from 0.922 – 0.976. The linear curve shows a straight relationship between phosphorus concentration (Ce) and phosphorus adsorption (Q). Based on the results, precipitation condition may occur at concentration 4 – 6 mg L^{-1}. The value of n increases as the level of liming increases, which ranged between 1.346 – 2.006. This indicates that the energy of attraction at the surface sites decreased, while the intermolecular bonds strengthened (Qayyum et al., 2015; Simonsson et al., 2018). The Freundlich coefficient (Kf) decreased with increasing liming dose, ranging from 1.723 to 2.195 mg kg^{-1}. The adsorption curve at the highest dose of 100% liming seemed to be steeper than other liming levels, suggesting the significant effect of liming 100% to phosphorus adsorption. The results show that the intervention of indigenous phosphorus suppressed the adsorption of added phosphorus so that the Kf value decreased (Hughes et al., 2000; Shafqat & Pierzynski, 2014).

4.2.2. The co-effects of citric acid and liming ratio

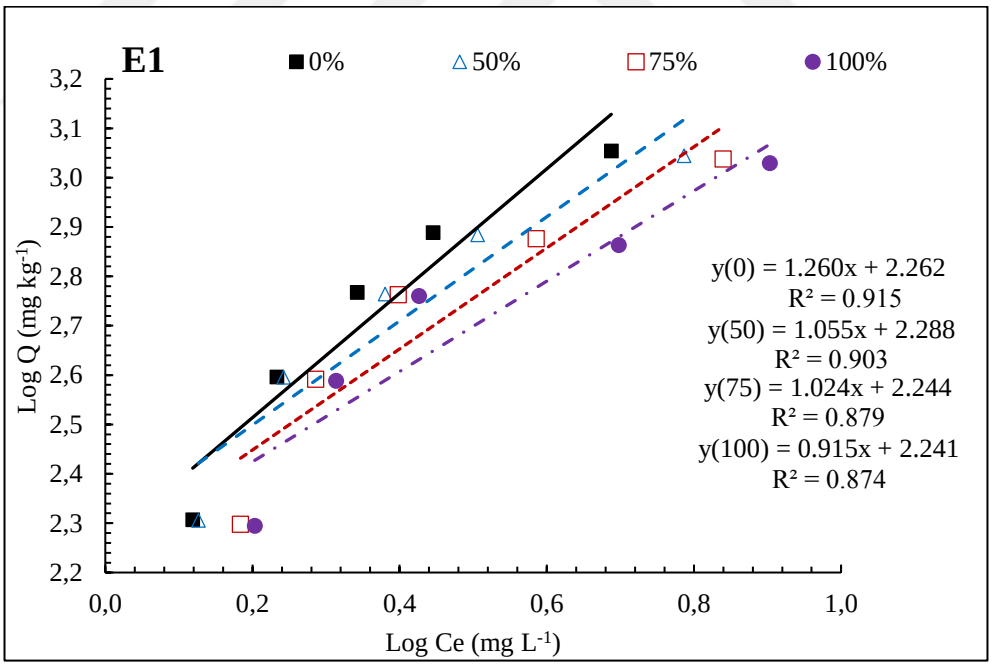

Figure 4.12. Linear Freundlich isotherms of E1 soil treated with differing lime requirements

Figure 4.12 shows the adsorption of phosphorus on E1 soil applied with citric acid using the Freundlich isotherm. The determination coefficient of the regression models of E1 soil ranged from 0.874 – 0.915. Thus, the rise in the determination coefficient

with the isotherm's curvature suggests the possibility of almost two distinct sorption mechanisms. It was highly probable that the isotherm's shape falls into the S-class category (Myers, 1999). However, the linear form of Freundlich adsorption isotherm model was justified. The n value of E1 soil varied between 0.915 – 1.260. In contrast to the results in $CaCl_2$ background, the n value decreases as the liming dose rises. The n values at 50% and 75% liming, indicating that the Freundlich Isotherm was linier. It means that adsorption occured with relatively uniform intensity over the entire concentration range. The n value of 0% liming was more than 1, indicating favorable adsorption at higher concentrations. Meanwhile, the n value of 100% liming was less than 1, suggesting favorable adsorption at lower concentrations. Under alkaline conditions or at higher concentrations, citric acid could also compete with phosphorus for adsorption sites. The complexing ability of citric acid may hinder the binding of phosphorus to the adsorbent surface, resulting in reduced phosphorus adsorption (Yang et al., 2019a). The Freundlich constant (Kf) of E1 soil ranged from 2.241 – 2.288 mg kg^{-1}. In this case, the surface site phosphorus adsorption capacity for all liming rates was similar. It Indicates the adsorption capacity was stagnant, allowing phosphorus not to be adsorbed and to be more available in the soil solution.

Based on Figure 4.13 and Figure 4.14, the value of the coefficient of determination of E2 soil implied that 70%, 80%, and 90% of the variance in the dependent variable is explained by the independent variables in the model, which suggested a good fit for the results. The coefficient of determination (R^2) ranged from 0.749 – 0.964. Meanwhile, the determination coefficient of the regression models of E3 soil varied between 0.926 – 0.945. The R^2 was close to 1 (in this case, 0.9), which means that the model was providing a very reliable prediction. As the liming ratio increases, the R^2 value decreased in E2 soil, particularly at 100% liming. This indicates the existence of more than one adsorption mechanism in one Freundlich isotherm representation. The n value of E2 soil varied between 1.220 – 1.328 and increase as the liming functions Meanwhile E3 soil ranged between 1.056 – 1.190. The Freundlich constant (Kf) of E3 soil decreased as the increase of liming rates. In soil E2, there was a sign of precipitation starting from 4 – 6 ppm. The curve forms more like type 5 in the adsorption isotherm classification (Myers, 1999), where the affinity energy between molecules is stronger than the adsorption site. In this case, Ca-P precipitation might be the source (Hughes et al., 2000).

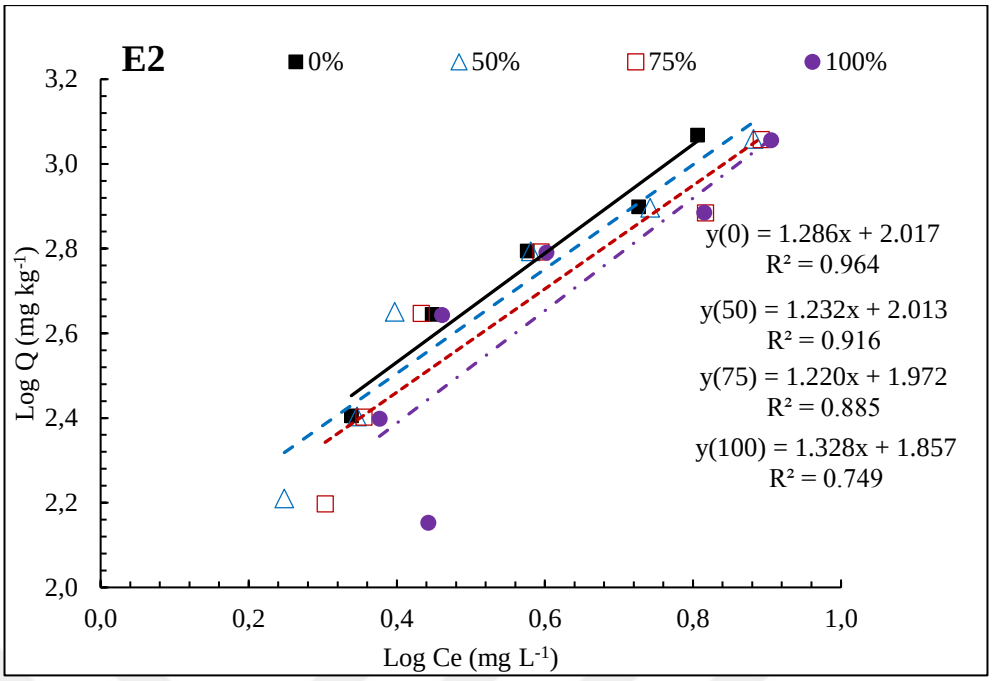

Figure 4.13. Linear Freundlich isotherms of E2 soil treated with differing lime requirements

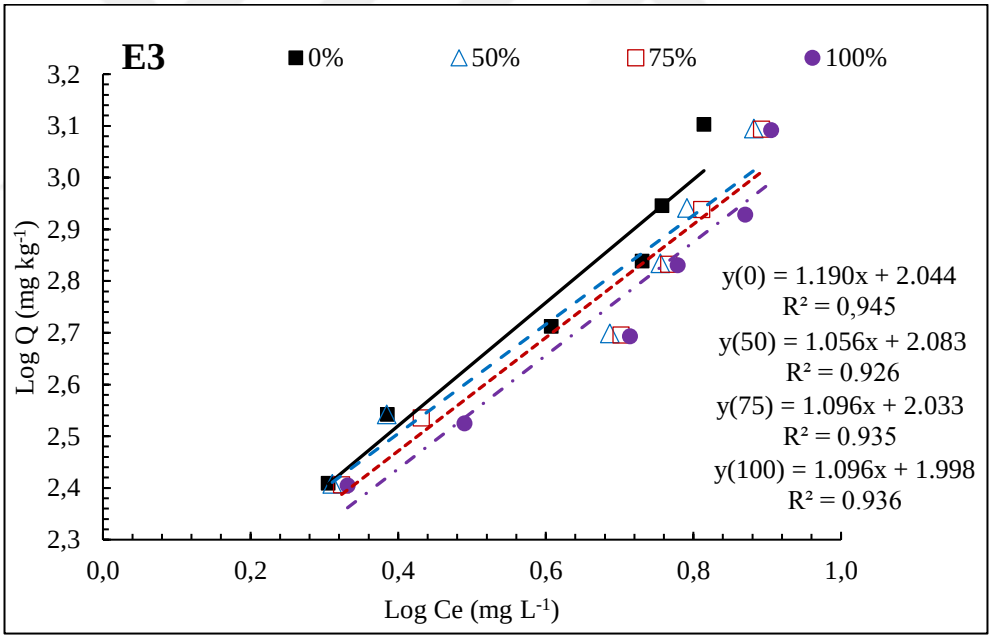

Figure 4.14. Linear Freundlich isotherms of E3 soil treated with differing lime requirement

In contrast to the effect on E2 soil, citric acid positively affected phosphorus adsorption's mechanism on E3 soil. In this case, citric acid might acted as a chelating agent, forming soluble complexes with phosphorus in the solution (Yang et al., 2019). Then, these complexes interact more effectively with the adsorption sites on the surface of minerals or other adsorbents, promoting phosphorus more available in the

soil (Hughes et al., 2000; Sui & Thompson, 2000; Jiao et al., 2007). The Kf value ranged from 1.857 – 2.017 mg kg^{-1} for E2 and 1.998 – 2.083 mg kg^{-1} for E3, furthermore there was a decrease in the descending liming level. This implies that there was an effect of solubility of indigenous phosphorus in the soil, which affected the adsorption of added phosphorus. The more solubility of native phosphorus, the adsorption capacity would be decreased and enhanced the availability of phosphorus in the soil (Barrow, 1984; Zhang et al., 2014).

Based on Figures 4.15 and 4.16, the range of R^2 on the regression model of Freundlich isotherm on E4 soil was 0.923 – 0.986 and E5 soil was 0.885 – 0.965. This means the experimental sorption data confirmed the Freundlich equation and the n and Kf values obtained are highly acceptable. The Freundlich constant (Kf) of E4 soil varied between 2.065 – 2.270 mg kg^{-1}. The Kf value of E5 soil ranged from 2.194 – 2.246 mg kg^{-1}. The Kf value of E4 increased after the application of liming. The increased Kf value of E4 implied that the soil adsorption ability became stronger with the rise in liming levels. Meanwhile, E5 soil showed similar Kf values. It indicates that there was no place for added phosphorus anymore to be adsorbed. As the soluble phosphorus from soil has taken the adsorption sites (Hughes et al., 2000).

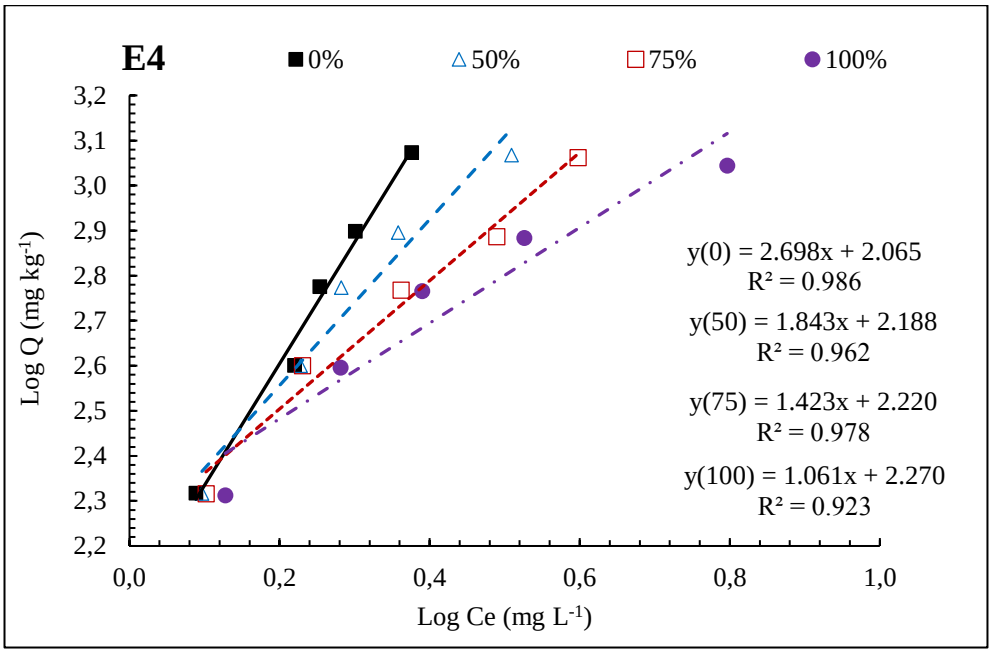

Figure 4.15. Linear Freundlich isotherms of E4 soil treated with differing lime requirements

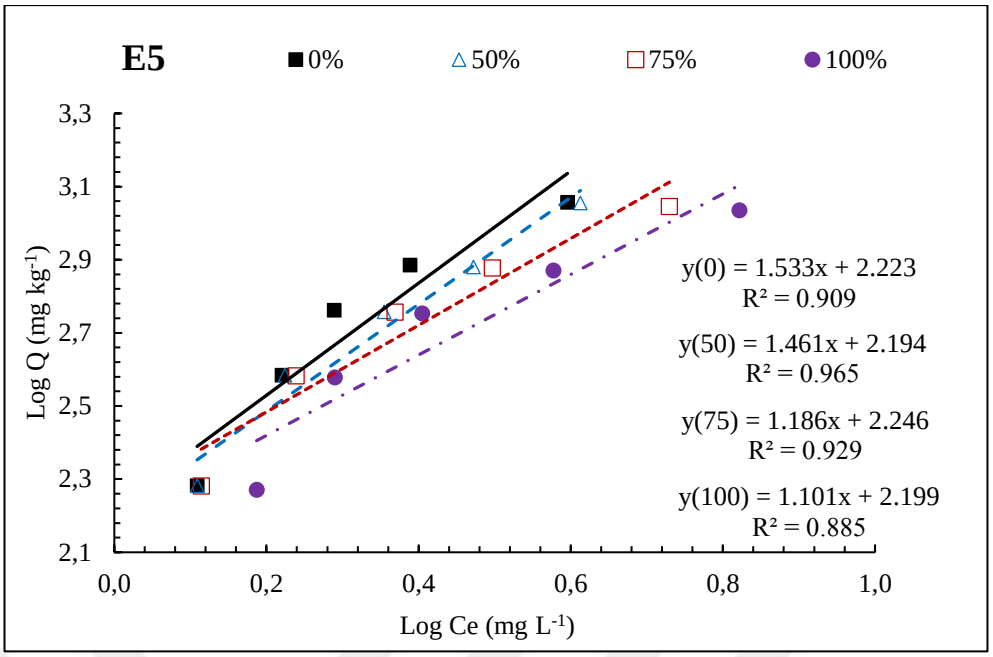

Figure 4.16. Linear Freundlich isotherms of E5 soil treated with differing lime requirements

In line with this, the n values of E4 and E5 decreased with the increase in liming levels. In soil E4, the range of n values decreased from 2.698 to 1.061, while in soil E5, it decreased from 1.533 to 1.100. Fe-P precipitation was observed to form in E4 and E5 soil without the use of liming. When liming was applied, precipitation occurred at high phosphorus concentrations until at 100% liming (E4) precipitation was absent. Although there was still an increase in adsorption at the endpoint of concentration equilibrium at 100% liming at E5. Based on this, the adsorption sites on E4 and E5 soils continue to be active and form diverse adsorption mechanisms (Shafqat & Pierzynski, 2014).

The coefficients of regression values for soils E7 and E8 exhibited a declining trend in response to the Freundlich adsorption isotherm as shown in Figure 4.17 and Figure 4.18. In soil E7, the regression coefficient ranged from 0.913 to 0.947, while in soil E8, it varied between 0.957 and 0.988. Moreover, the n values, representing the Freundlich isotherm constant, for soils E7 and E8 showed a normal adsorption pattern with the application of liming. In soil E7, the n value ranged from 1.083 to 1.155; in soil E8, it varied from 1.014 to 1.074. However, there was precipitation at the higher phosphorus concentration, which was at 6 – 9 mg L^{-1}. This indicates that chemisorption process happened at the low P concentration, if the phosphorus is continuously added it could be physisorption (Shafqat & Pierzynski, 2014).

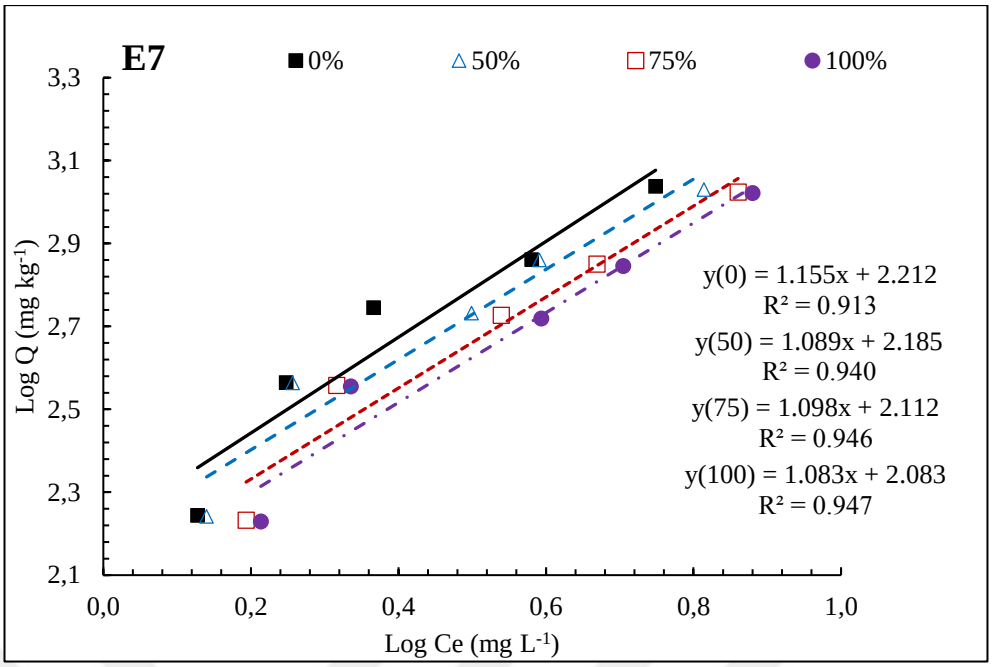

Figure 4.17. Linear Freundlich isotherms of E7 soil treated with differing lime requirements

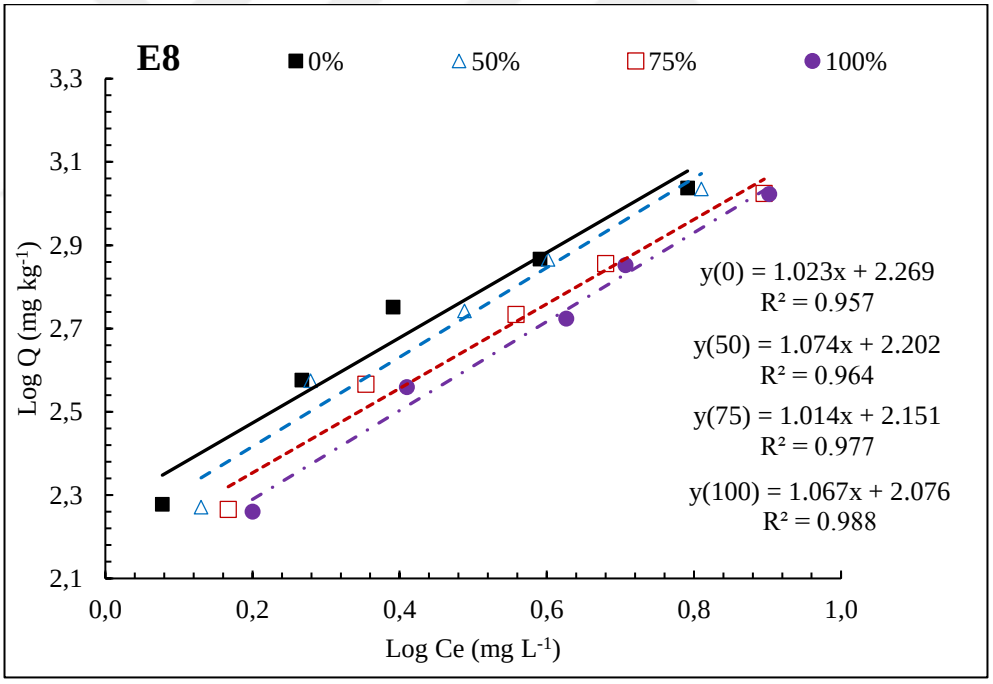

Figure 4.18. Linear Freundlich isotherms of E8 soil treated with differing lime requirements

Additionally, the Kf values for soils E7 and E8 demonstrated a similar diminishing trend with increased liming levels. In soil E7, the Kf value ranged from 2.083 to 2.212 mg kg^{-1}, while in soil E8, it varied from 2.076 to 2.269 mg kg^{-1}. This suggests that phosphorus adsorption decreased as the use of liming application. Liming was able to

netralized the soil by increasing pH and hindered phosphorus retantion. At the end, phosphorus would be more available for plants (Anderson, 2013).

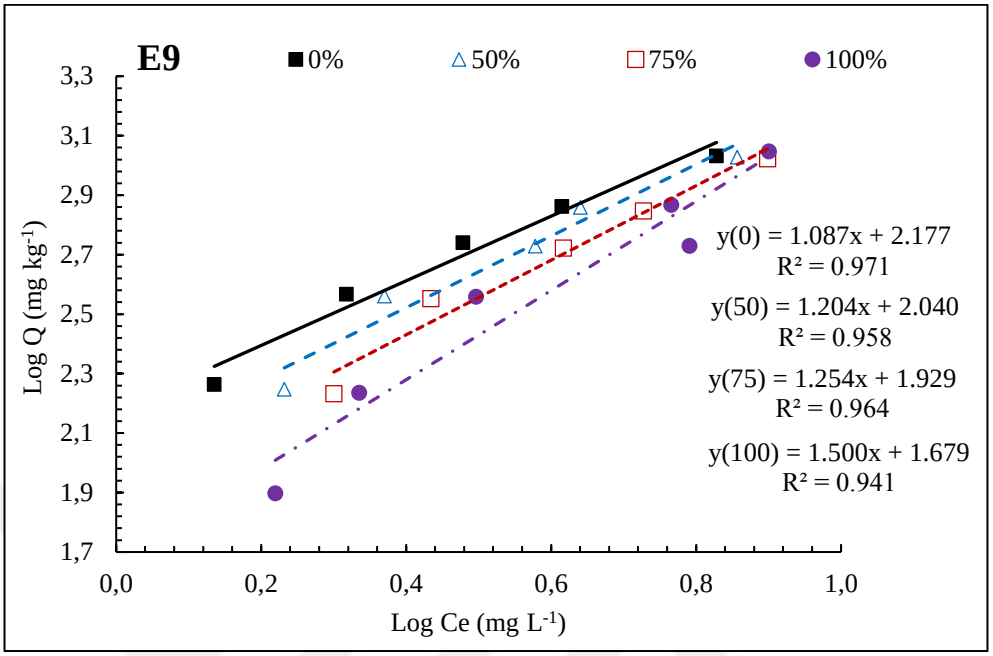

Figure 4.19. Linear Freundlich isotherms of E9 soil treated with differing lime requirements

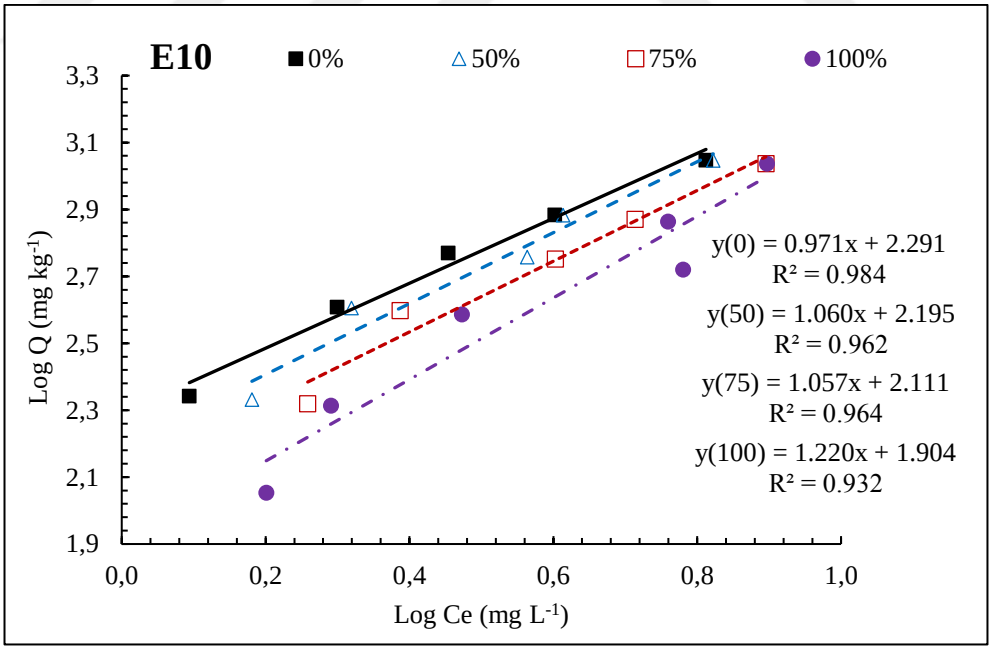

Figure 4.20. Linear Freundlich isotherms of E10 soil treated with differing lime requirements

Based on Figure 4.19 and Figure 4.20, in soil E9, the regression coefficient ranged from 0.941 to 0.971, while in soil E10, it varied from 0.932 to 0.984. It means that the regression results was justified. On the other hand, the n values for soils E9 and E10

exhibited an increment with the application of liming. In soil E9, the n value ranged from 1.087 to 1.500; in soil E10, it varied from 0.971 to 1.220. This is related to the precipitation of phosphorus with calcium and it happened around at 8 mg L^{-1} P concentration on liming 100%. The Kf values for soils E9 and E10 displayed a declining trend with the increase of liming levels. In soil E9, the Kf value ranged from 2.177 to 1.679 mg kg^{-1}, while in soil E10, it varied from 2.291 to 1.904 mg kg^{-1}. Although the solubility of native P and P addition allows for increased adsorption capacity, the use of citric acid suppressed the higher adsorption process because it could form chelates and made P available in the soil (Qayyum et al., 2015; Simonsson, et al., 2018).

Based on Figure 4.21 and Figure 4.22, the obtained Kf and n values are reliable based on the R^2 values of regression models, which ranged from 0.940 to 0.989 for E11 and 0.927 to 0.968 for E14. The n values of E11 and E14 ranged from 0.878 to 1.065 and 1.016 to 1.067, which the values approximately described the normal adsorption. Even so, the curve describes the precipitation Ca-P happened on 8 ppm concentration at liming 100%. The Kf value in soil E11 started at 2.369 mg kg^{-1} and steadily decreased to 2.055 mg kg^{-1}.

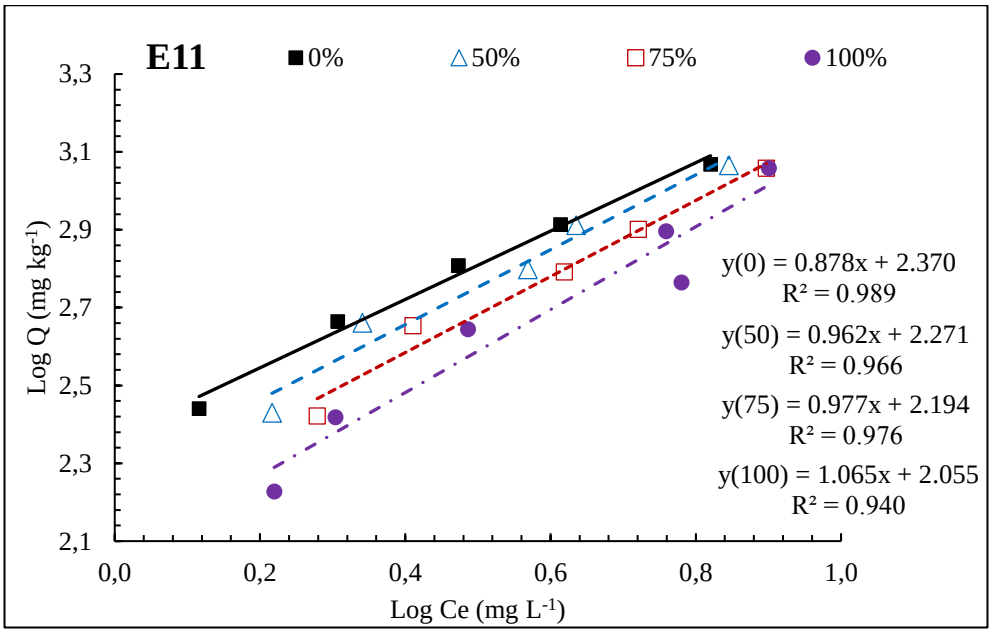

Figure 4.21. Linear Freundlich isotherms of E11 soil treated with differing lime requirements

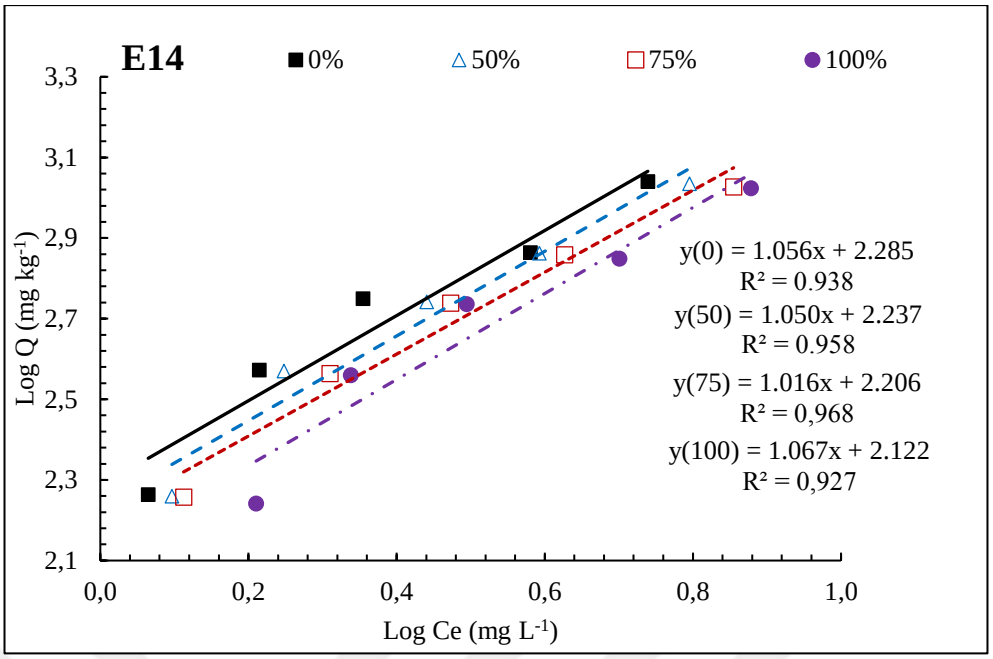

Figure 4.22. Linear Freundlich isotherms of E14 soil treated with differing lime requirements

Meanwhile, the Kf value for soil E14 decreased from 2.285 to 2.122 mg kg^{-1}. It means that the adsorption decreased as the increased of liming ratio. However, the strength of the bond between phosphorus and soil became weaker, making phosphorus more readily released from soil particles and more available for plants (Shafqat & Pierzynski, 2014; Qayyum et al., 2015; Simonsson et al., 2018). In addition, due to application of citric acid the soil became less effective in adsorbing and holding onto phosphorus, which may have led to higher levels of phosphorus leaching or becoming more available for plant uptake (Zhu et al., 2022).

4.2.3. The co-effects of malic acid and liming ratio

The P sorption data of malic acid applied soils were subjected to the linear form of Freundlich adsorption isotherm model. Figure 4.23 and Figure 4.24 present the adsorption isotherms and model parameters of E1 and E2 soil. The coefficient of determination for the regression models of E1 soil varied from 0.939 to 0.972 and 0.960 to 0.977 for E2, indicating that the obtained n and Kf values were reliable. Consequently, the experimental sorption data validated the applicability of Freundlich equation.

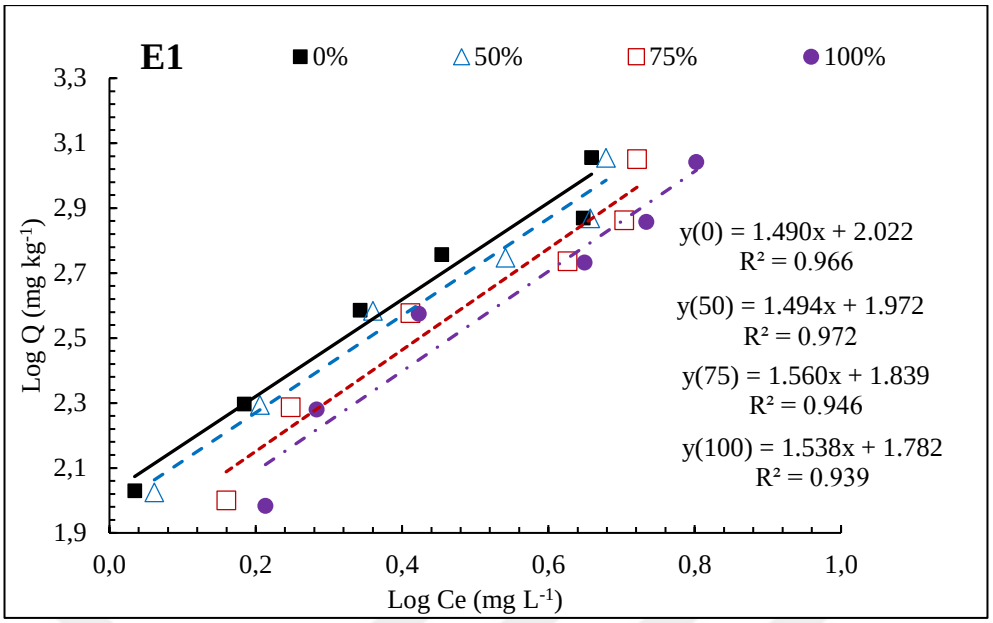

Figure 4.23. Linear Freundlich isotherms of E1 soil treated with differing lime requirements

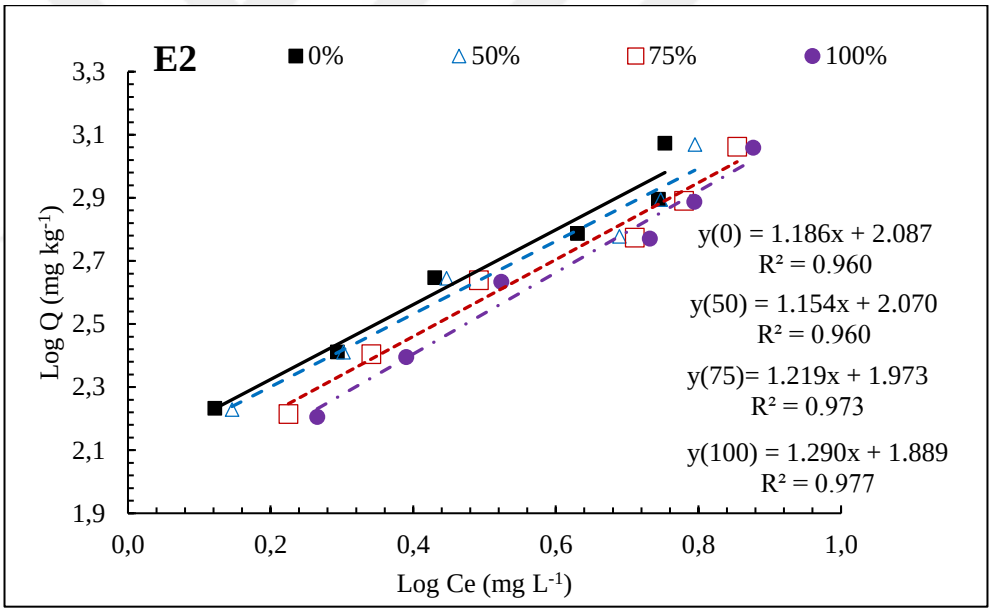

Figure 4.24. Linear Freundlich isotherms of E2 soil treated with differing lime requirements

The n values increased with the incremental liming levels, ranging from 1.490 to 1.560 for E1 and 1.186 to 1.290 for E2. The adsorption rate was observed to be high at low P concentrations. In addition, the formation of a distinct adsorption region was observed at concentrations between 6 and 8 mg L^{-1} as in the type 2 isotherm. This indicates that the adsorbate molecules have relatively strong mutual interactions, leading to a tendency for multilayer formation (Myers, 1999). The Kf value of E1 and E2 soil decreased as the liming function increased, with values ranging from 2.022 to

1.782 mg kg^{-1} for E1 and 2.087 to 1.889 mg kg^{-1} for E2. This indicated adsorption processes decreased as the liming increase and application of malic acid, enhance the more available for plant uptake (Sui & Thompson, 2000; Jiao et al., 2007).

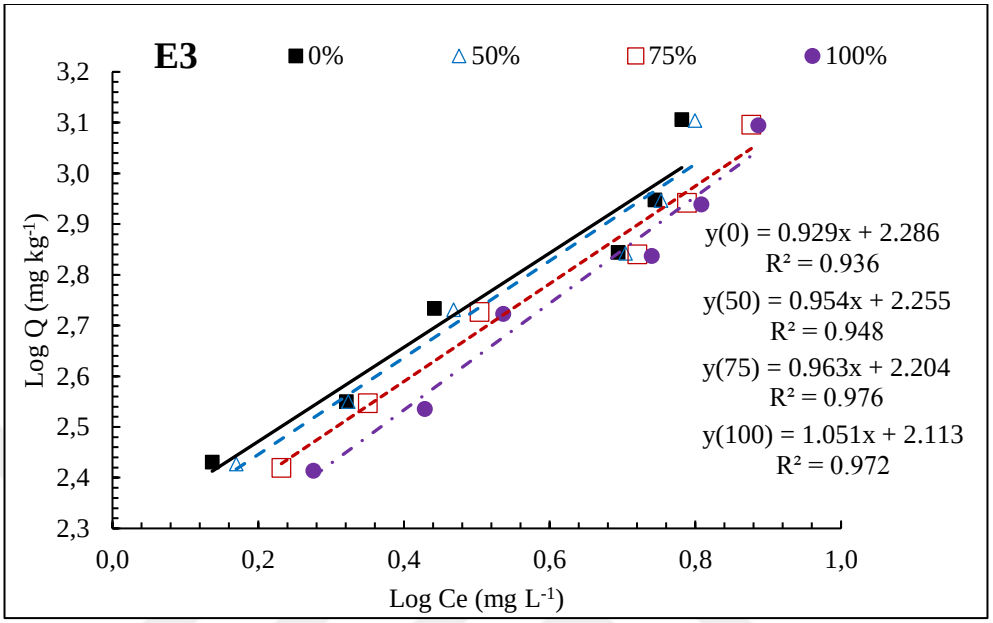

Figure 4.25. Linear Freundlich isotherms of E3 soil treated with differing lime requirements

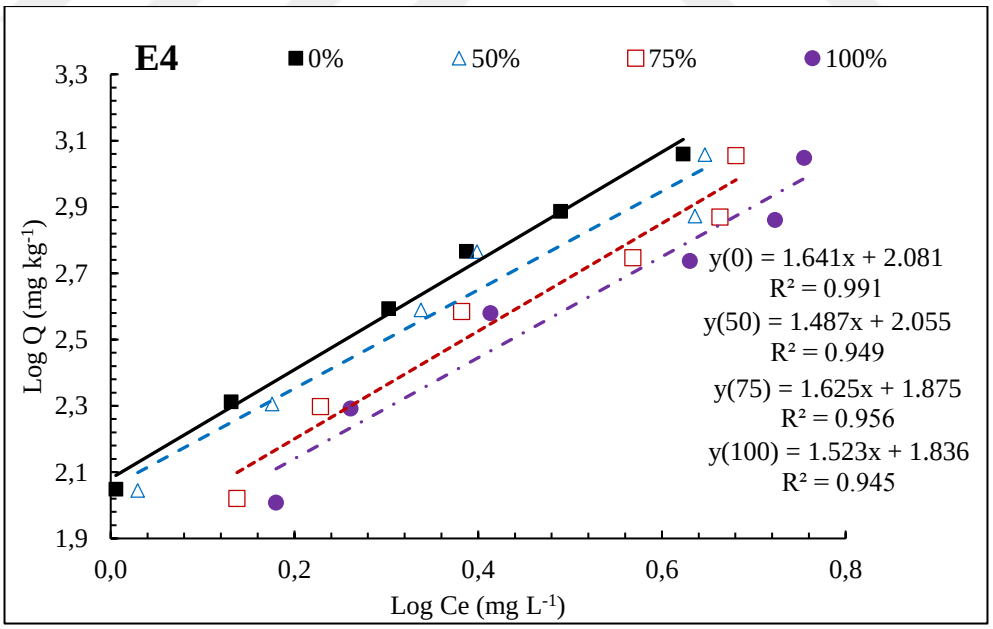

Figure 4.26. Linear Freundlich isotherms of E4 soil treated with differing lime requirements

The highest Freundlich coefficient value (n) for soil E4 was 1.641 without liming application. When liming 50% is applied, the n values decreased but totally changed at liming 75% and 100%. It ranged from 1.487 to 1.641. The S-type adsorption was

observed as the liming increase. Soil with liming 0% had favorable adsorption at higher concentrations. After the application of liming, the adsorption started to be benefit at low concentrations. This suggest that interaction intermolecular increased than adsorption sites and adsorbate. In this case, there was precipitation Ca-P around 7 – 8 mg L^{-1} P concentration. The Kf values decreased as the liming rates increased, ranging from 2.286 to 2.113 mg kg^{-1} for E3 and 2.091 to 1.836 mg kg^{-1} for E4. This decline in Kf values suggest adsorption inhibition In this case, it was expected that higher levels of liming and malic acid could enhance the release of phosphorus from soil particles into the soil solution, thereby increasing its availability for plant uptake (Hughes et al., 2000, Sui & Thompson, 2000; Jiao et al., 2007; Zhang et al., 2014).

Based on Figures 4.27 and 4.28, the coefficient of regression for soil E5 ranged from 0.941 to 0.971, while for soil E7, it ranged from 0.926 to 0.962. As indicated by the coefficient of regression values, the regression models for both soil E5 and E7 were acceptable and provided a good fit to the experimental data.

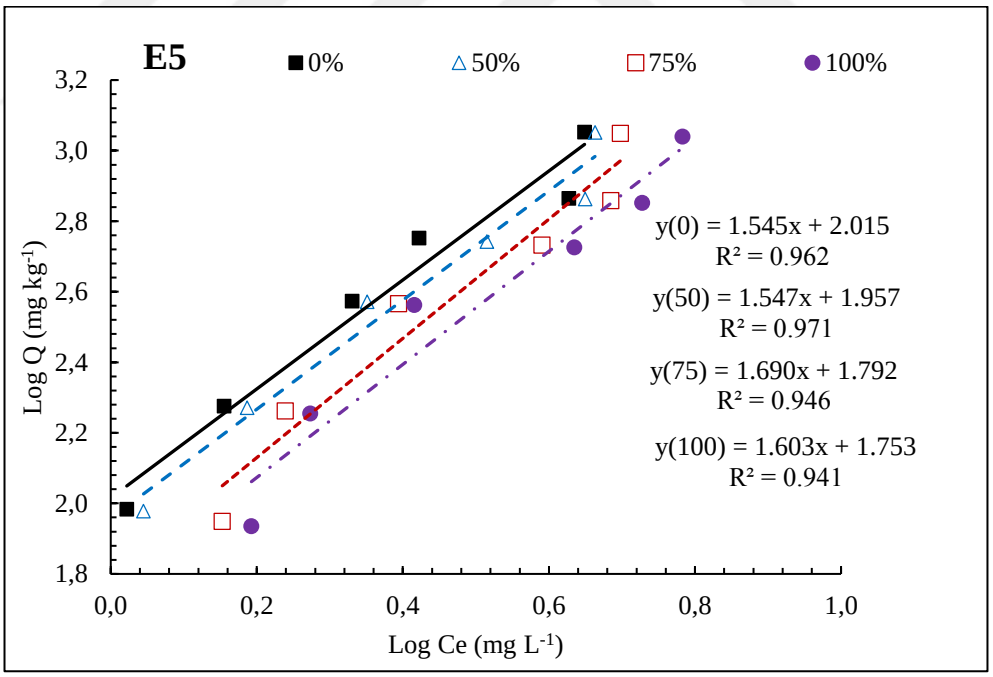

Figure 4.27. Linear Freundlich isotherms of E5 soil treated with differing lime requirements

The n values for both soil E5 and E7 increased with the increasing level of liming, with E5 ranging from 1.545 to 1.690 and E7 ranging from 1.622 to 1.712. The surface's affinity declines, and P and Ca from the background solution may precipitate through

ionic contact. With an increased liming ratio and a lower initial concentration, the depletion of the data point to S type was noticed.

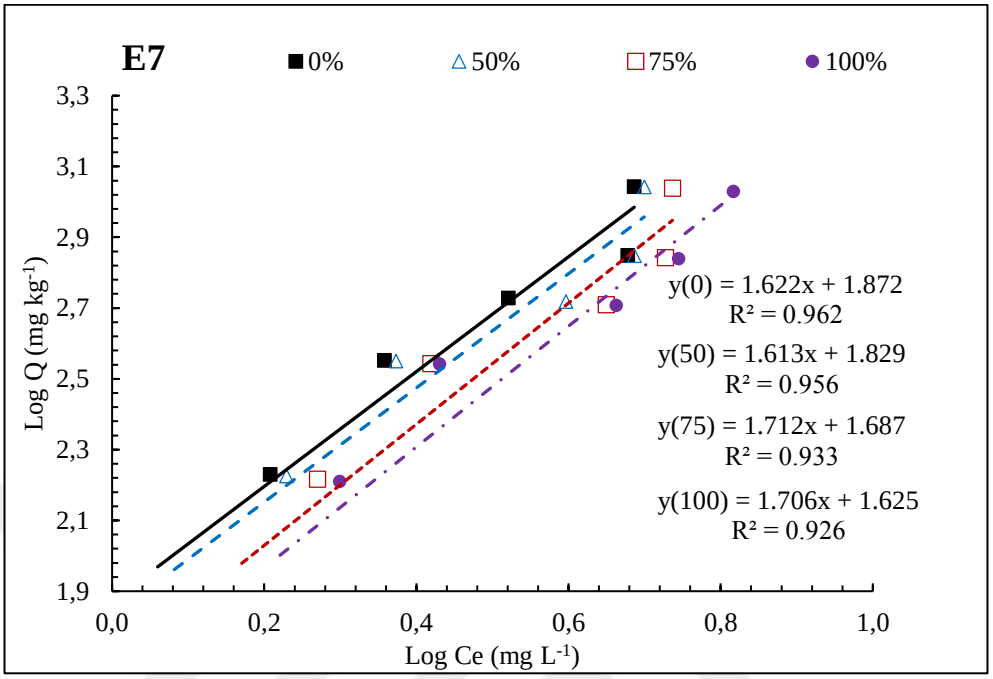

Figure 4.28. Linear Freundlich isotherms of E7 soil treated with differing lime requirements

The Kf values for soil E5 and E7 decreased with the increasing function of liming, with E5 ranging from 2.015 to 1.753 mg kg^{-1} and E7 ranging from 1.872 to 1.625 mg kg^{-1}. The decrease in Kf values for soil E5 and E7 with increasing liming levels indicated a reduction in the soil's adsorption capacity for phosphorus. This means that with higher liming levels, the soil's ability to adsorb and retain phosphorus was diminished, potentially leading to a higher release of phosphorus into the soil solution (Shafqat & Pierzynski, 2014). This is related to the increased solubility of indigenous phosphorus in the soil due to the pH increment (Barrow, 1984).

Based on Figure 4.29 and Figure 4.30, the coefficient of regression for E8 soil ranged from 0.937 – 0.963, while for E9 soil, it ranged from 0.958 – 0.965. This indicated a good fit relationship between the variables in the regression model. The n values of E8 and E9 soil increased as the function of liming ranged between 1.548 – 1.644 and 1.556 – 1.694. Isotherms shaped like the S-type, which occurred due to the solute attraction force on the surface could lead to cooperative adsorption and solute absorption was

inhibited by the competition of complexation reactions with malic acid ligands (Shafqat & Pierzynski, 2014).

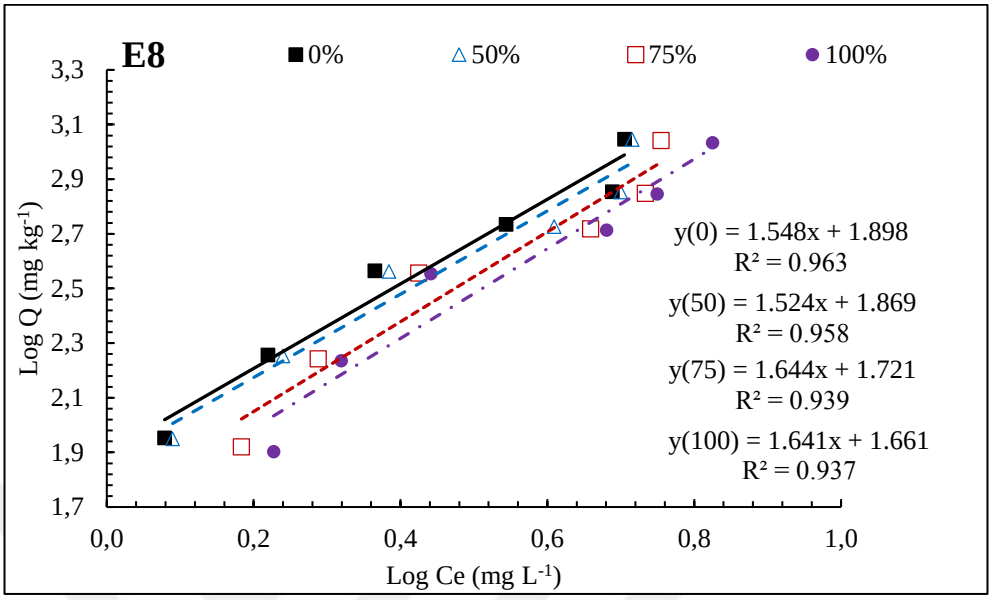

Figure 4.29. Linear Freundlich isotherms of E8 soil treated with differing lime requirements

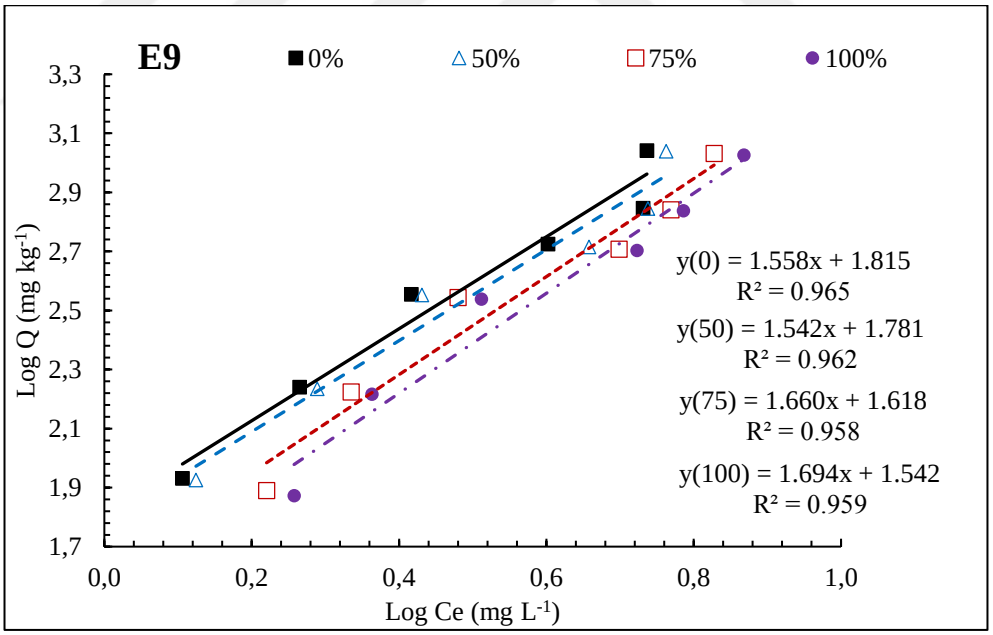

Figure 4.30. Linear Freundlich isotherms of E9 soil treated with differing lime requirements

On the other hand, the Kf values of both E8 and E9 decreased as the application of liming increased. It varied from 1.898 – 1.661 mg kg^{-1} for E8 and 1.815 – 1.542 mg kg^{-1} for E9. This indicated that the soil's capacity for phosphorus adsorption diminished with higher levels of liming. The decreasing Kf values suggest that the adsorption

decreased, resulting the soil's ability to bind and hold phosphorus decreased, potentially leading to higher phosphorus mobility and availability in the soil solution, which can be advantageous for plant uptake (Hughes et al., 2000; Sui & Thompson, 2000).

Based on Figure 4.31 and Figure 4.32, the coefficient of regression for E10 soil was found to be 0.946 to 0.964, while for E11 soil, it ranged from 0.961 to 0.971. These values indicated a relatively stable relationship between the variables in the regression model, which means that the n and Kf values were acceptable.

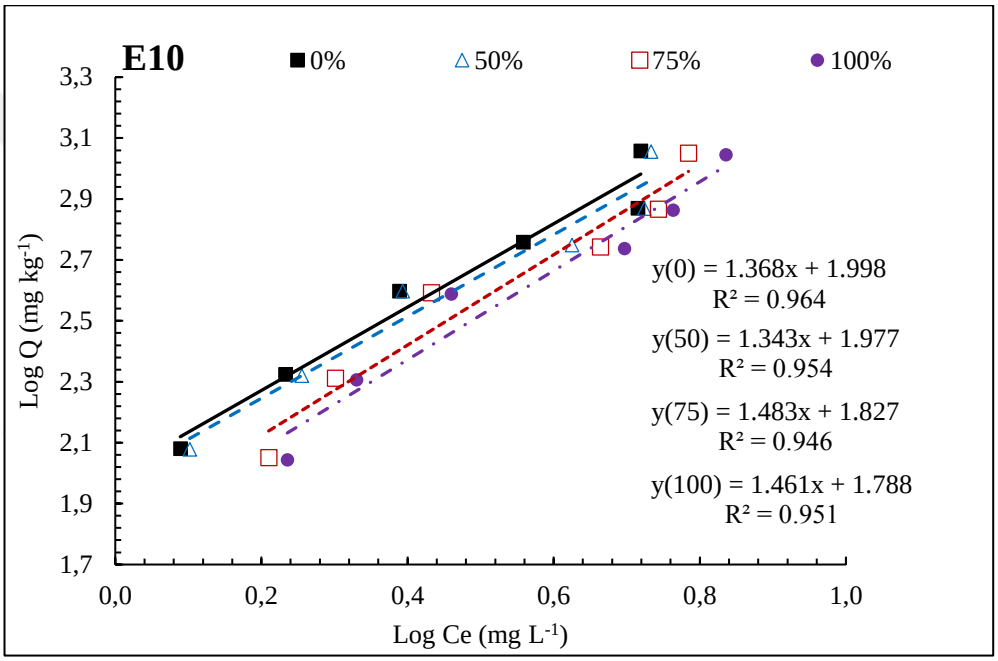

Figure 4.31. Linear Freundlich isotherms of E10 soil treated with differing lime requirements

Moreover, the n values of E10 and E11 soil increased as the liming levels ranged between 1.343 to 1.483 for E10, and 1.171 to 1.240 for E11. The increasing n values indicated that the soil had more active binding sites available to adsorb phosphorus, leading to enhanced phosphorus retention. Consequently, the application of liming positively influenced the phosphorus adsorption capacity of both E10 and E11 soils, indicating the affinity of the surface is weakining and possible ionic interaction or precipitation of P with Ca which was supplied by background solution. The S-type on-set of the experimental data can also indicate such behavior. The depletion of the data point to S type was observed at lower initial concentration corresponding with the increasing liming ratio.

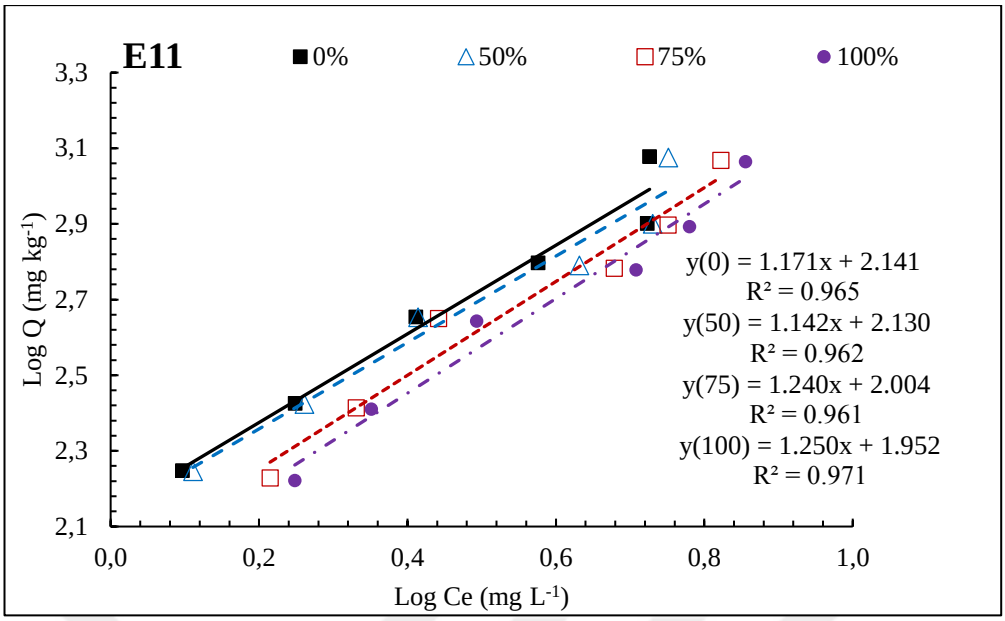

Figure 4.32. Linear Freundlich isotherms of E11 soil treated with differing lime requirements

On the contrary, the Kf value of both E10 and E11 decreased with the increasing application of liming, ranging from 1.998 to 1.788 mg kg^{-1} for E10 and 2.141 to 1.953 for E11 mg kg^{-1}. The declining Kf values suggested that the strength of the phosphorus-soil interactions weakened, resulting in a reduced ability of the soil to retain phosphorus through adsorption. As a result, with higher levels of liming, the soil's ability to bind and hold phosphorus decreased, potentially leading to a greater mobility and availability of phosphorus in the soil solution. This increased availability of phosphorus can be beneficial for plant uptake (Hughes et al., 2000; Sui & Thompson, 2000; Jiao et al., 2007).

Based on Figure 4.33, the regression coefficient for E14 soil ranged from 0.927 to 0.963. It suggested a good fit of the data to the regression model. This implied that the model could effectively explain the variation in phosphorus adsorption based on the liming levels and phosphorus concentration. In this case, the results were considered acceptable. The n value of E14 soil ranged between 1.595 and 1.691. This indicated that the relationship between phosphorus concentration and its adsorption onto the soil became stronger as the liming levels increased.

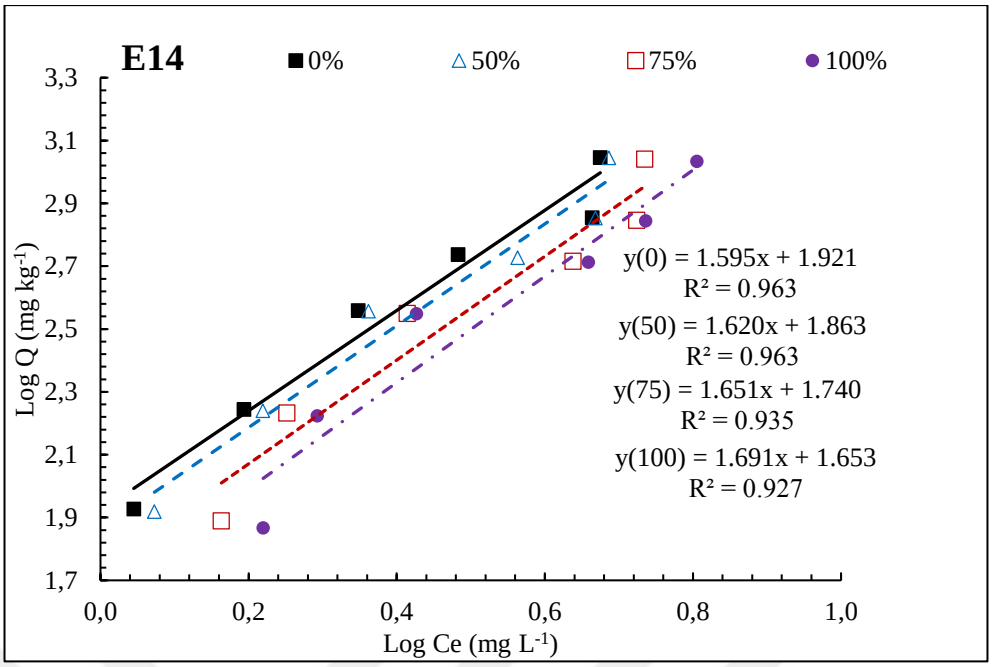

Figure 4.33. Linear Freundlich isotherms of E14 soil treated with differing lime requirements

The Kf value of E14 soil showed a reverse pattern, decreasing as the application of liming increased. It varied from 1.921 to 1.653 mg kg^{-1}. The decreasing Kf values implied that the strength of the phosphorus-soil interactions weakened with higher liming levels, resulting in a reduced ability of the soil to retain phosphorus through adsorption (Sui & Thompson, 2000; Jiao et al., 2007). The results suggested that liming has a significant influence on the adsorption behavior of phosphorus in E14 soil. The increase in n values indicates improved phosphorus retention capacity, while the decrease in Kf values suggests reduced phosphorus adsorption capacity with higher liming levels (Shafqat & Pierzynski 2014; Qayyum et al., 2015; Simonsson et al., 2018).

4.2.4. The co-effects of oxalic acid and liming ratio

According to Figure 4.34 and Figure 4.35, the regression coefficient (R^2) for E1 soil ranged from 0.834 – 0.884. Meanwhile, R^2 for E2 varied between 0.944 – 0.981. These values represent the goodness of fit of the regression model for E1 and E2 soil data. A regression coefficient close to 1 indicated a strong fit between Freundlich isotherm data and regression model, suggesting that the model was admissible. As the decrease in the determination coefficient with the shaper of the isotherm indicated potential two

or thre different mechanisms or sorption regions. The shape of the isother is very likely to be the S-type. However, the higher regression coefficient for E2 soil indicated a more robust correlation and less variability in the data points.

The freundlich exponent (n) of E1 and E2 rose as the increased of liming application. It ranged from 1.226 – 1.462 for E1 and 1.157 – 1.331 for E2. This meant that there was weaker sorption strength of phosphorus adsorption with increasing liming. This result implied more heterogeneous surface or cooperative adsorption behavior. The freundlich constant (Kf) of E1 and E2 ranged between 2.077 – 1.822 mg kg^{-1} and 2.068 – 1.847 mg kg^{-1}. In contrast, with the rise in liming levels, the Kf values of both E1 and E2 soils declined. This suggests that the soil's capacity to adsorb phosphorus decreased as liming increased. This showed that over a very large range of initial P concentration the availability and mobility of either indigenous or fertilizer P was to increase. Correspondingly, the decrease in Kf values signifies a weakening of the phosphorus-soil interactions, resulting in a reduced ability of the soil to retain phosphorus through adsorption (Hughes et al., 2000; Sui & Thompson, 2000; Jiao et al., 2007).

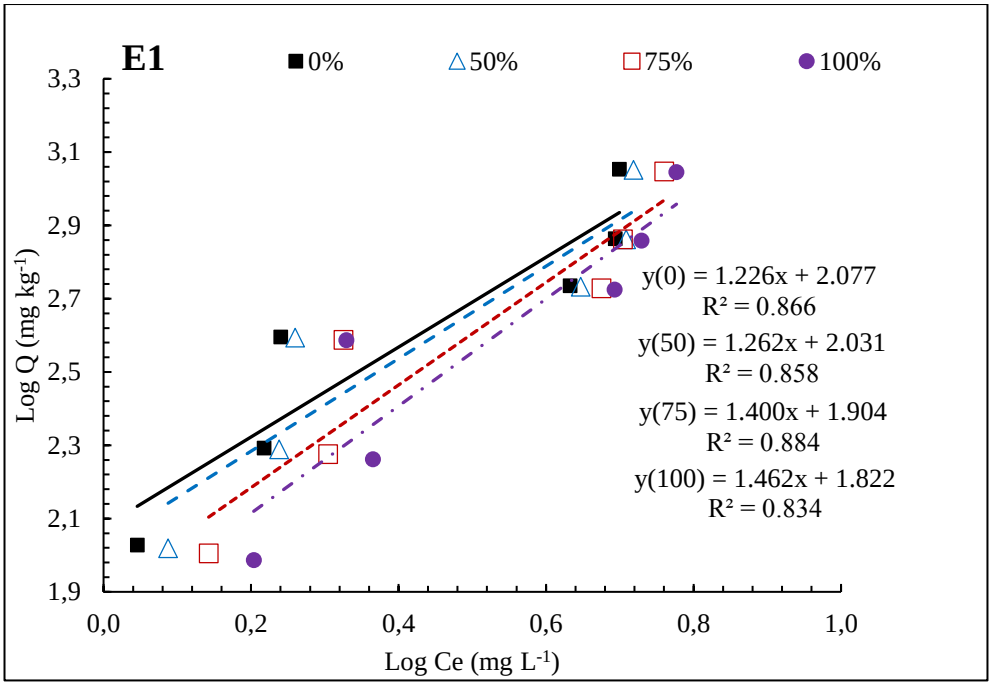

Figure 4.34. Linear Freundlich isotherms of E1 soil treated with differing lime requirement

According to Figure 4.36 and Figure 4.37, the coefficient of determination for the regression models of E3 and E4 soil ranged from 0.945 to 1.030 and 0.804 to 0.920. This indicates that the model effectively captured a substantial portion of the variability in the dependent variable using the included predictors. With an R^2 value close to 1 (in this case, 0.9), the model provided highly reliable predictions. However, the scattering nature of the experimental data for E4 especially at higher level of liming ratio was apparent. The depletion in the equilibrium P concentration at low P loadings was eyecatching for E4 that the co-effects of liming and the oxalic acid was more evident than the higher P loadings.

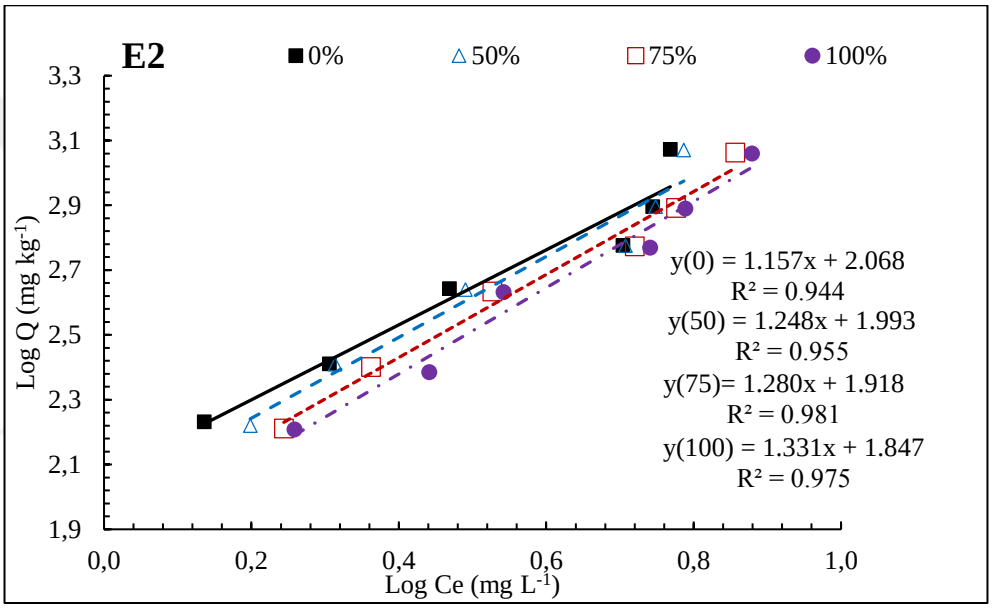

Figure 4.35. Linear Freundlich isotherms of E2 soil treated with differing lime requirements

The freundlich exponents (n) of E3 and E4 improved as the increased of liming application. It varied between 0.945 to 1.030 for E3 and 1.312 to 1.558 for E4. The n value in E3 soil tends to be lower than in other soils. This implies that phosphorus adsorption in E3 soil is relatively influenced smaller extent by the treatments. On the other hand, in E4 soil, treatment effects were more evident with very large depletion in the n coefficient due to liming levels with the most substantial change were obtained for 100% liming. In this case, the increase in soil pH led to the solubilization of indigenous phosphorus in the soil, which enhanced ion interactions.

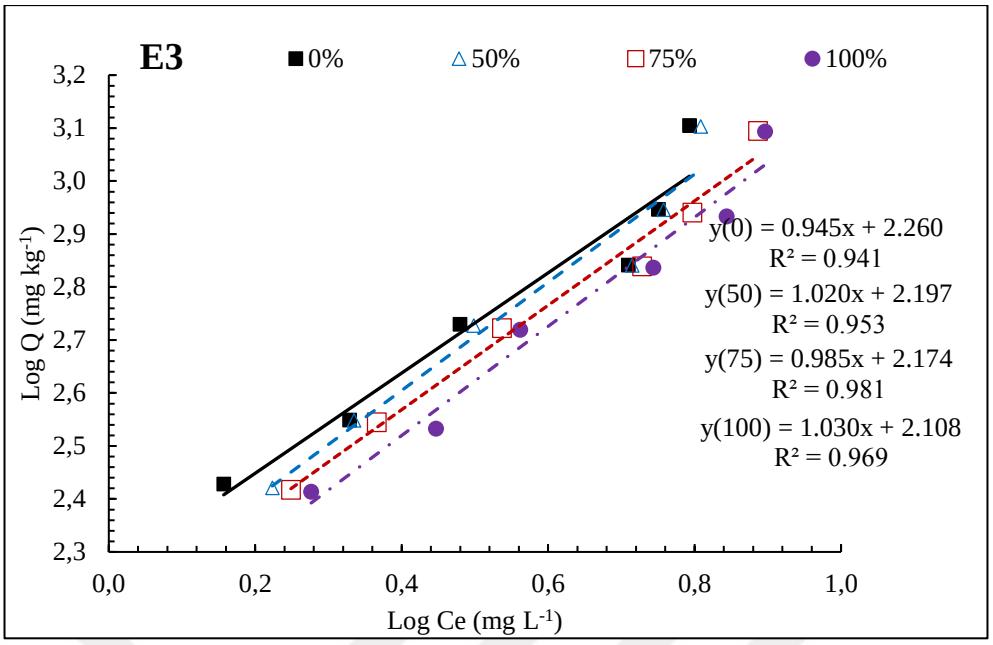

Figure 4.36. Linear Freundlich isotherms of E3 soil treated with differing lime requirements

The Freundlich constant (Kf) of E3 and E4 decreased as the liming levels. It ranged from 2.260 – 2.108 mg kg^{-1} for E3 and 2.163 – 1.877 mg kg^{-1} for E4. The decreasing Kf values suggested that the strength of the phosphorus-soil interactions weakened and the dissolution of indigenous P resulted in a reduced ability of the soils to retain loaded phosphorus through adsorption (Shafqat & Pierzynski, 2014).

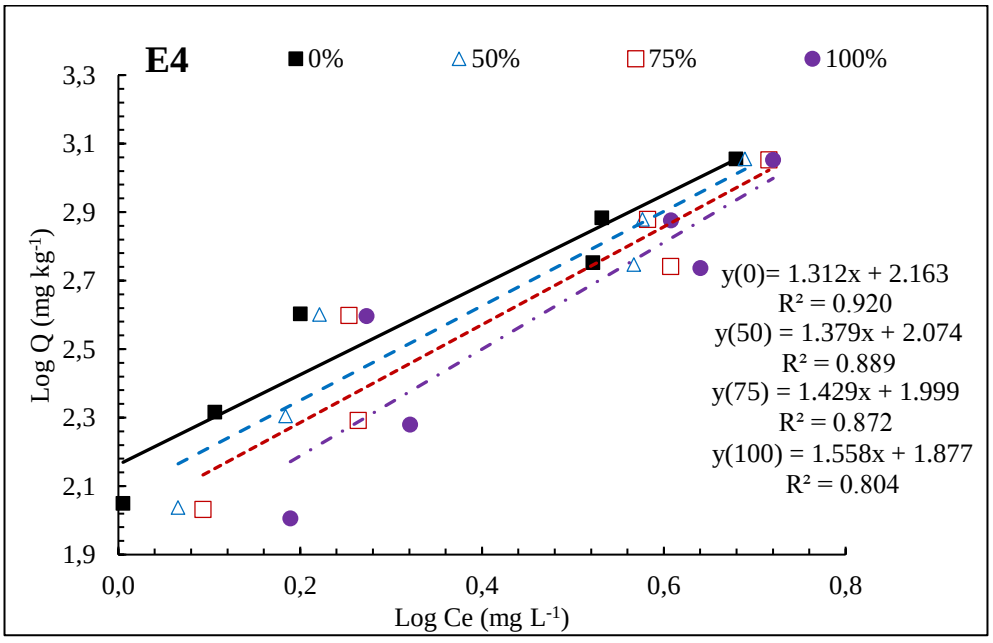

Figure 4.37. Linear Freundlich isotherms of E4 soil treated with differing lime requirements

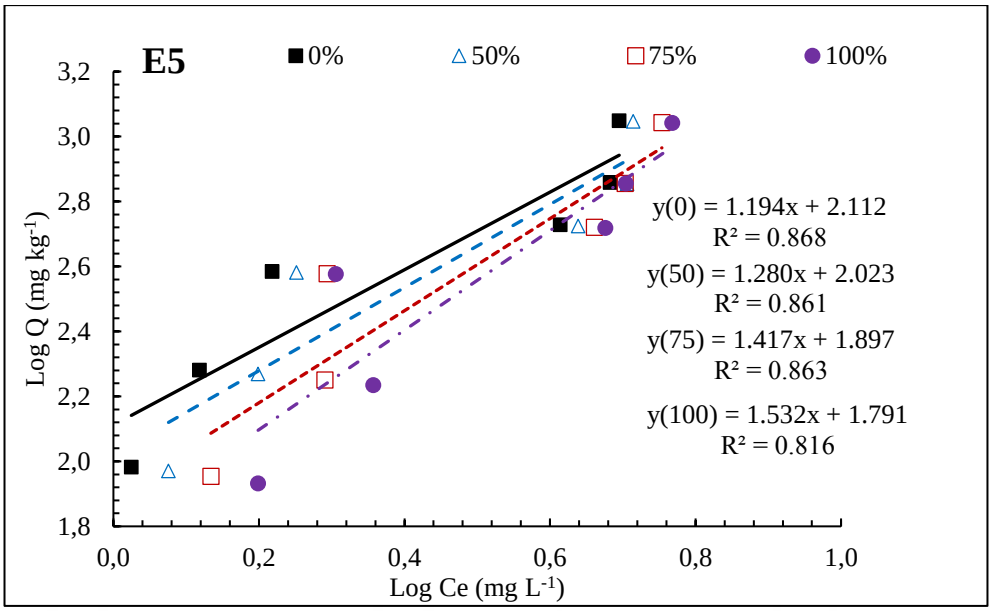

Figure 4.38. Linear Freundlich isotherms of E5 soil treated with differing lime requirements

Based on Figure 4.38 and Figure 4.39, the E5 and E7 soils had a coefficient of determination ranging from 0.816 – 0.868 and 0.738 – 0.805. This means that phosphorus adsorption on E5 and E7 soils analyzed by Freundlich isotherm soil was justifiable.The phosphorus adsorption in E5 and E7 soil exhibited relatively high heterogeneity, as indicated by n values ranging from 1.194 to 1.532 and 1.376 to 1.680, respectively. Additionally, the n values increased with higher levels of liming dependency, demonstrating stronger changes at lower solute concentrations with increasing liming practices. The Freundlich constant (Kf) revealed that the adsorption capacity decreased as the liming dose increased. The Kf values ranged from 2.112 to 1.791 mg kg^{-1} for E5 and 1.886 to 1.563 mg kg^{-1} for E7. This observation suggests that liming influences the soil pH, affecting phosphorus sorption and inducing indigenous P solubilization (Barrow, 1984).

Based on Figure 4.40 and Figure 4.41 the value of the coefficient of determination of E8 and E9 soil implied that 70%, 80%, and 90% of the variance in the dependent variable is explained by the independent variables in the model, which suggested a good fit for the results. The coefficient of determination (R^2) ranged from 0.760 – 0.893 for E8 and 0.931 – 0.967 for E9. The depletion from the linear behaviour was observed at higher P loadings for the original soil whereas in the intermediate P loadings caused larger depletion for 100% liming treatment.

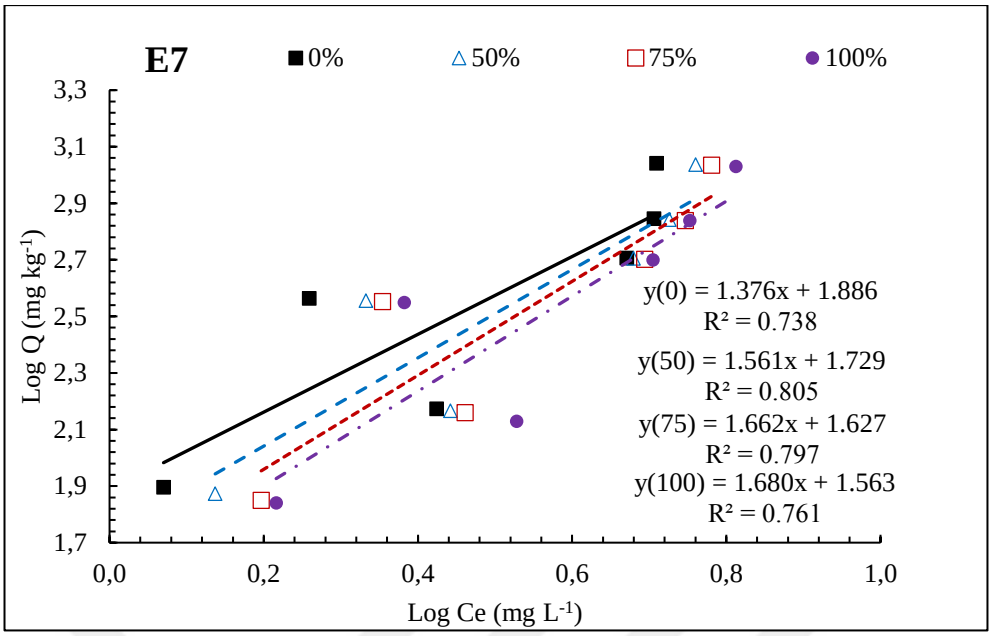

Figure 4.39. Linear Freundlich isotherms of E7 soil treated with differing lime requirements

The n value of E8 soil ranged from 1.281 to 1.512. In this case, the n value increased with the increasing lime application but experienced a drastic reduction at the 100% lime dose. This could be attributed to the possible precipitation reactions occurred at the upper end of the isotherm. As the on set of the experimental data considered there was no increase in the Ce-P despite a huge increase in the adsorbed P. This resulted in some depletion from the linear behaviour of the sorption which accompanied with lower determination coefficient. The increase in pH caused phosphorus to become more available in the soil solution and accessible to plants. On the other hand, the n value of E9 soil ranged from 1.474 to 1.789, increasing with higher levels of liming. Unlike E8 soil, the 100% lime application resulted in the highest phosphorus adsorption. This might be due to indigenous phosphorus solubility in the soil and low potential acidity of soil both of which reduces the affinity of surfaces to newly added phosphorus (Zhang et al., 2014). The Freundlich constant (Kf) represented the soil's adsorption capacity. Higher Kf value indicated a greater adsorption capacity coefficient, meaning the soil adsorbed higher amounts of P genetically or antropogenically. The Kf value ranged from 1.965 to 1.768 mg kg^{-1} for E8 and 1.817 to 1.475 mg kg^{-1} for E9. As the liming level increased, the Kf value decreased, indicating that the soil's affinity for phosphorus reduced with higher liming. This allowed to transform the indigenous and fertilizer phosphorus to the plant-available forms (Shafqat & Pierzynski, 2014; Qayyum et al., 2015; Simonsson et al., 2018).

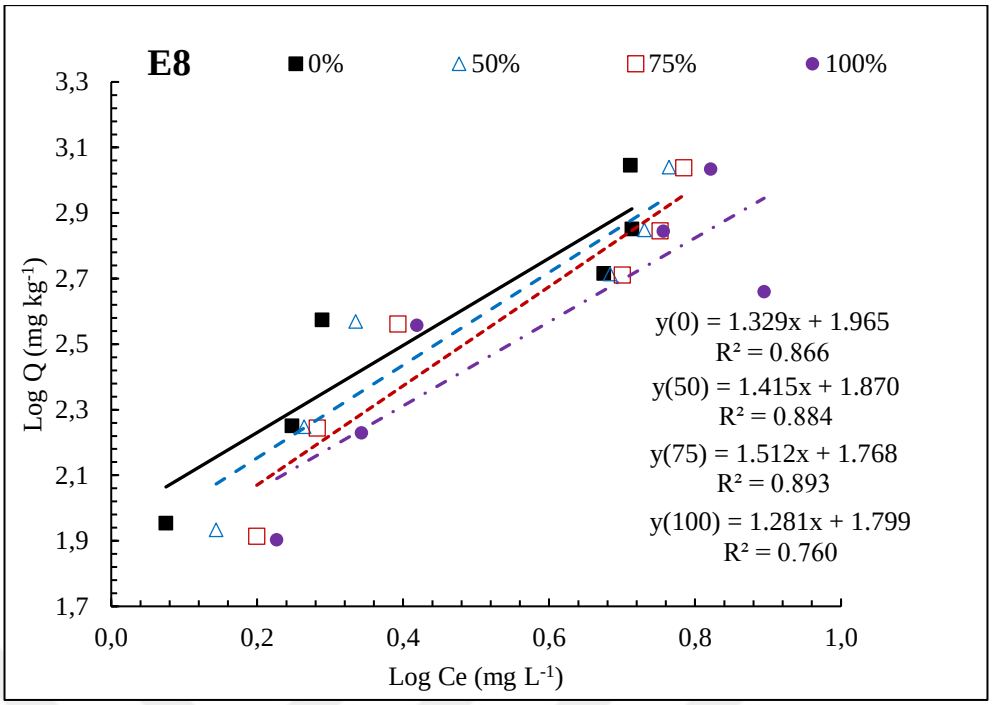

Figure 4.40. Linear Freundlich isotherms of E8 soil treated with differing lime requirements

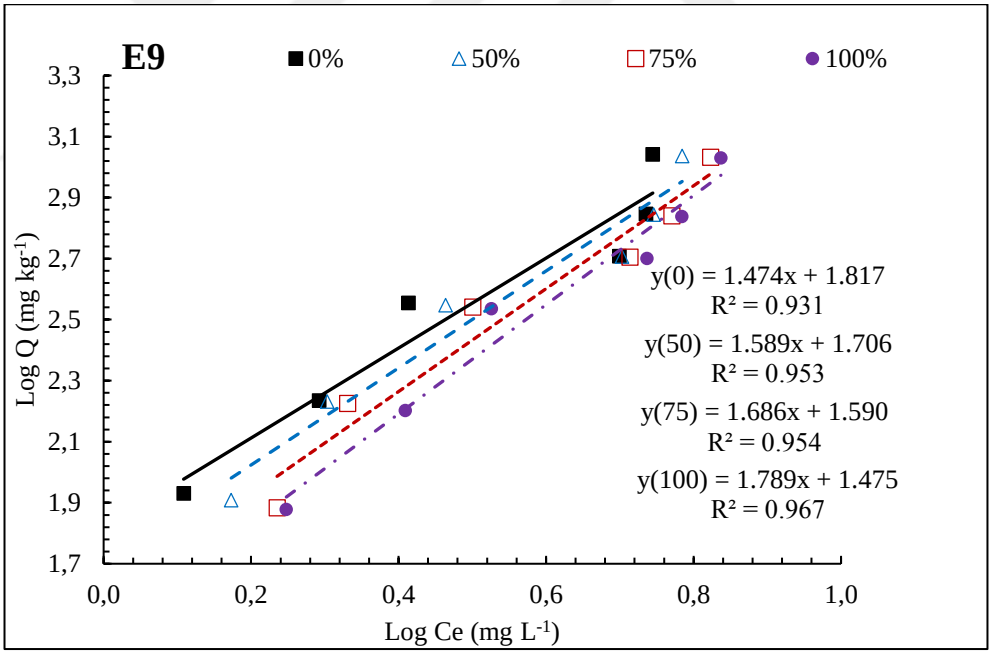

Figure 4.41. Linear Freundlich isotherms of E9 soil treated with differing lime requirements

Based on Figure 4.42 until Figure 4.44, the coefficient of determination or R-squared of regression analysis of phosphorus adsorption on E10, E11, and E14 soil with Freundlich isotherm ranged from 0.909 – 0.964 for E10, 0.952 – 0.970 for E11, and 0.739 – 0.817 for E14. This suggests a robust correlation between the variables investigated in the experiment. As a result, the findings indicate that the data obtained

from soil E10 are dependable and suitable for further analysis and interpretation. The n values of E10, E11, and E14 soils showed an increase with the application of liming, ranging between 1.120 – 1.534 for E10, 0.956 – 1.293 for E11, and 1.347 – 1.569 for E14.

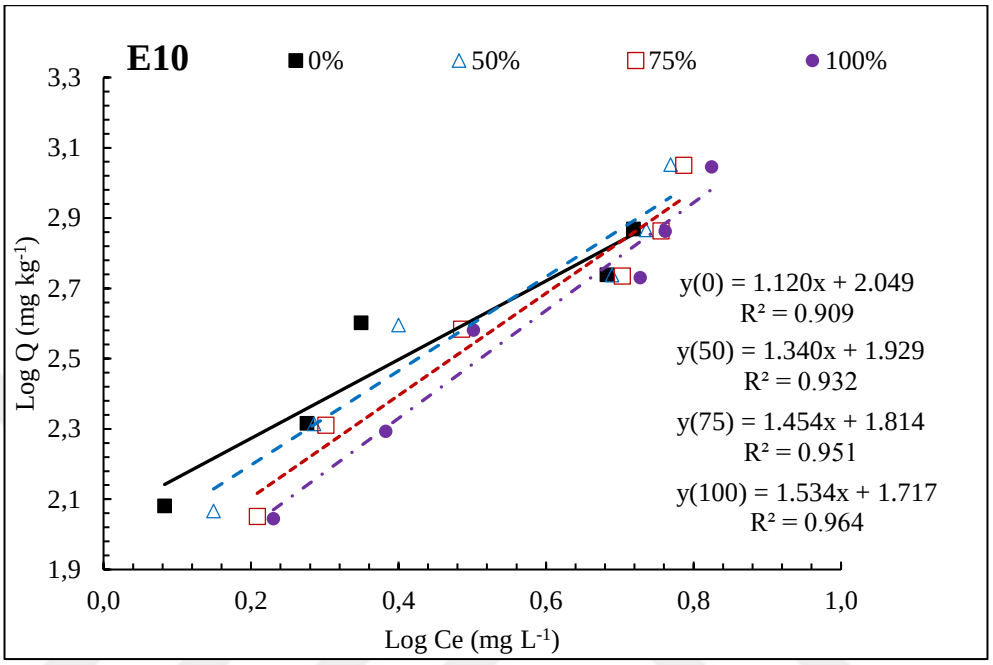

Figure 4.42. Linear Freundlich isotherms of E10 soil treated with differing lime requirements

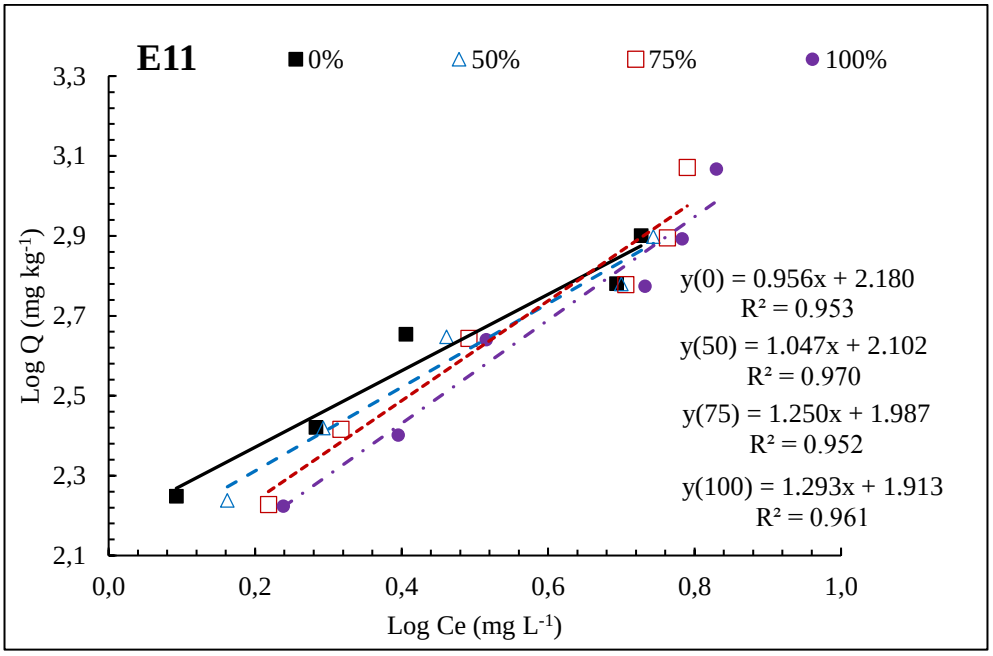

Figure 4.43. Linear Freundlich isotherms of E11 soil treated with differing lime requirements

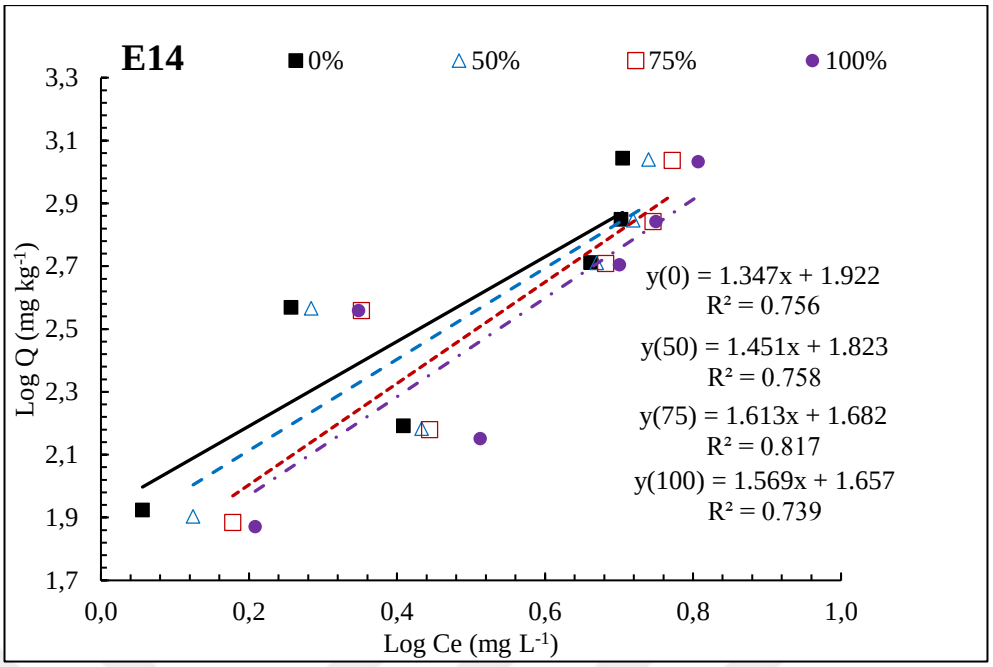

Figure 4.44. Linear Freundlich isotherms of E14 soil treated with differing lime requirements

The rising n values suggested that the ion-ion interaction increased and the soil bind the P with weaker strength. Consequently, the application of liming positively influenced the phosphorus availability of the soils. In contrast, the Kf values of E10, E11, and E14 soils declined with the increasing application of liming, ranging from 2.049 – 1.717 mg kg^{-1} for E10, 2.180 – 1.913 mg kg^{-1} for E11, and 0.739 – 0.817 mg kg^{-1} for E14. The decreasing Kf values suggested a weakening of the interactions between phosphorus and the soil, resulting in a reduced ability of the soil to retain phosphorus through adsorption. As a result, with higher liming, the soil's capacity to bind and retain phosphorus diminishes, potentially leading to greater mobility and availability of phosphorus in the soil solution (Sui & Thompson, 2000; Jiao et al., 2007; Shafqat & Pierzynski, 2014). The other point is that liming to a neutral pH around 6.5 maximize P availability because the solubility lines of both the precipitates of Al/Fe and Ca crosses at this pH (Lindsay, 2001). Below this pH favour the precipitation of Al/Fe-P whereas above this pH Ca-P pecipitates. At relatively lower LR treatment the added P can react with the secondary Al/Fe oxides bring about by displacement of these elements from the exchange sites. These may initially increase the P affinity in soils by forming the Fe/Al-P precipitates but increasing pH results in the dissolution of them.

4.3. Effect of The Liming Ratio and Organic Acids with Langmuir Isotherm

4.3.1. Liming effect

Figure 4.45 shows the relationship between phosphorus concentration and phosphorus adsorption by Langmuir adsorption isotherm. The determination coefficient of the regression models for E1 and soil varied between 0.752 – 0.892. Decreasing values indicate a decrease in the solubility of native phosphorus as liming increases. The Langmuir adsorption constant (Kl) ranged from 2.444 to 4.621 L mg^{-1}. An increase in the Kl values suggest a stronger affinity between the adsorption sites and phosphorus. It is observed that energy affinity of sites was strong at low P concentration, but there was precipitation at concentration of 3 mg L^{-1} on liming application and 2.7 mg L^{-1} on liming 0%. This indicates that there was precipitation by Ca and Fe of P resulting in reduced P adsorption (Anderson et al., 2013). However, the maximum adsorption in soil E1 decreased with the increase in liming, which ranged from 1 136 – 746 mg kg^{-1}. The addition of calcium through liming formed insoluble calcium phosphate minerals in the solution. These minerals tended to precipitate out of the solution rather than being adsorbed onto the surface. This further reduces the effective adsorption capacity for phosphorus (Anderson et al., 2013).

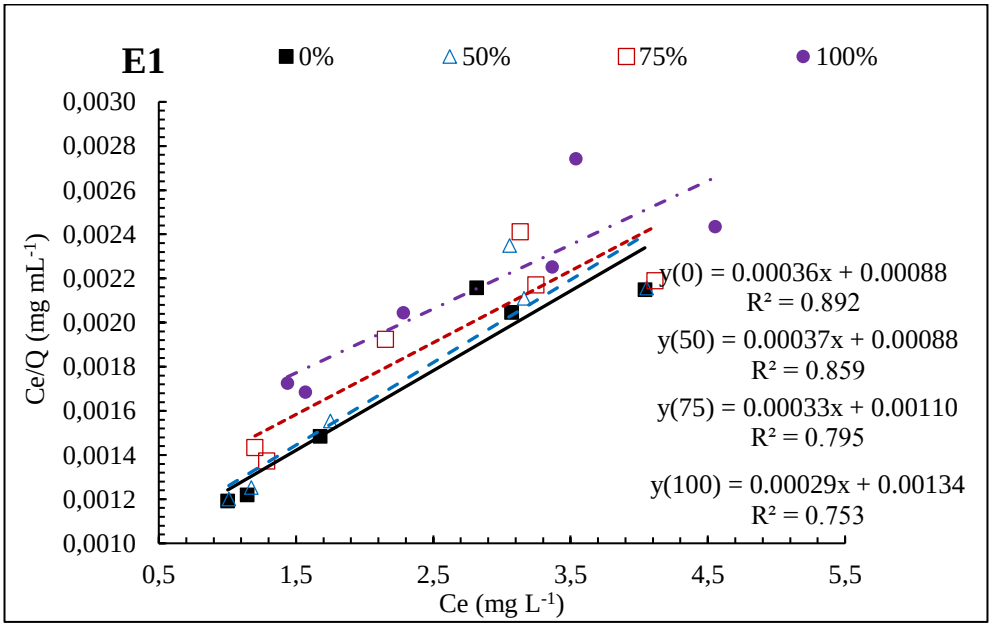

Figure 4.45. Linear Langmuir isotherms of E1 soil treated with differing lime requirements

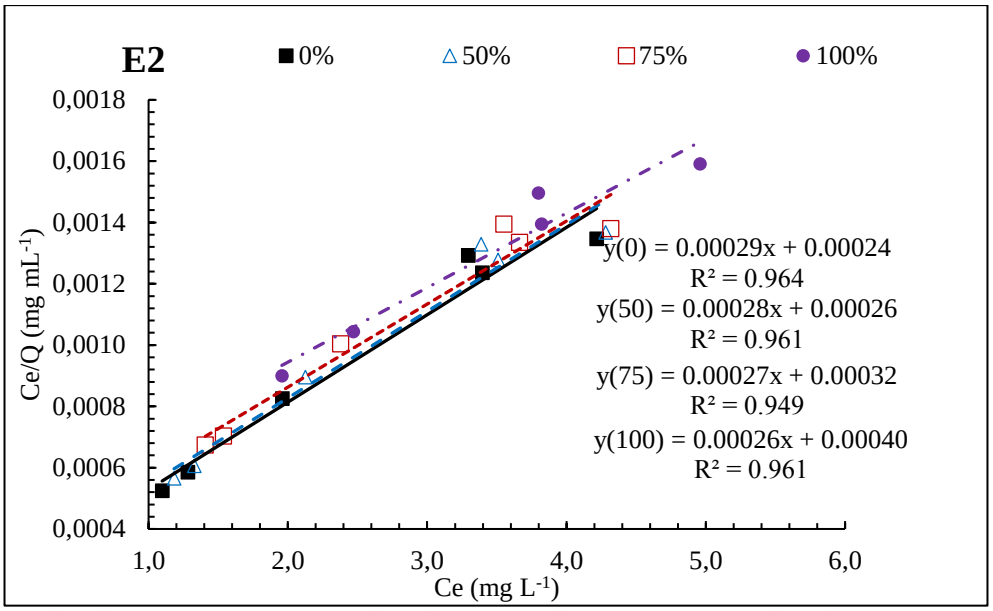

Figure 4.46. Linear Langmuir isotherms of E2 soil treated with differing lime requirements

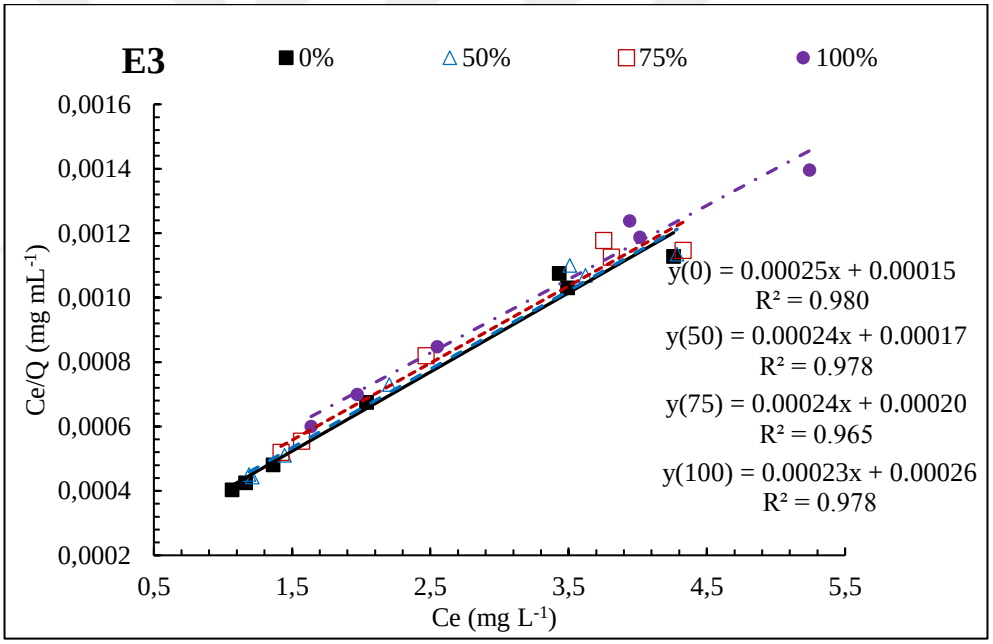

Figure 4.47. Linear Langmuir isotherms of E3 soil treated with differing lime requirements

As shown in Figure 4.46 and Figure 4.47, the regression coefficient of E2 soil and E3 soil ranged between 0.949 – 0.964 and 0.965 – 0.980. The regression results indicate that the parameter's value of Langmuir isotherm was justifiable. The Kl values of E2 and E3 ranged from 0.828 to 1.538 L mg^{-1} and 0.600 to 1.130 L mg^{-1}, respectively. The values was almost similar for all liming ratios, even there was increase in Kl values from E2 and E3. The two of soils had precipitation of Ca-P between 3.5 – 4 mg L^{-1} of P concentration. Even so, there was increase of adsorption along with the liming ratio.

This indicates that solubility of native phosphorus enhanced the mechanism of adsorption. The maximum adsorptions ranged from 4 167 to 2 500 mg kg^{-1} for E2 and 6 667 to 3 846 mg kg^{-1} for E3. The E3 soil has a higher maximum adsorption capacity than E2, suggesting that the solid surface in E3 condition can adsorb a tremendous amount of the adsorbate than in E2 condition. If lime ions compete with phosphorus for adsorption sites, it can reduce the amount of phosphorus adsorbed on solid surface (Lee & Kim, 2007).

According to Figure 4.48 and Figure 4.49, the coefficient of determination for the E4 and E5 soil ranged between 0.911 – 0.929 and 0.868 – 0.943, respectively. Liming 100% has lowest R^2, indicating low amount of indigenous phosphorus in the soils. However, the regression results was justified. The Kl values of E4 and E5 varied between 1.471 – 2.586 L mg^{-1} and 1.609 – 2.650 L mg^{-1}, respectively.

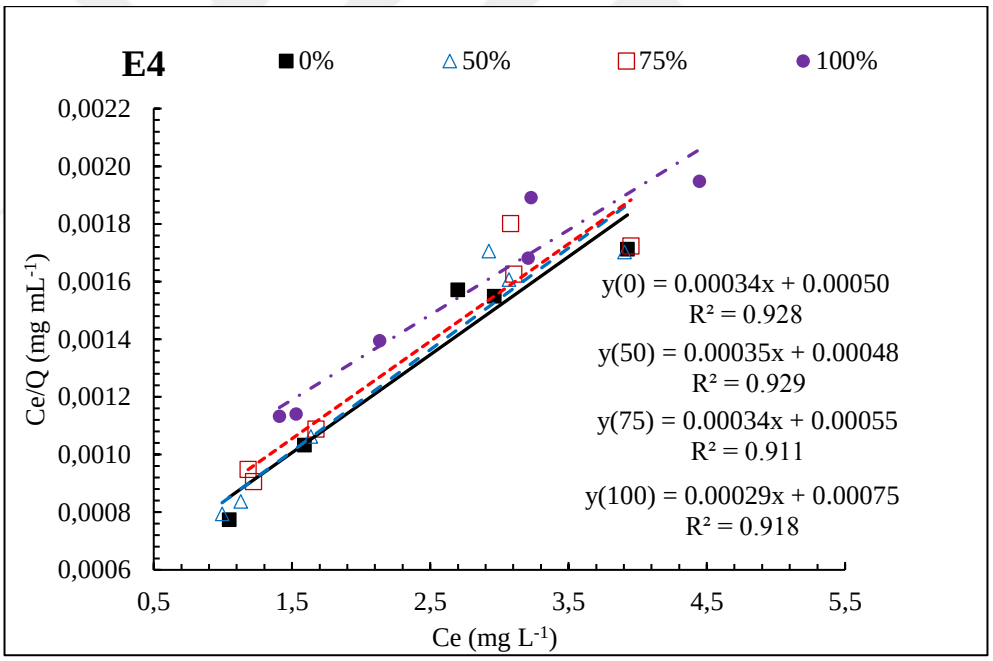

Figure 4.48. Linear Langmuir isotherms of E4 soil treated with differing lime requirements

There was a drastic decrease in adsorption at 50% lime application, but adsorption increased again at 75% and 100% liming. The presence of dissolved P ions from indigenous sources could contribute to the ionic strength of the solution. Higher ionic strength could lead to stronger electrostatic interactions between phosphorus ions and the soil surfaces, promoting adsorption (Simonsson et al., 2018). The maximum adsorption values of E4 and E5 decreased as the liming level increases, which ranged

between 2 000 – 1 333 mg kg^{-1} for E4 and 1 149 – 943 mg kg^{-1} for E5. The variations in the maximum adsorption could be influenced by changes in the surface area, surface charge, or the availability of active sites on solid surface (Errassifi et al., 2010). With the addition of lime, it might decrease the quantity of phosphorus by increasing soil pH (Wei et al., 2014; Simonsson et al., 2018).

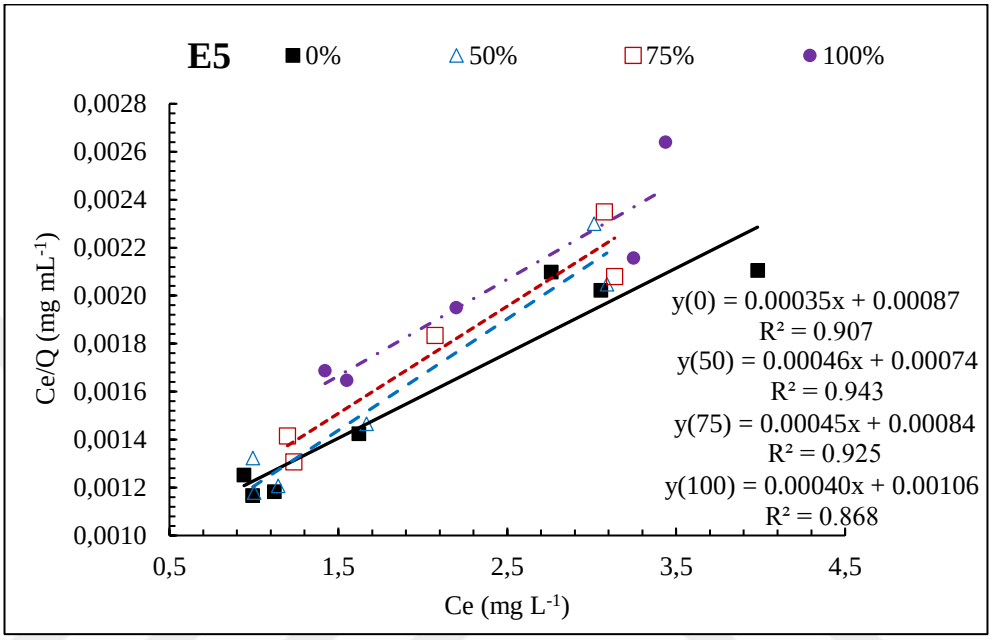

Figure 4.49. Linear Langmuir isotherms of E5 soil treated with differing lime requirements

Based on Figures 4.50 and 4.51, the regression coefficient for E7 and E8 soil ranged from 0.874 - 0.938 and 0.875 - 0.919. The lowest R^2 on liming ratio 100% suggests the adsorption of added P increased rather than native P. However, this indicates a good fit of the regression models to the experimental data. The Kl values for E7 ranged from 1.935 to 3.200 L mg^{-1}, while E8 ranged from 1.583 to 3.138 L mg^{-1}. The increase in Kl values indicates that there was presence of dissolved P ions from indigenous sources enhanced the adsorption (Simonsson et al., 2018). Moreover, precipitation P with Fe/Ca was observed even at low P concentrations followed by increased adsorption and adsorption rates started to reduce at higher P concentration. Maximum adsorptions (E7: 1 124 – 781 mg kg^{-1} and E8: 1 754 – 1 099 mg kg^{-1}) demonstrated reduction of adsorption capacity of soil surface. Higher values of maximum adsorption for E8 indicate that the solid surface in this condition can adsorb immense amount of the adsorbate compared to the E7 soil. This implies that the E8 soil provides a more favorable environment for adsorption, accommodating a higher quantity of the

adsorbate on the solid surface. Calcium phosphate had a tendency to precipitate out of the solution rather than being adsorbed onto the surface, thereby diminishing the soil's effective capacity for phosphorus adsorption (Anderson et al., 2013; Liu, 2015).

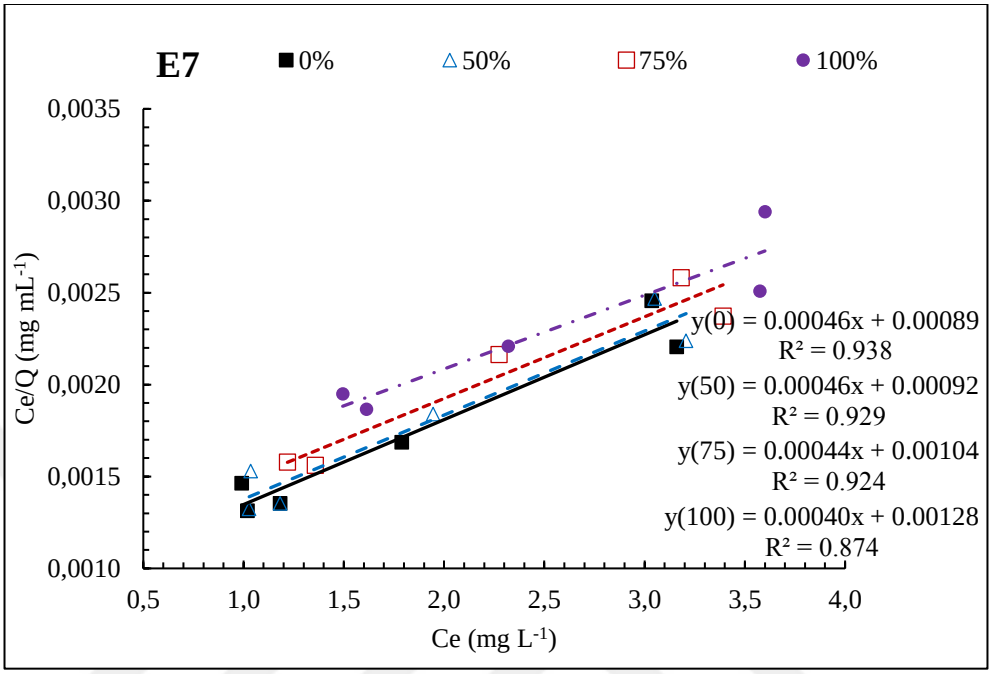

Figure 4.50. Linear Langmuir isotherms of E7 soil treated with differing lime requirements

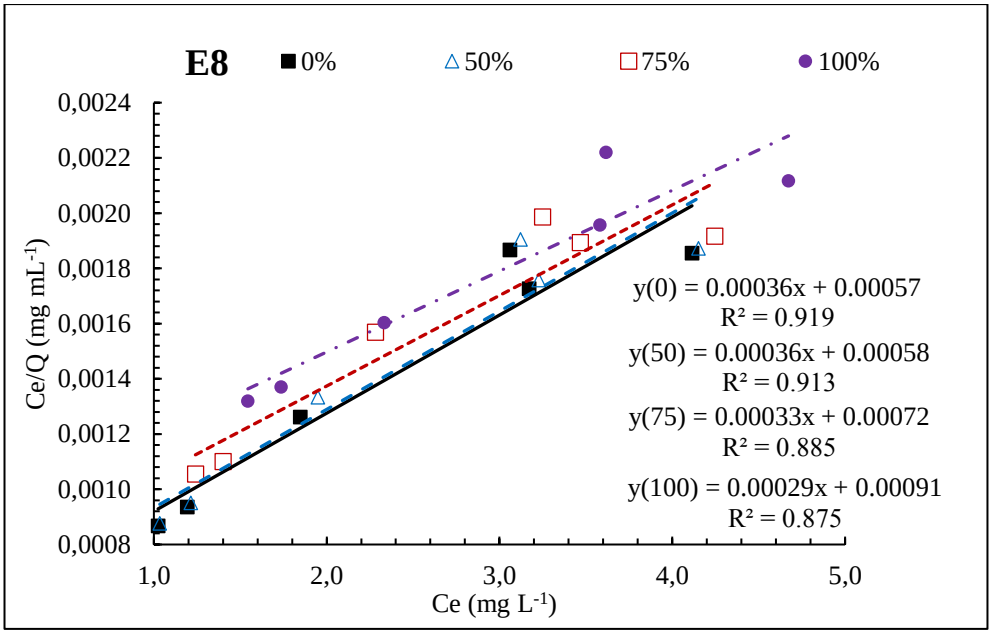

Figure 4.51. Linear Langmuir isotherms of E8 soil treated with differing lime requirements

Based on Figure 4.52 and Figure 4.53, there was a higher scatter of data in E9 than E10 in the high phosphorus concentration section. This causes the R^2 value in E9 to

range between 0.820 to 0.895, and E10 ranged from 0.902 to 0.932. However, the data points for E9 and E10 are well-fitted to the regression lines, suggesting a reliable relationship between the phosphorus concentration and its adsorption on the solid surface.

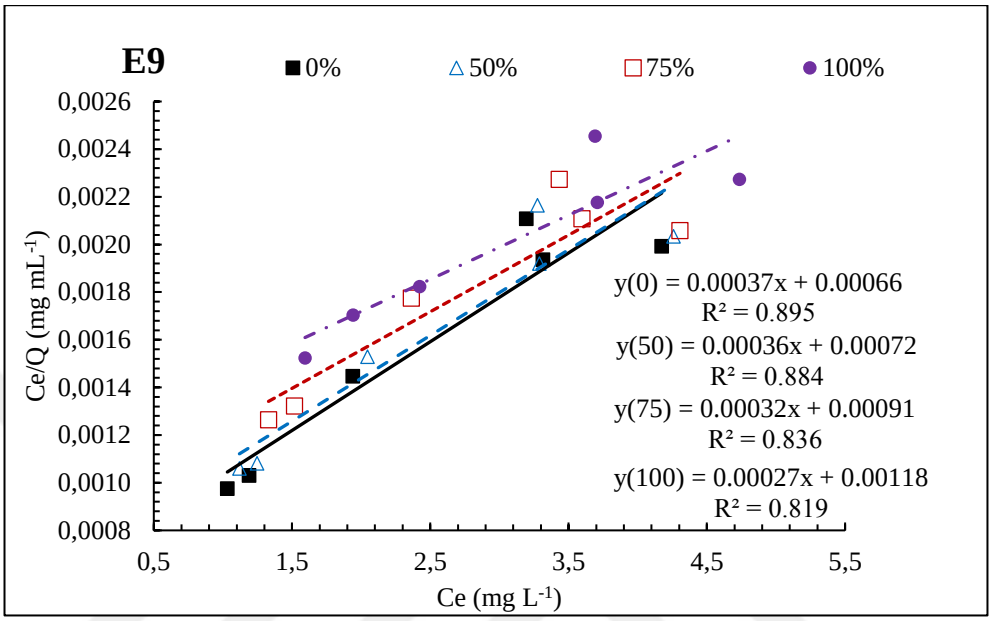

Figure 4.52. Linear Langmuir isotherms of E9 soil treated with differing lime requirements

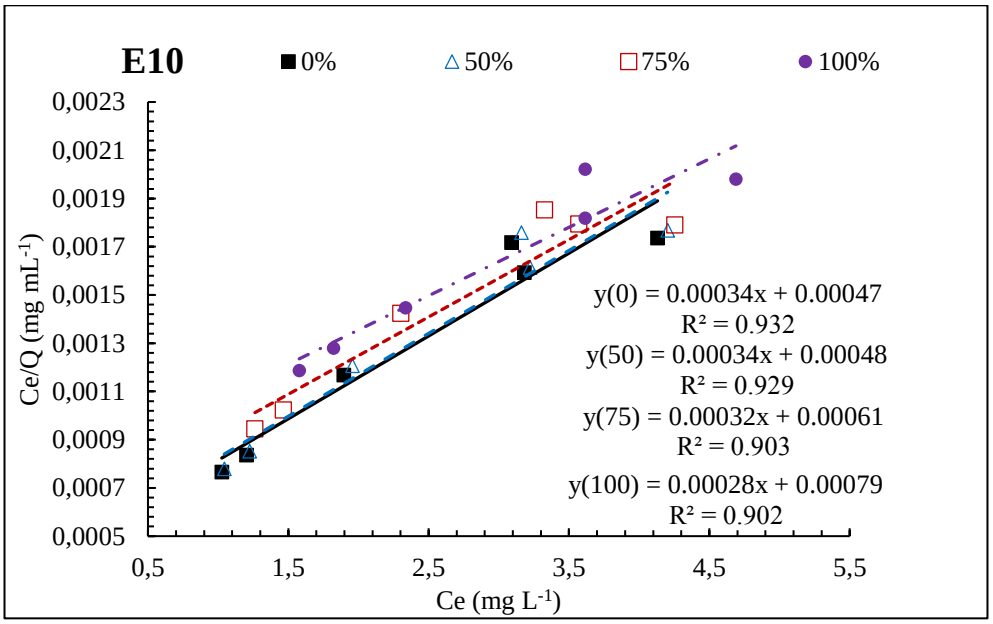

Figure 4.53. Linear Langmuir isotherms of E10 soil treated with differing lime requirements

The Kl values for E9 ranged from 1.784 to 4.370 L mg^{-1}, and E10 ranged from 1.382 to 2.821 L mg^{-1}. There was strong adsorption at initial concentration for both of soils

until reached concentration around 3.5 mg L^{-1}, it started to decrease because of the competition with other moleculs. Due to the application of liming, Ca^{2+} could bind P to be calcium phosphate and as this complex form hindered the phosphorus adsorption (Ghasemi & Asadpour, 2007). Meanwhile, the maximum adsorptions for E9 ranged from 1 515 to 847 mg kg^{-1} while, E10 ranged from 2 128 to 1 266 mg kg^{-1}. The maximum adsorptions (Qmax) decreased as the liming increased, indicating liming affected the soil pH by promoting Ca^{2+} in the soils, which could be competitor for soil surfaces to adsorp P. This case influenced Qmax values of E9 and E10 soils to be reduced as liming function (Ejigu et al., 2023).

According to Figure 4.54 and Figure 4.55, the regression data reveals distinct adsorption behaviors between E11 and E14 soil with a range of 0.923 – 0.945 (E11) dan 0.844 – 0.911 (E14). E11 and E14 show a strong and reliable correlation (represented by high R-squared values) between the adsorbate concentration and its adsorption on the solid surface. The high R-squared values indicate that the data points for both E11 and E14 fit well with the regression lines, indicating a robust relationship between the variables.

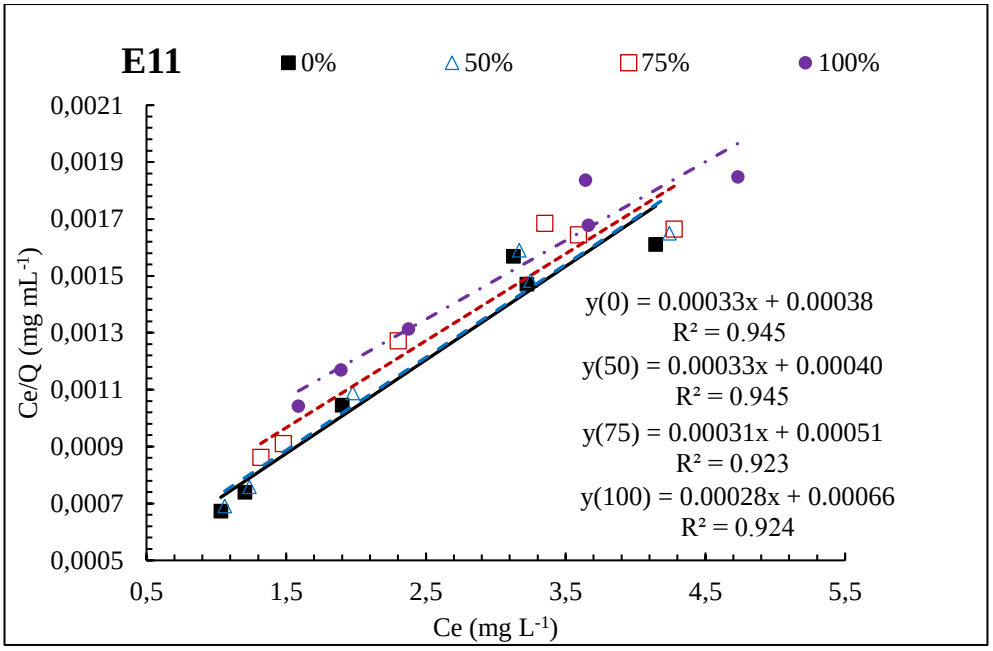

Figure 4.54. Linear Langmuir isotherms of E11 soil treated with differing lime requirements

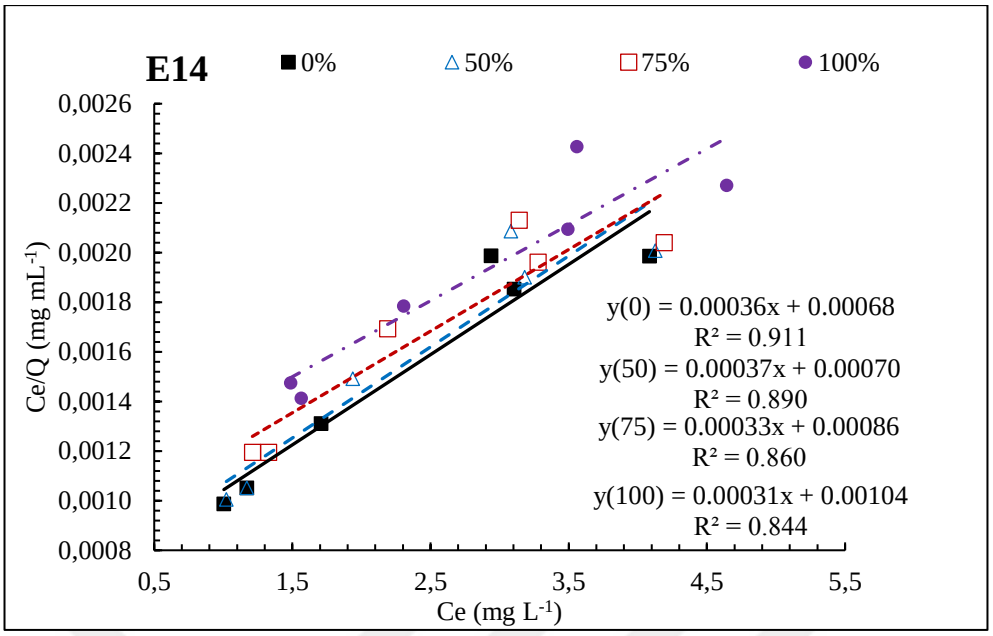

Figure 4.55. Linear Langmuir isotherms of E14 soil treated with differing lime requirements

Regarding Kl values, E11 exhibits values ranging from 1.152 to 2.357 L mg^{-1}, while E14 ranges from 1.889 to 3.355 L mg^{-1}. The increase in Kl values from 0 – 100% liming signifies a strengthening of the interactions between phosphorus and the soil surface in the E11 and E14 condition. The adsorption was robust at initial concentration then precipitation carried out on liming 0 – 75% at P concentration of 3 – 3.5 mg L^{-1}. Meanwhile, there was increasing of intermolecular interaction above 3.5 mg L^{-1} of P concentration at liming 100%. Furthermore, considering the maximum adsorptions, E11 showed values ranging from 2 632 to 1 515 mg kg^{-1}, whereas E14 displays a range of 1 471 to 962 mg kg^{-1}. Higher values of maximum adsorption for E11 suggest that the solid surface in this condition can adsorb a more significant amount of the adsorbate than E14. The Qmax decreased as the liming increased, indicating liming significantly affected the maximum adsorption by enhancing complexation of Ca-P (Gisi et al., 2016; Ejigu et al., 2023).

4.3.2. The co-effects of citric acid and liming ratio

The phosphorus (P) sorption data from soils treated with citric acid were analyzed using the linear version of Langmuir adsorption isotherm model. Figure 4.56 illustrates the adsorption isotherms and model parameters for the E1 soil. The coefficient of

determination for the regression models of E1 soil ranged from 0.987 to 0.999, suggesting that the obtained values were highly reliable.

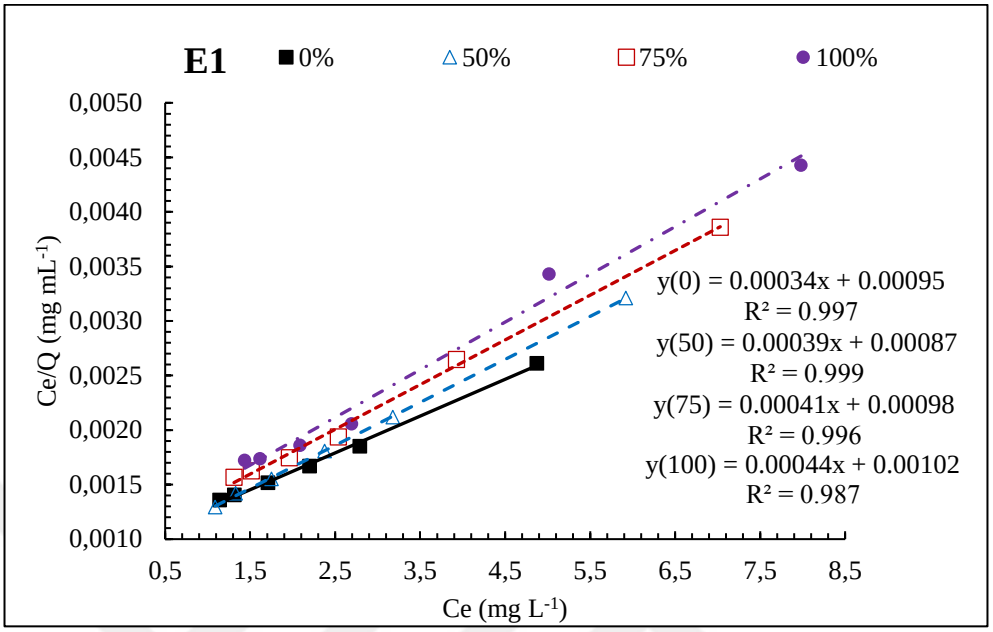

Figure 4.56. Linear Langmuir isotherms of E1 soil treated with differing lime requirements

The Kl values decreased as a function of liming, which ranged from 2.794 – 2.318 L mg^{-1}. Adsorption was rapid at the initial concentration, although as the concentration increased adsorption was further depressed by ion competition at 75% and 100% liming at P concentrations of 4 mg L^{-1} and 5 mg L^{-1}. This indicates the effect of increasing pH through liming to decrease adsorption. This case enhanced availability of phosphorus in the solution due to the addition of citric acid (Schmitt et al., 2017; Dunne et al., 2020). In line with this, the maximum adsorption decreased in the range of 1 149 – 980 mg kg^{-1}. The liming promoted Ca^{2+} to the soils and caused binding with phosphorus. That form known as complex binding and it was hard to be adsorb to the adsorption sites. In results, maximum adsorption E1 soils decreased due to liming application (Perassi & Borgnino, 2014).

Based on Figure 4.57 and Figure 4.58, the value of the coefficient of determination of E2 and E3 soil implied that 90% of the variance in the dependent variable is explained by the independent variables in the model, which suggested a good fit for the results. The coefficient of determination (R^2) ranged from 0.981 – 0.993 for E2 and 0.966 – 0.973 for E3 soil.

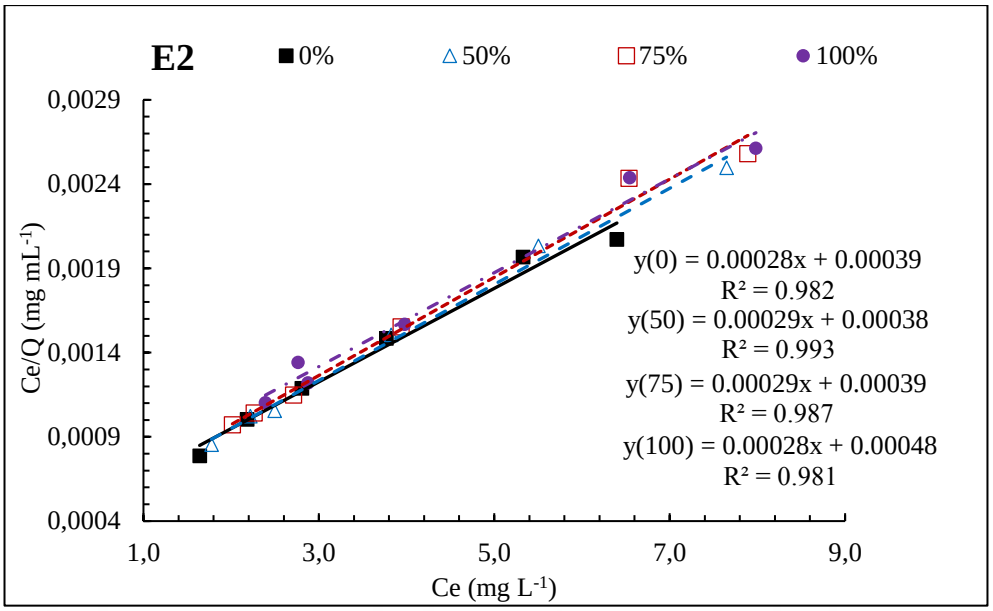

Figure 4.57. Linear Langmuir isotherms of E2 soil treated with differing lime requirements

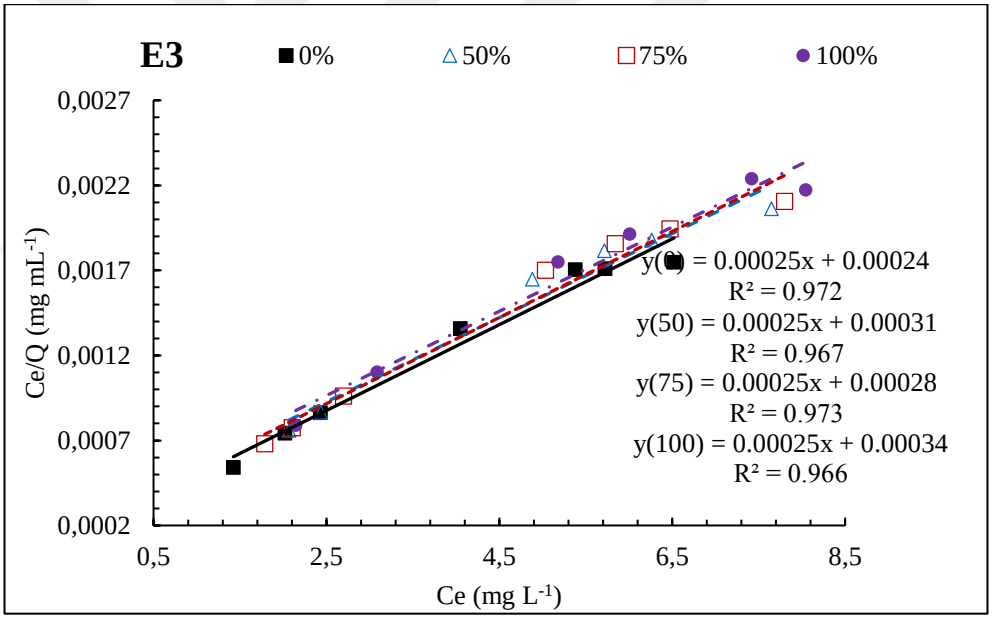

Figure 4.58. Linear Langmuir isotherms of E3 soil treated with differing lime requirements

The Kl values ranged from 1.310 to 1.714 L mg^{-1} for E2 and 0.960 to 1.360 L mg^{-1} for E3. The phosphorus adsorption in E3 soil was lower than E2 soil. Moreover, adsorption rates were robust at initial concentration of phosphorus for both soils. At liming 75% and 100%, adsorption reduced due to competition with other ions. This indicates when the soil pH is increased through liming, the calcium ions (Ca^{2+}) released during the liming process can compete with phosphorus ions (P^{-3} or $H_2PO_4^-$) for binding sites on soil particles (Wang et al., 2106a). However, the

maximum adsorption decreases with increasing liming, ranging from 2 564 – 2 083 mg kg^{-1} for E2 and 4 167 – 2 941 mg kg^{-1} for E3. The most probable influence for Qmax decline was from citric acid, which could form complex bonds with the certain compounds that was difficult to be adsorbed to the phosphorus sites. Adding lime dosage could lead to physical and chemical changes on the soil surface (Moradi et al., 2012).

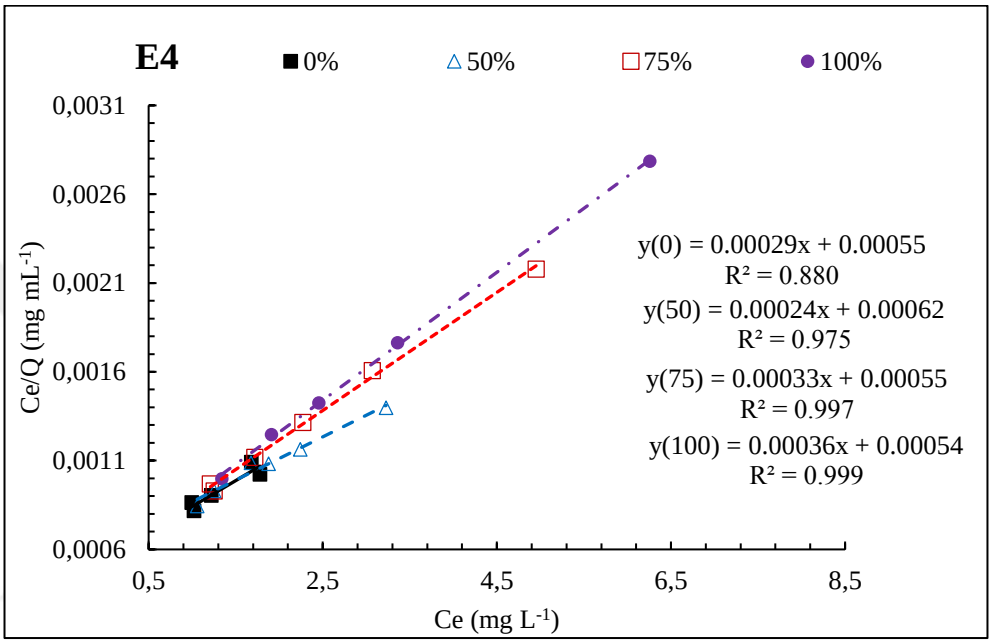

Figure 4.59. Linear Langmuir isotherms of E4 soil treated with differing lime requirements

Based on the regression analysis results presented in Figure 4.59 and Figure 4.60, the coefficient of determination (R^2) ranged from 0.880 to 0.999 for E4 and 0.982 to 0.999 for E5. There was a large scatter of data in E4 soil without liming. However, these R^2 values signify a strong correlation between phosphorus concentration and its adsorption on E4 and E5 soils. The Kl values ranged from 1.500 – 2.583 L mg^{-1} for E4 and 3.630 – 2.425 L mg^{-1} for E5. At 0% and 50% liming on E4 soil there was more than one adsorption mechanism involved. Even the phosphorus precipitation mechanism occurred at low concentrations. This caused the formation of re-adsorption sites which led to high adsorption (Akrawi et al., 2021). But along with the addition of liming, adsorption continued to decrease. While in E5 soil, there was a not so significant decrease in adsorption. Compared to E4, E5 soil had a higher adsorption rate. Meanwhile, the maximum adsorption ranged from 1 613 – 1 852 mg kg^{-1} for E4 and 1 020 – 1 111 mg kg^{-1} for E5. The lowest value of maximum adsorption for E4

was observed at 50% lime dosage. This suggests that liming had significant effect to decrease maximum adsorption. In contrast, E5 showed no significant influence of liming on the maximum adsorption, as implies that E5 soil has similar Qmax values. This indicates that with liming use might enhance complexation of Ca-P and minimazed the capacity of adsorption sites (Gunary, 2006).

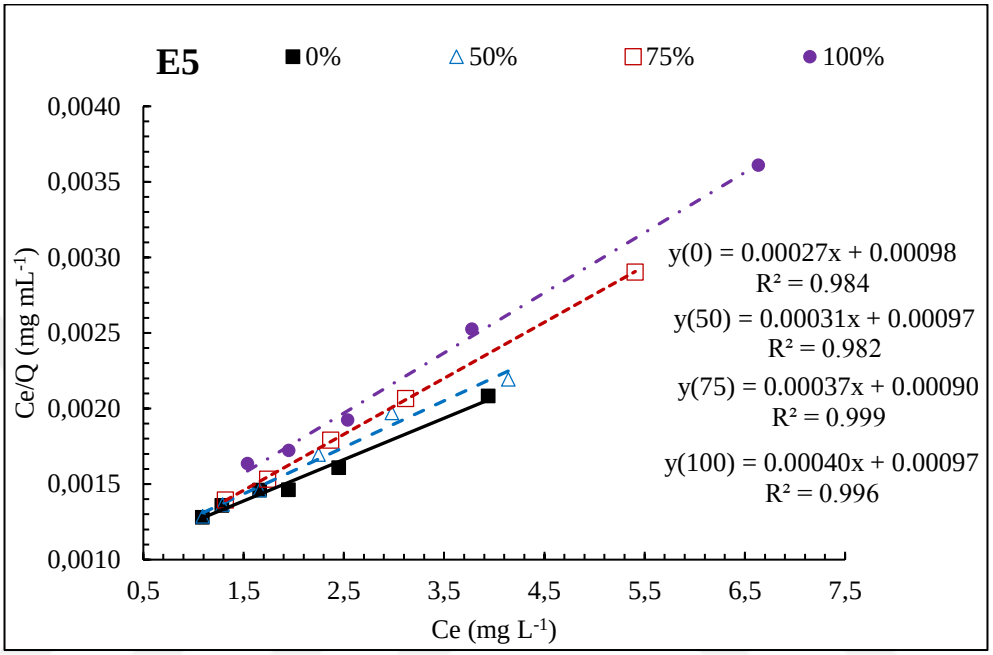

Figure 4.60. Linear Langmuir isotherms of E5 soil treated with differing lime requirements

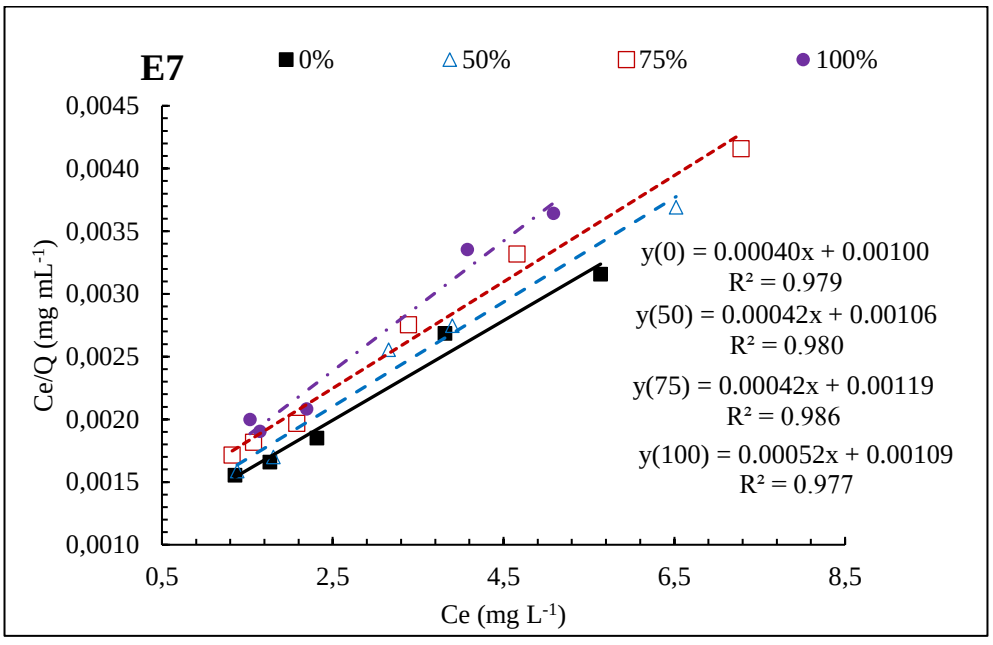

Figure 4.61. Linear Langmuir isotherms of E7 soil treated with differing lime requirements

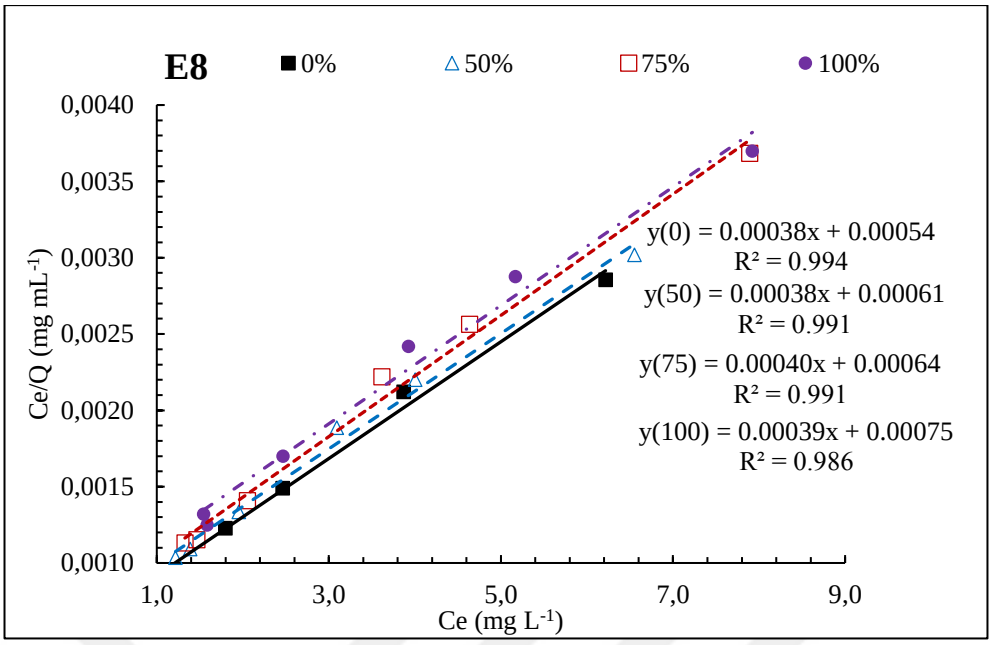

Figure 4.62. Linear Langmuir isotherms of E8 soil treated with differing lime requirement

Based on Figure 4.61 and Figure 4.62, the regression coefficient (R^2) for E7 soil ranged from 0.977 – 0.986. Meanwhile, R^2 for E8 varied between 0.986 – 0.994. These values represented the fit of the regression model for E7 and E8 soil data. The Kl values of E7 and E8 ranged from 2.096 – 2.833 L mg^{-1} for E7 and 1.421 – 1.923 L mg^{-1} for E8. The maximum adsorption for E7 varied between 1 000 – 840 mg kg^{-1} and E8 ranged between 1 852 – 1 333 mg kg^{-1}. The rise in Kl values of two soils suggests the enhance of adsorption affinity, leading to a more favorable adsorption process at higher lime dosages but the liming 100% on E7 soil had adsorption weaker at initial concentration because of precipitation to be calcium phosphate. The maximum adsorption of E7 and E8 soil decreased as the liming rates improved. The adsorption capacity of both soils was significantly influenced by higher lime dosages, resulting in a low ability to adsorb phosphorus from the solution (Eslamian et al., 2021).

As seen in Figure 4.63 and Figure 4.64, the regression coefficient of E9 ranged from 0.968 to 0.992, while in soil E10, it varied from 0.946 to 0.993. These R-squared values indicate a robust and acceptable correlation between the phosphorus concentration and its adsorption on the soil surface for E9 and E10 conditions. The Kl values for E9 and E10 soils varied from 1.377 to 2.684 L mg^{-1} and 1.270 to 1.816 L mg^{-1}, respectively. The increase in Kl values for both soils indicates an improvement in adsorption affinity, making the adsorption process more favorable at higher lime application rates.

The mechanism underlying this enhancement involves the creation of additional adsorption sites, facilitating the uptake of phosphorus by the soil (Hasan et al., 2016). However, when 100% lime was applied to the E7 soil, the initial concentration showed weaker adsorption due to the formation of calcium phosphate precipitation (Eslamian et al., 2021).

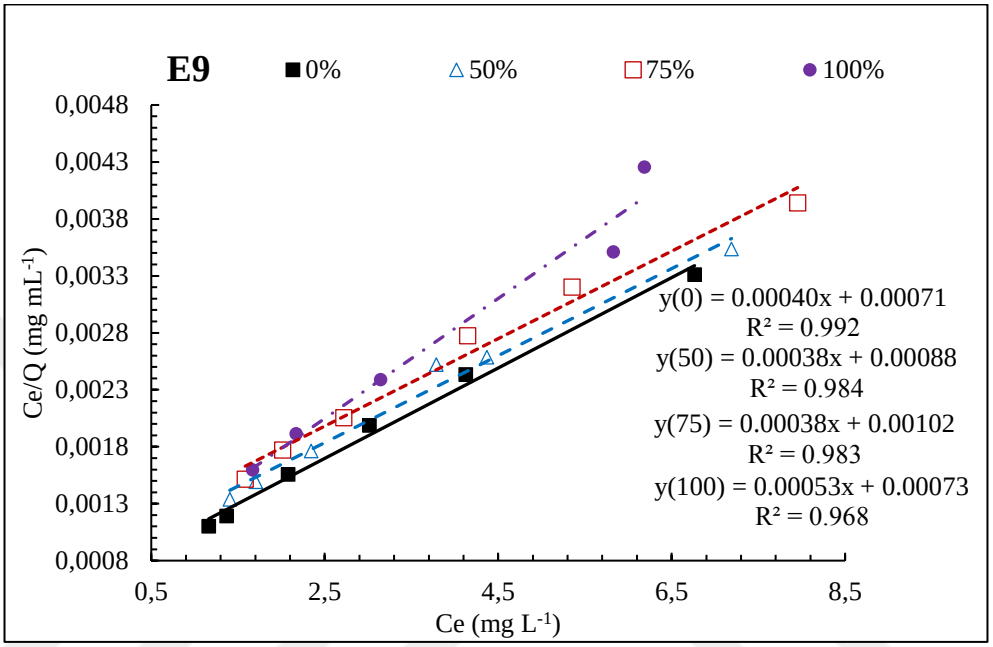

Figure 4.63. Linear Langmuir isotherms of E9 soil treated with differing lime requirements

The maximum adsorption for E9 soil continued to decrease with increasing lime dosage until reaching 75%, which increased when the dosage was further increased to 100%. The maximum adsorption for E9 soil ranged from 1 408 to 980 mg kg^{-1}. On the other hand, for E10 soil, the maximum adsorption steadily decreased with the escalation of lime dosage, which ranged between 2 128 to 1 449 mg kg^{-1}. This indicates that there was present of calcium in the environment that compete with phosphorus for adsorption sites. This could lead to a decrease in the maximum adsorption (Hasan et al., 2016).

Based on Figure 4.65 and Figure 4.66, the regression coefficients (R-squared) for E11 ranged from 0.960 to 0.993, while E14 ranged from 0.988 to 0.992. These high R-squared values indicate strong correlations between the phosphorus concentration and its adsorption on E11 and E14 soils. This suggests that the Langmuir isotherm model is appropriate for representing phosphorus adsorption on both soils.

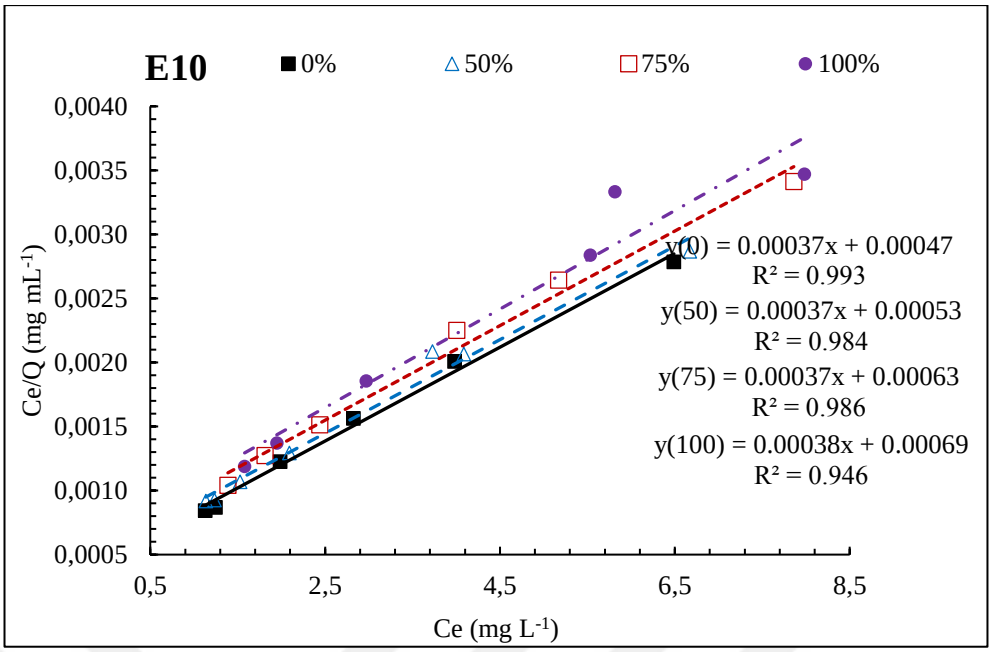

Figure 4.64. Linear Langmuir isotherms of E10 soil treated with differing lime requirements

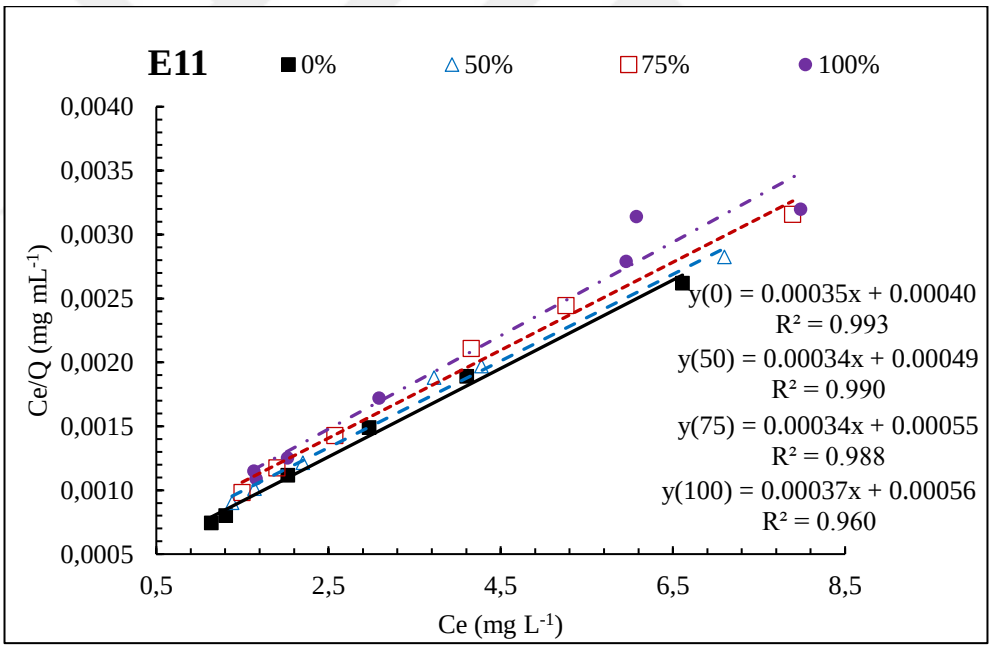

Figure 4.65. Linear Langmuir isotherms of E11 soil treated with differing lime requirements

Regarding the Kl values, E11 exhibited values ranging from 1.143 to 1.618 L mg^{-1} and 1.366 to 1.976 L mg^{-1} for E14. The data suggest that the Kl values increased with higher lime dosage for E11 and E14 soils. This implies that the interaction strength between phosphorus and the solid surface of both soils became stronger with increasing lime dosage because of solubility of native phosphorus. In addition, an increase in the surface charge of the soil enhances the electrostatic interactions

between ions in the solution and the adsorption sites on the soil surface. This increases the attraction between the soil surface and the solution's phosphate ions (PO_4^{3-}) (Bolan et al., 2003; Amin, 2018).

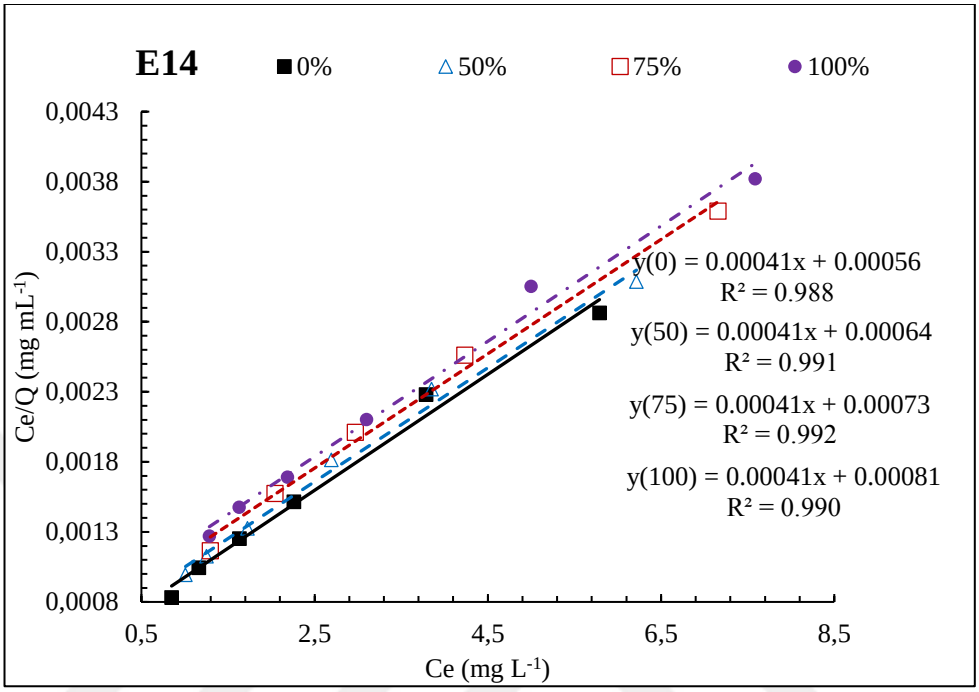

Figure 4.66. Linear Langmuir isotherms of E14 soil treated with differing lime requirements

The maximum adsorptions for E11 ranged from 2 500 to 1 786 mg kg^{-1}; and E14 ranged from 1 786 to 1 235 mg kg^{-1}. The data indicate that the maximum adsorptions decreased with higher lime dosage for E11 and E14 soils. This indicates the presence of calcium in the surroundings can compete with phosphorus (P) for available adsorption sites, resulting in a reduction in the maximum adsorption capacity of the desired substance (Ström et al., 2002; Yang et al., 2019b). Furthermore, citric acid could facilitate the breakdown of some calcium compounds in the lime into more soluble forms in the solution. As a result, dissolved calcium reacted with phosphates in the soil, forming more soluble calcium phosphate complexes. Adding citric acid enhances the availability of phosphorus in the solution (Khademi et al., 2010; Zhang et al., 2021; Zhu et al., 2022).

4.3.3. The co-effects of malic acid and liming ratio

In Figure 4.67, the adsorption of phosphorus on E1 soil treated with malic acid is presented using the Langmuir isotherm model. The coefficient of determination (R-squared) for E1 soil ranged from 0.986 to 0.992. This indicates that the values obtained from the analysis were justifiable.

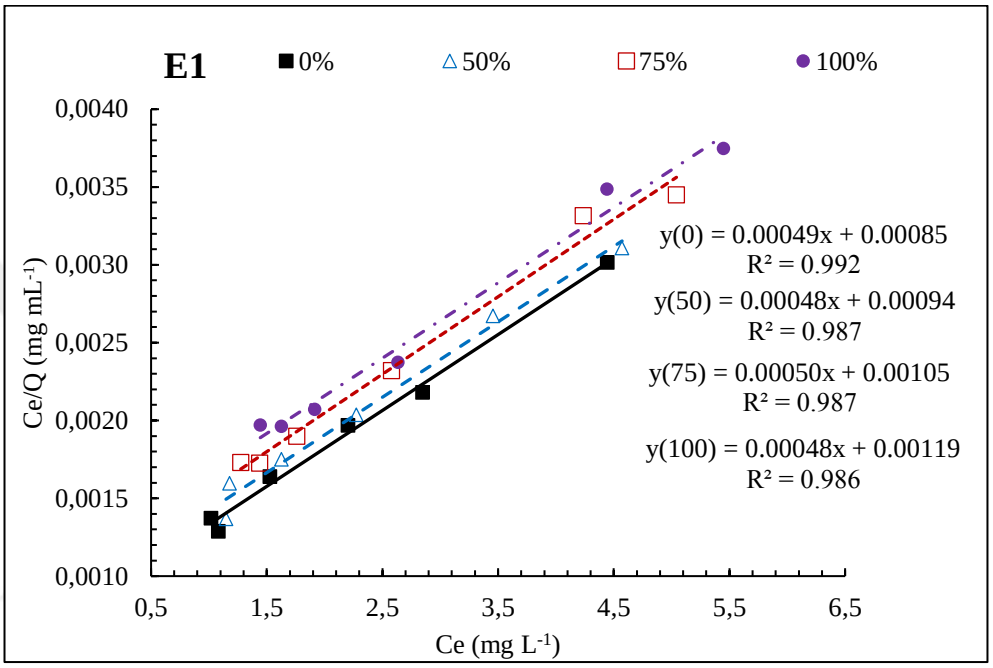

Figure 4.67. Linear Langmuir isotherms of E1 soil treated with differing lime requirements

Based on the presented data, the Kl values (E1: 1.735 – 2.479 L mg^{-1}) showed improvement of adsorption concerning the increase in lime dosage. This indicates that the interaction strength between the phosphorus and the soil surface of E1 soil was strong at initial concentration across different lime dosage levels. However, at 75% and 100% liming, Ca-P precipitation was formed at a P concentration of 4.5 mg L^{-1}. On the other hand, the maximum adsorptions (E1: 1 176 – 840 mg kg^{-1}) demonstrated a decrease trend with the escalation of lime dosage. If the adsorption sites on a material or surface were already occupied by adsorbed substances, the maximum adsorption capacity would be reached, and further adsorption of the same substance might not be possible without desorbing some of the previously adsorbed material. This suggests that liming had a more pronounced impact on the adsorption capacity of E1 soil,

leading to an improved ability to enhance phosphorus availability (Eslamian et al., 2021).

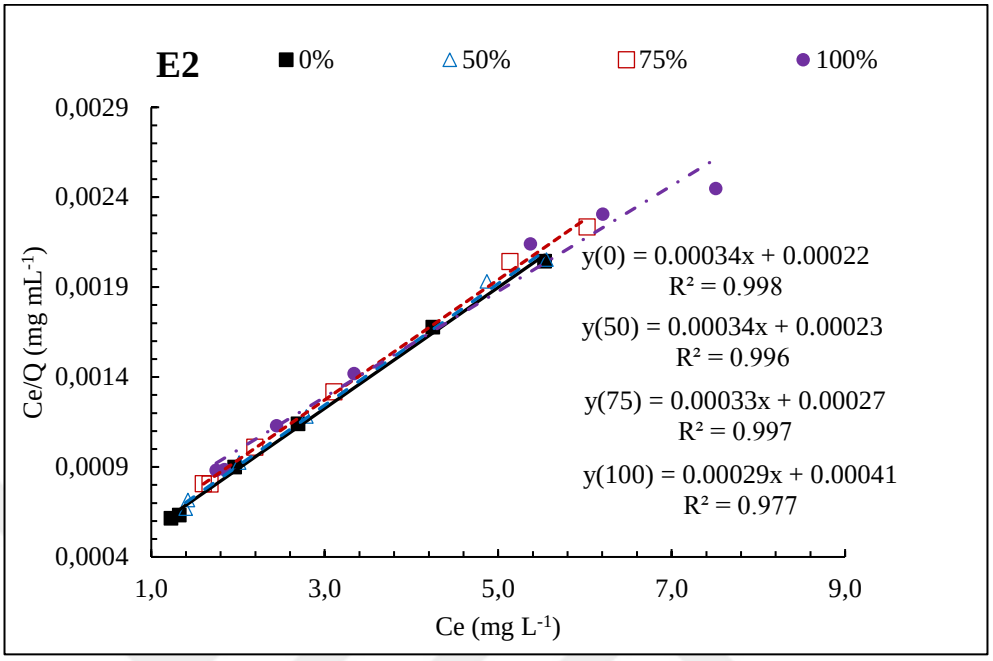

Figure 4.68. Linear Langmuir isotherms of E2 soil treated with differing lime requirements

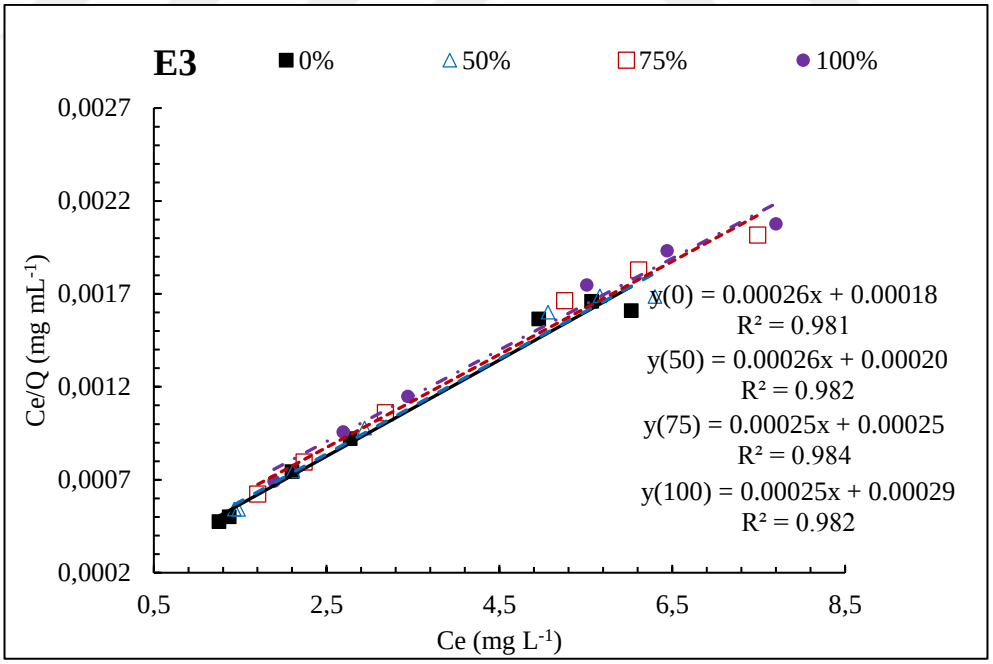

Figure 4.69. Linear Langmuir isotherms of E3 soil treated with differing lime requirements

Based on Figures 4.68 and 4.69, the regression coefficients (R-squared) for E2 ranged from 0.977 to 0.998, while E3 ranged from 0.981 to 0.984. These high R-squared

values indicate strong correlations between the phosphorus concentration and adsorption in E2 and E3 soils. This suggests that the Langmuir isotherm model is suitable for representing phosphorus adsorption on both soils. The Kl values of E2 exhibited values varying from 0.647 to 1.414 L mg^{-1}, and the values were 0.692 to 1.160 L mg^{-1} for E3. The Qmax values ranged between 4 554 – 2 439 mg kg^{-1} for E2 and 5 556 – 3 448 mg kg^{-1} for E3. The adsorption maximum continued to decrease as liming increased. The addition of lime and malic acid indicates competition for phosphorus, lime and organic acid groups that could bind P, thus reducing the maximum adsorption of the soil (Eslamian et al., 2021).

Figure 4.70 and Figure 4.71 presents the adsorption isotherms and model parameters of E4 and E5 soil. The coefficient of determination for the regression models of E4 soil varied from 0.929 to 0.967, and E5 ranged from 0.859 to 0.992. This means that the obtained values were reliable. Consequently, the experimental sorption data validated the Langmuir equation usage. The Kl values of E4 ranged between 1.528 – 1.946 L mg^{-1}, and E5 ranged from 2.188 –2.641 L mg^{-1}.

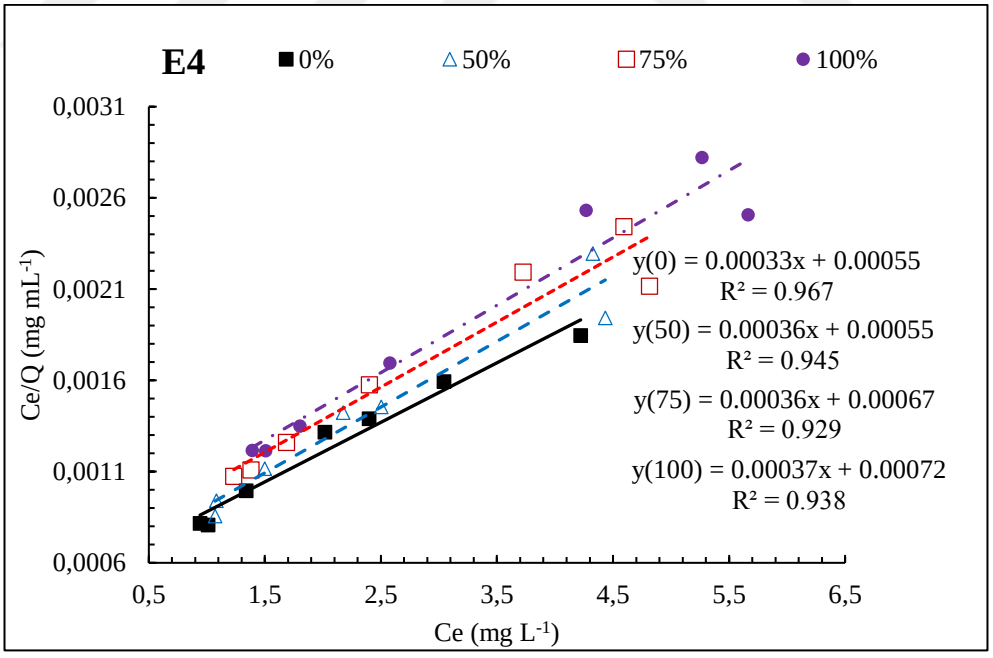

Figure 4.70. Linear Langmuir isotherms of E4 soil treated with differing lime requirements

The Kl values increased with higher lime dosage for E4 and E5 soils. In E4 soils, the adsorption rate was high at low P concentrations, then with 50% lime application at a P concentration of 4.5 mg L^{-1} there was a decrease in adsorption due to Ca or Fe

competition to bind P while at 75% and 100% liming Ca-P precipitation occurred at concentrations of 4.5 – 6 mg L^{-1}. While the process was reversed in E5 soil, where precipitation occurred in 0% and 50% liming while competition with Ca^{2+} occurred in 75% and 100% liming. The maximum adsorption of E4 ranged from 1 818 to 1 493 mg kg^{-1}, while E5 ranged from 1 053 to 885 mg kg^{-1}. The maximum adsorptions decreased with higher lime dosage for both E4 and E5 soils. The data indicate that higher lime dosage enhanced the bonding between phosphorus and calcium, formed into calcium phosphate (Moradi et al., 2012).

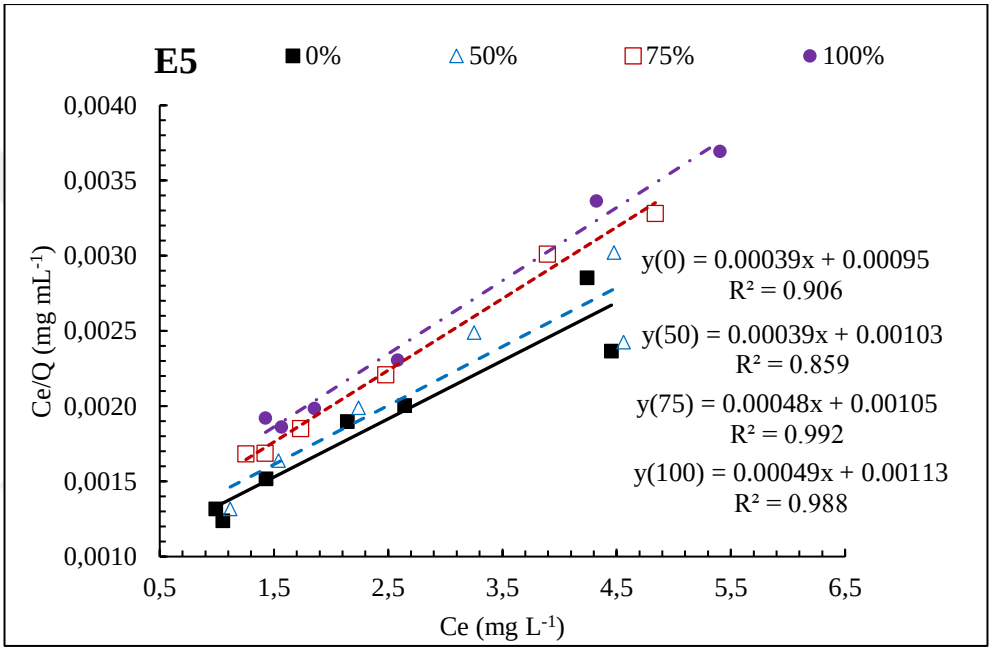

Figure 4.71. Linear Langmuir isotherms of E5 soil treated with differing lime requirements

According to Figure 4.72 and Figure 4.73, the R-squared values for E7 ranged from 0.981 to 0.994, whereas E8 varied from 0.923 to 0.997. These significant R-squared values imply a robust relationship between the phosphorus concentration and its adsorption on E7 and E8 soils. This indicates that the Langmuir isotherm model is appropriate for describing phosphorus adsorption on these soils. The Kl values of E7 demonstrated values ranging from 1.887 to 2.837 L mg^{-1}, while for E8, the values ranged from 1.178 to 2.405 L mg^{-1}. In soil E7, Fe or Ca precipitation was observed at low phosphorus concentrations followed by strong adsorption throughout liming. Lime application showed stronger phosphorus affinity energy and adsorption sites until P concentrations of 4 – 4.5 mg L^{-1} showed Ca competition for adsorption sites. While the E8 soil showed normal adsorption followed by Ca-P precipitation in the P

concentration range of 5 – 7 mg L^{-1}. Furthermore, the maximum adsorption capacities for E7 varied from 719 to 1 000 mg kg^{-1}; E8 ranged from 1 124 to 1 887 mg kg^{-1}. The data suggest that increasing lime dosage for both E7 and E8 soils decreased the maximum adsorptions. This implies that liming application was able to form Ca-P which difficult to be adsorbed (Wang et al., 2106a).

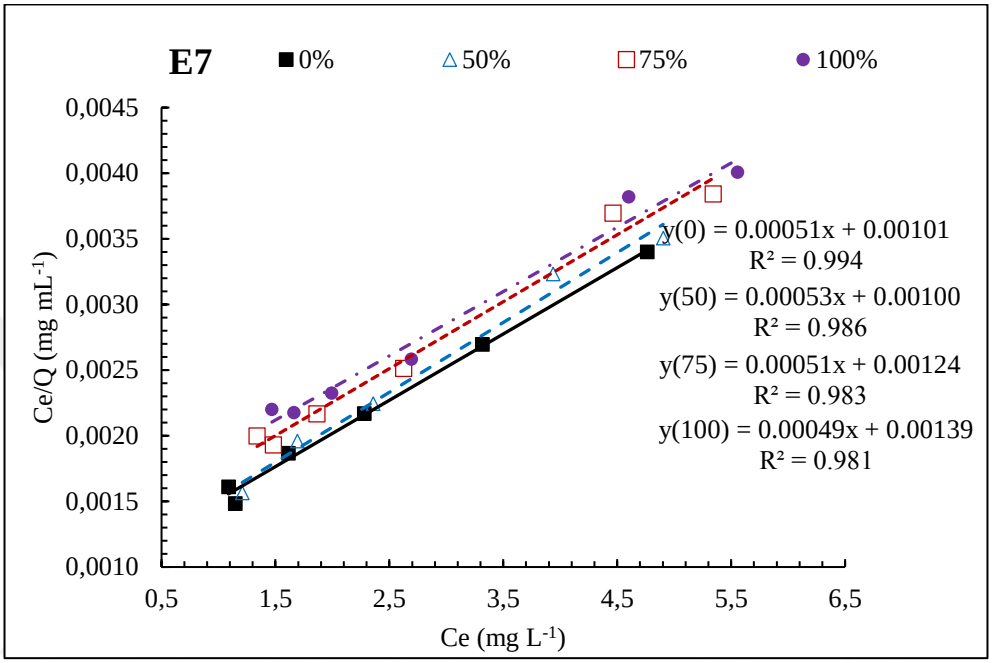

Figure 4.72. Linear Langmuir isotherms of E7 soil treated with differing lime requirements

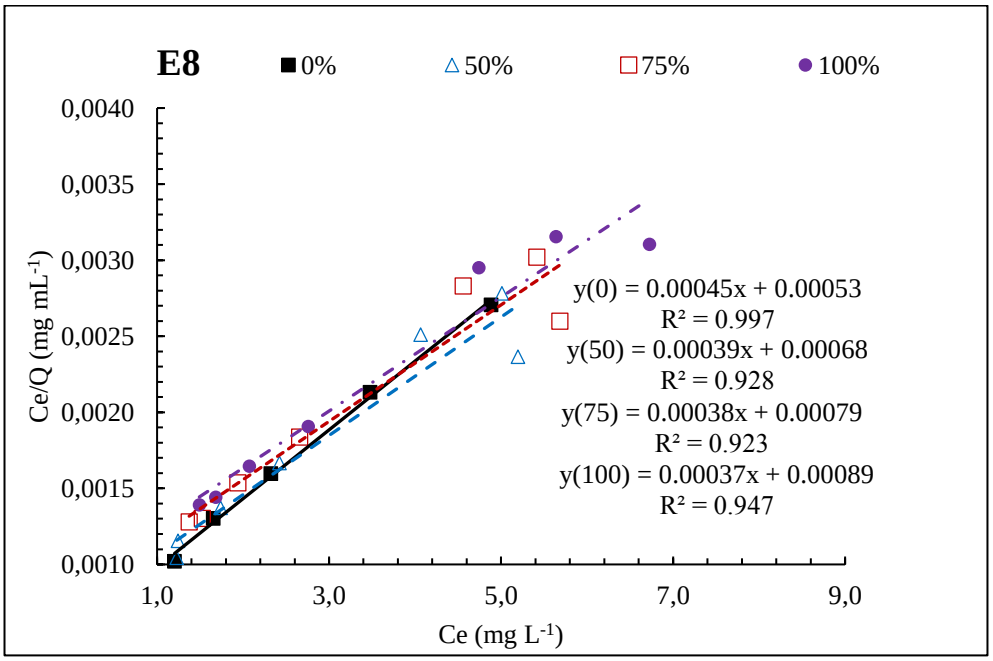

Figure 4.73. Linear Langmuir isotherms of E8 soil treated with differing lime requirements

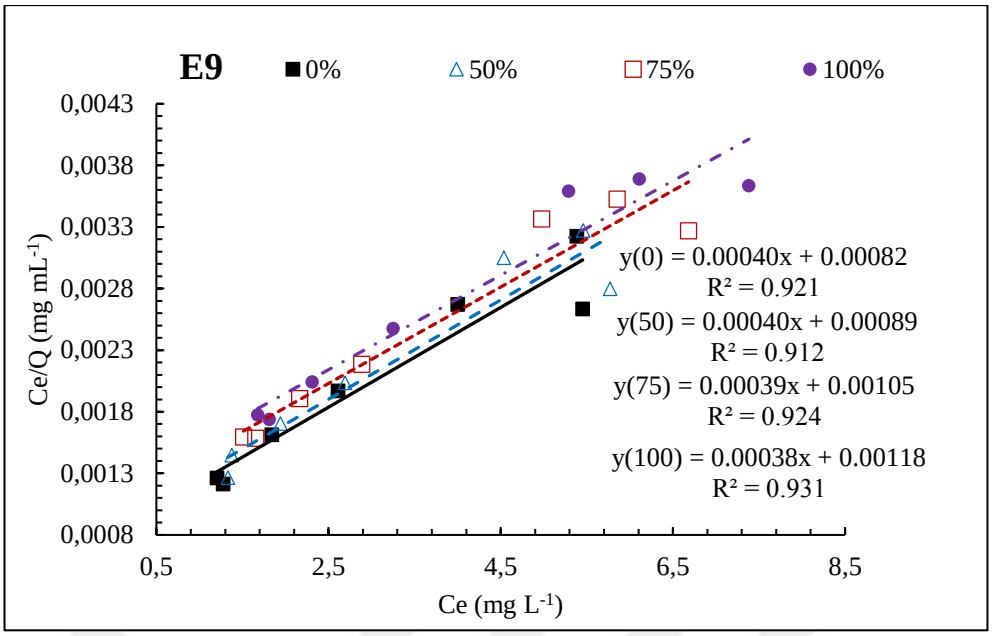

Figure 4.74. Linear Langmuir isotherms of E9 soil treated with differing lime requirements

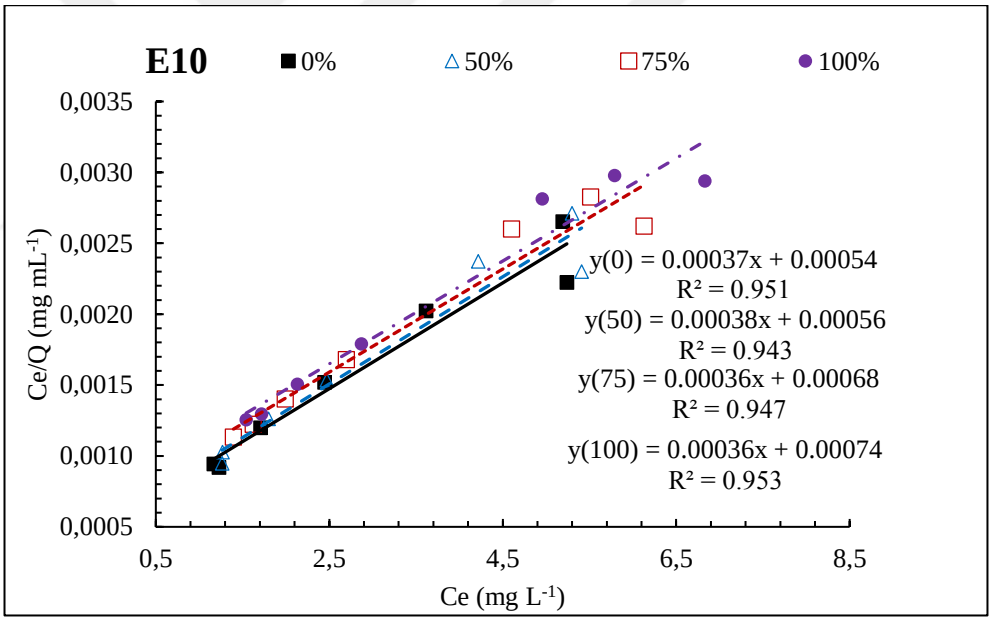

Figure 4.75. Linear Langmuir isotherms of E10 soil treated with differing lime requirement

Based on Figures 4.74 and 4.75, the regression coefficients (R-squared) for E9 ranged from 0.912 to 0.931 and E10 from 0.943 to 0.953. These R-squared values indicate reasonably strong correlations between the phosphorus concentration and adsorption on E9 and E10 soils. While both soils exhibit good correlations, E10 shows a narrower range of R-squared values, suggesting that the Langmuir isotherm model is suitable for representing phosphorus adsorption on both soils, with a slightly better goodness of fit for E10.

Concerning the Kl values, E9 showed values ranging from 2.050 to 3.105 L mg^{-1}; for E10, the values were 1.459 to 2.056 L mg^{-1}. The binding energy of adsorption sites in soils E9 and E10 increased with the increase of liming. In this case, rapid adsorption occurred at low phosphorus concentrations and then reached the point of precipitation at P concentrations of 4.5 – 5 mg L^{-1} upon liming application. Especially at 100% liming in soil E9, precipitation occurred at the initial concentration. This indicates the precipitation of phosphorus by Ca^{2+} caused by the use of lime. Additionally, the maximum adsorptions for E9 and E10 ranged from 1 220 to 847 mg kg^{-1} and 1 852 to 1 351 mg kg^{-1}, respectively. The datas indicate that the maximum adsorptions decreased with higher lime dosage for E9 and E10 soils. A decrease in the availability of adsorption sites on solid surfaces occurred when certain substances reached their solubility limits and formed solid, insoluble precipitates, which could obstruct or cover the surfaces where adsorption typically took place (Dunne et al., 2020).

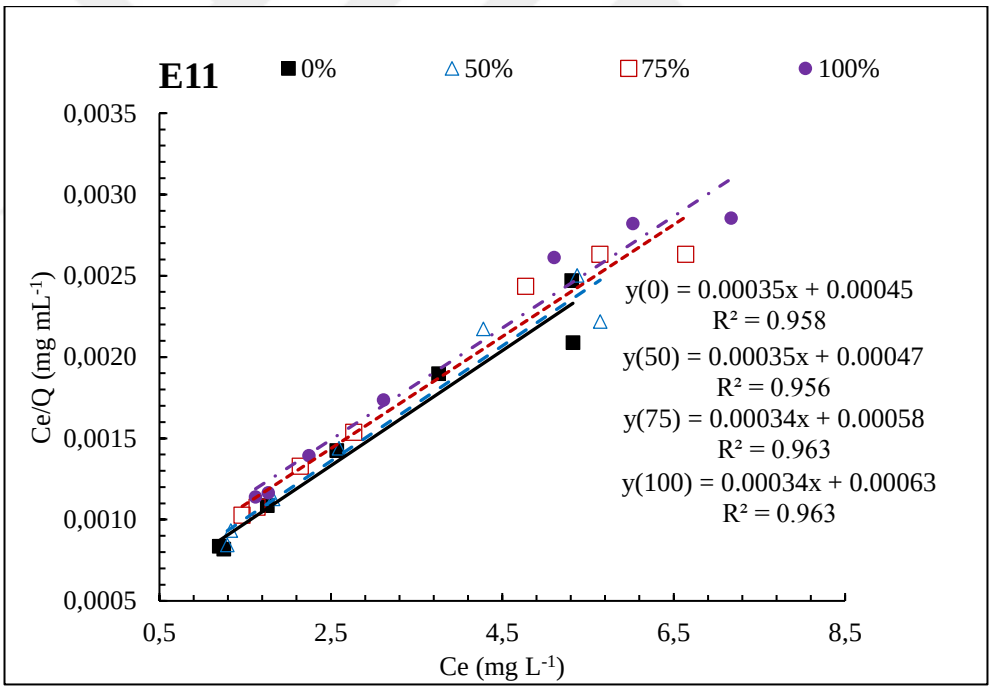

Figure 4.76. Linear Langmuir isotherms of E11 soil treated with differing lime requirements

As seen in Figure 4.76 and Figure 4.77, the regression coefficients (R-squared) for E11 ranged from 0.912 to 0.931, while E14 ranged from 0.943 to 0.953. These R-squared values indicate reasonably strong correlations between the phosphorus concentration and adsorption on E11 and E14 soils. The Kl values of E11 and E14 ranged from 1.286 to 1.853 L mg^{-1} and 1.974 to 2.842 L mg^{-1}, respectively. Precipitation was observed in

both soils at all liming ratios occurring between P concentrations of 5 – 7 mg L^{-1}. This precipitation was related to the increase in Ca in the soil which then had a tendency to bind phosphorus to form calcium phosphate (Wang et al., 2016a).

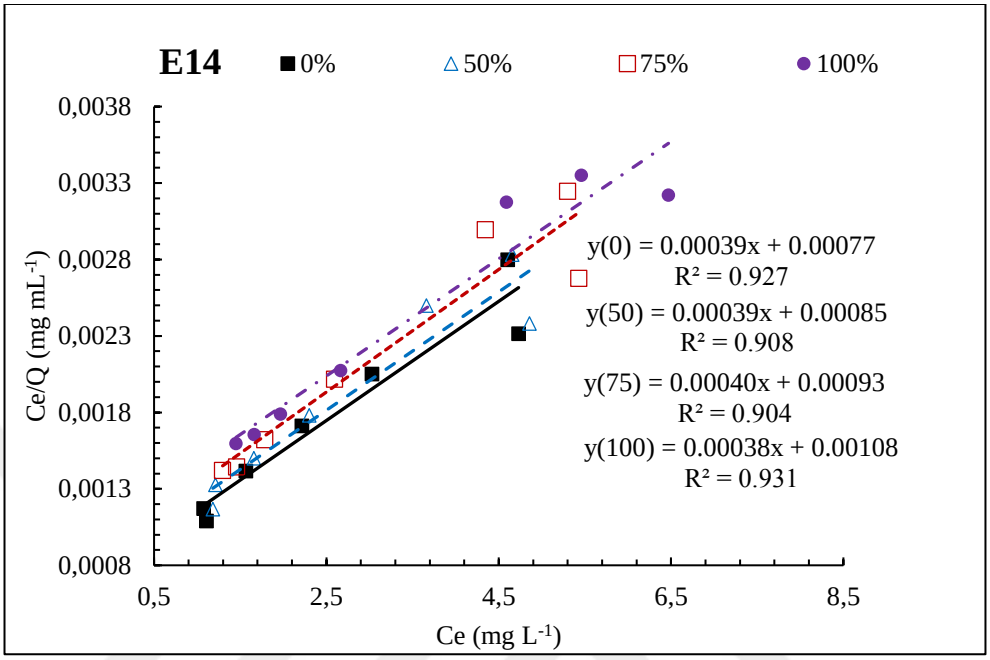

Figure 4.77. Linear Langmuir isotherms of E14 soil treated with differing lime requirements

The maximum adsorptions for E11 ranged from 2 222 to 1 587 mg kg^{-1} and E14 varied between 1 299 to 926 mg kg^{-1}, respectively. The data shows that for both E11 and E14 soils, the maximum adsorptions decreased with increased lime dosage. Some calcium compounds in liming could be broken down into a form more easily dissolved in solution with malic acid. As a result, the dissolved calcium could react with phosphate in the soil and form a more soluble calcium phosphate complex compound. This addition of malic acid increases the availability of phosphorus in the solution, thus decreasing the maximum adsorption (Naidu et al., 2006; Moradi et al., 2012; Wen et al., 2020).

4.3.4. The co-effects of oxalic acid and liming ratio

The phosphorus sorption data of treated soils were analyzed using the linear format of the Langmuir adsorption isotherm model. The adsorption isotherms and model parameters of E1 soil are shown in Figure 4.78. The coefficient of determination (R-squared) for the regression models of E1 soil ranged from 0.814 to 0.861, indicating a

strong correlation between the experimental data and the model. The Kl and Qmax values obtained from the analysis are acceptable, further validating the applicability of the Langmuir equation in describing the phosphorus adsorption on E1 soil.

The Kl value (E1) ranged from 1.851 to 3.525 L mg^{-1}. The data showed a positive linier trend with increasing lime dosage. There was early precipitation at all liming ratios. It then formed a new adsorption mechanism whose rate increased until the competition of Ca to P occurred at 75% and 100% liming at a concentration of 4.5 – 5 mg L^{-1}. The maximum adsorptions (E1) ranged from 1 149 to 709 mg kg^{-1}. The data indicated an decreasing trend with higher lime dosages. The pH of a solution affects the ionization state of adsorbates (molecules or ions). Changes in the charge or protonation state of adsorbates could influence their affinity for adsorption sites on the solid surface. In some cases, the pH that the adsorbate carried the same charge as the adsorption site, reducing adsorption capacity (Yigezu et al., 2023).

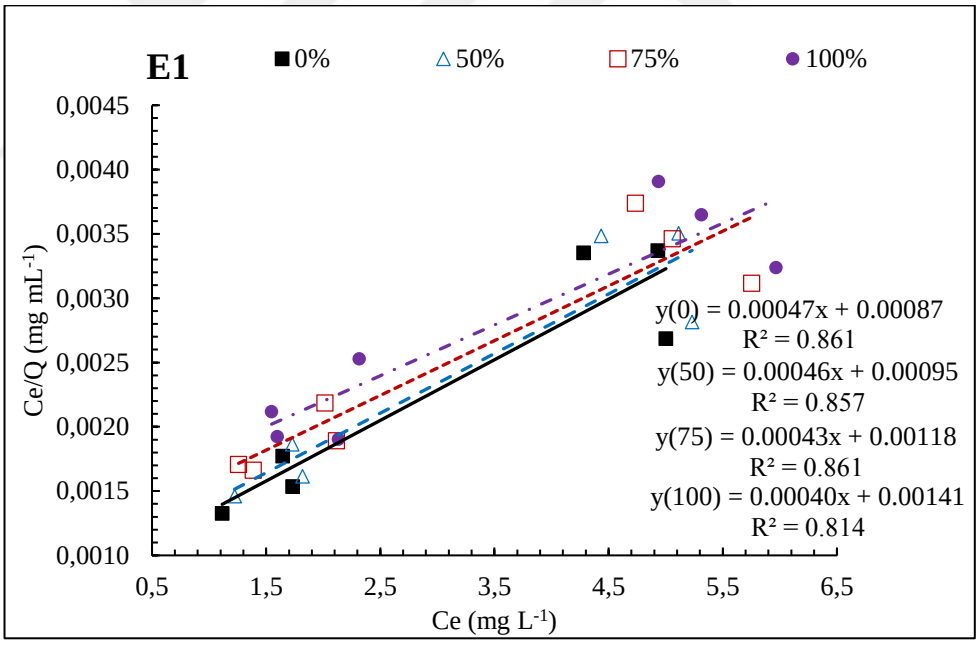

Figure 4.78. Linear Langmuir isotherms of E1 soil treated with differing lime requirements

Based on Figure 4.79 and Figure 4.80, the regression coefficients (R-squared) for E2 ranged from 0.967 to 0.975, while E3 ranged from 0.980 to 0.987. These high R-squared values indicate substantial correlations between the phosphorus concentration and adsorption in E2 and E3 soils. This suggests that the chosen regression model is

suitable for representing phosphorus adsorption on both soils. The Kl values of E2 ranged from 0.903 to 1.483 L mg^{-1}, and E3 ranged from 0.731 to 1.080 L mg^{-1}.

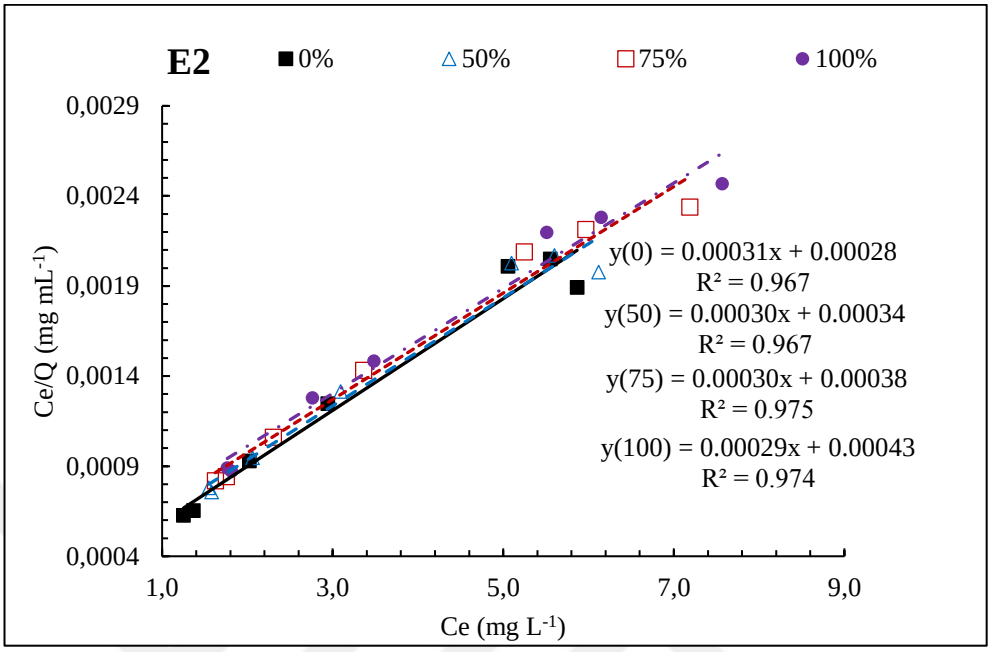

Figure 4.79. Linear Langmuir isotherms of E2 soil treated with differing lime requirements

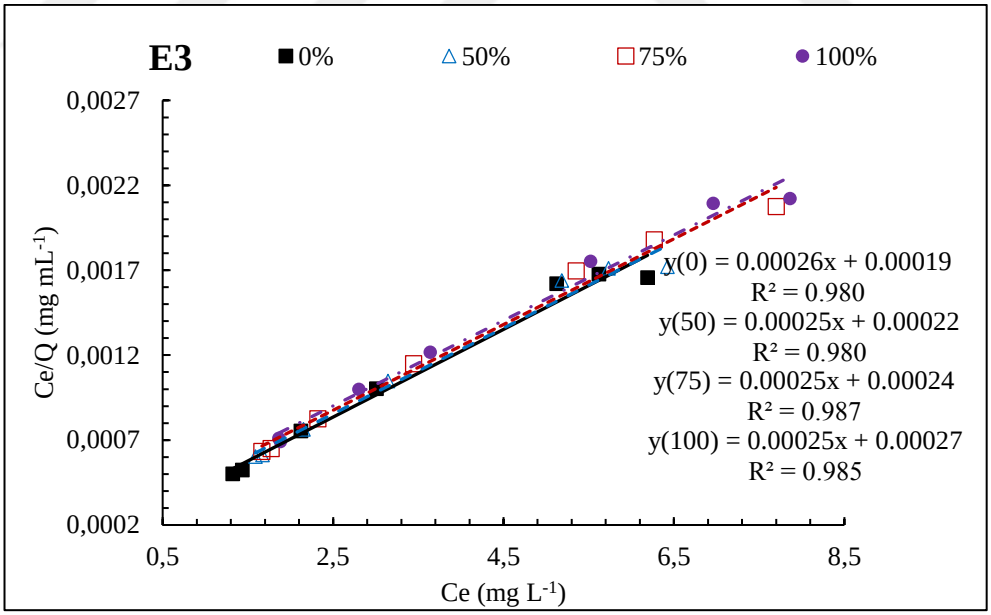

Figure 4.80. Linear Langmuir isotherms of E3 soil treated with differing lime requirements

As seen in Figure 4.81 and Figure 4.82, the regression coefficients (R-squared) for E4 ranged from 0.900 to 0.957, while E5 ranged from 0.839 to 0.983. A lower R^2 value than the others in E5 indicates a wide spread of data. In addition, it could be indicated

that the solubility of native phosphorus in the soil was reduced at 100% liming. However, the high R-squared values indicate that the selected regression model effectively represents the phosphorus adsorption process in the studied soils.

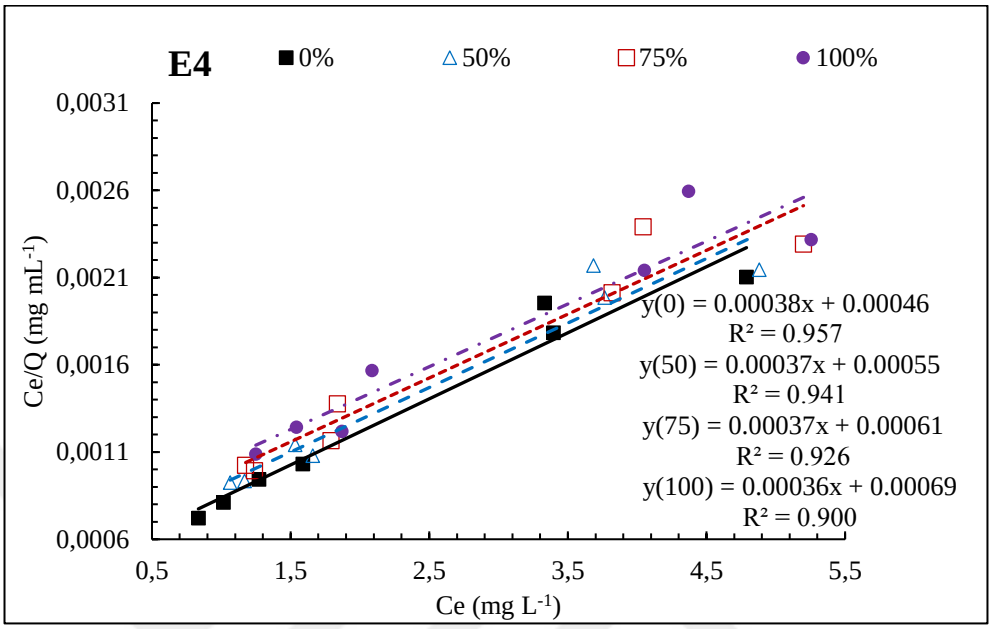

Figure 4.81. Linear Langmuir isotherms of E4 soil treated with differing lime requirements

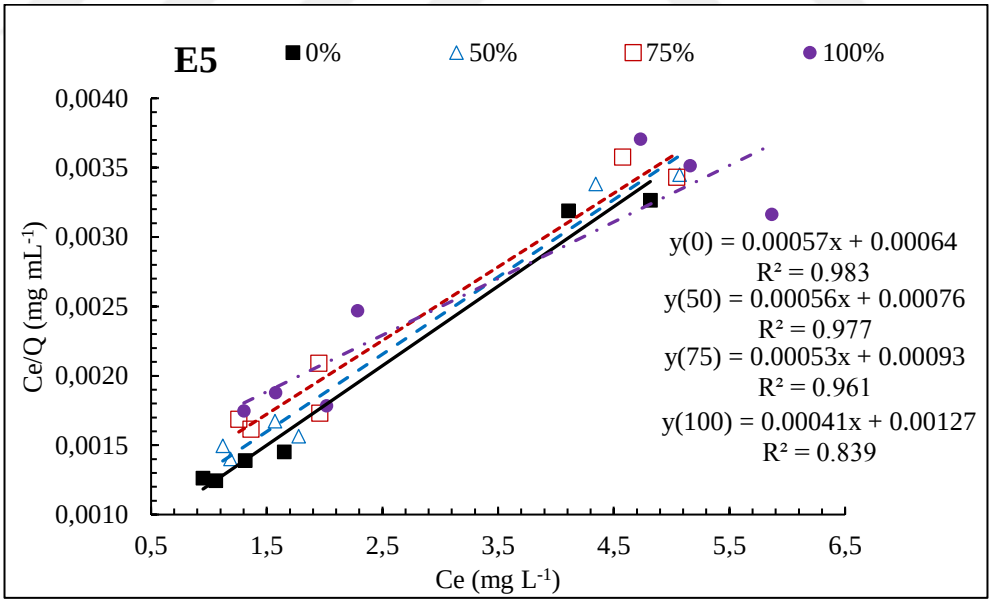

Figure 4.82. Linear Langmuir isotherms of E5 soil treated with differing lime requirements

The Kl values of E4 ranged from 1.211 to 1.917 L mg^{-1}, while E5 ranged from 1.123 to 3.098 L mg^{-1}. This improvement in Kl values suggest that the soils exhibit a strong affinity between adsorption and the adsorbates. Based on the results obtained, rapid

adsorption occurred at initial concentrations in soil E4 while at high concentrations in soil E5. In soils with liming, precipitation was observed at low P concentrations of 1 – 1.5 mg L^{-1}. Thereafter, the adsorption mechanism resumed followed by ion competition above the P concentration of 1.5 mg L^{-1} at 75% and 100% liming. The maximum adsorptions of E4 ranged from 2 174 to 1 449 mg kg^{-1}, whereas E5 ranged from 1 563 to 787 mg kg^{-1}. This reduction in adsorption maximum was attributed to the precipitation of P by Ca which formed insoluble complexes in the soil (Majumdar et al., 2005).

Based on Figures 4.83 and 4.84, the regression analysis showed that the R-squared values for E7 soil ranged from 0.798 to 0.912, and E8 varied between 0.925 to 0.995. The decrease in R^2 value in soil E7 indicates high dispersion of data and a decrease in solubility of indigenous phosphorus. However, The Langmuir adsorption isotherm model was suitable for representing phosphorus adsorption on E7 and E8 soil.

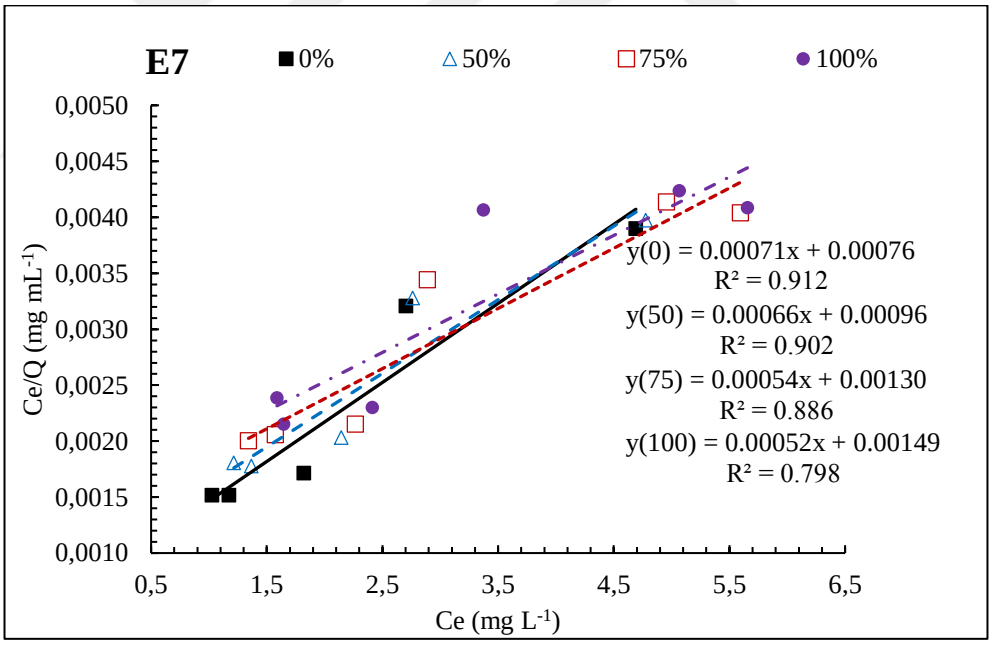

Figure 4.83. Linear Langmuir isotherms of E7 soil treated with differing lime requirements

The Kl values for E7 and E8 soil ranged from 1.070 to 2.865 L mg^{-1} and 0.746 to 1.875 L mg^{-1}. At least 2 or 3 adsorption mechanisms occurred in soils E7 and E8. In soil E7 there was ion competition at concentrations of 2.5 – 3.5 mg L^{-1} while in soil E8 there was precipitation in the range of 5 – 5.5 mg L^{-1}. Particularly at 100% liming, precipitation was observed at the beginning of the P concentration followed by high

adsorption thereafter (Eslamian et al., 2021). The maximum adsorption values for E7 soil ranged from 1 316 to 671 mg kg^{-1} and E8 varied between 1 333 to 2 273 mg kg^{-1}. There was a decrease in adsorption maximum due to precipitation at low P concentrations, while at 100% liming in soil E8 the adsorption maximum increased dramatically due to the formation of a strong phosphorus adsorption mechanism at high P concentrations. This case created more active adsorption sites, enhancing the soil's capacity to bind phosphorus from the solution (Eslamian et al., 2021).

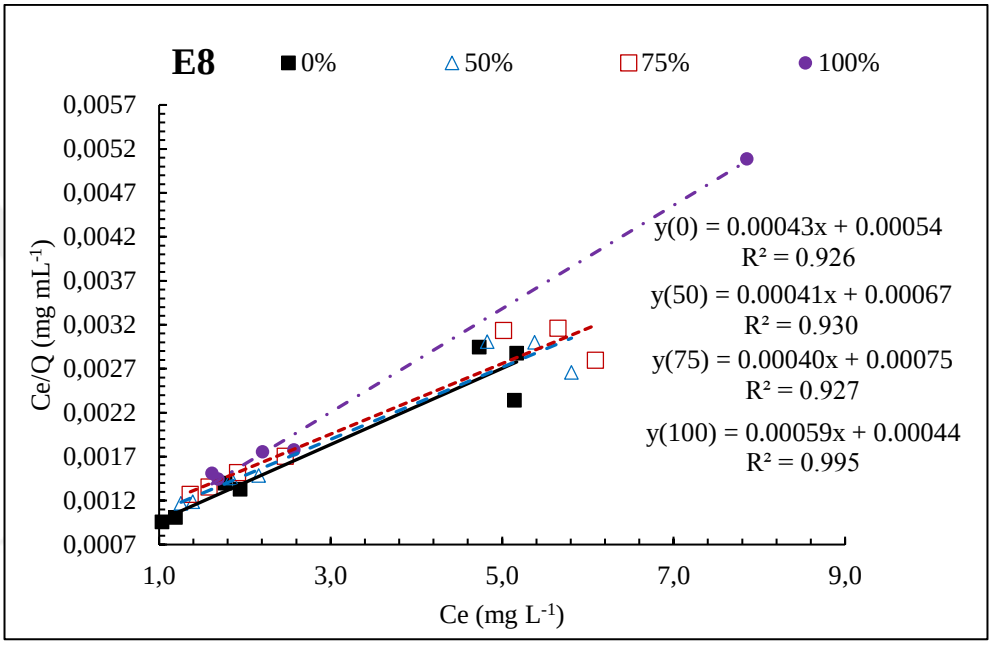

Figure 4.84. Linear Langmuir isotherms of E8 soil treated with differing lime requirements

Figure 4.85 and Figure 4.86 show the regression analysis of phosphorus adsorption using Langmuir Isotherm. Based on the result, the R-squared E9 and E10 ranged between 0.902 to 0.992 and 0.986 to 0.992. The values close to 1 indicate that the Langmuir isotherm model is suitable for representing phosphorus adsorption on these soils. The Kl values for E9 ranged from 1.531 to 1.773 L mg^{-1}, while E10 ranged from 0.848 to 1.442 L mg^{-1}.

E9 soil treated with 0 – 75% liming application showed high adsorption rate at P concentration and observed precipitation at 5 – 6 mg L^{-1} concentration while at 100% liming precipitation occurred at the beginning creating high adsorption at high P concentration. In addition, at least 2 adsorption mechanisms occurred in 0 and 100% liming in E10 soil causing precipitation at the beginning followed by high adsorption

at high P concentrations, while 50% and 75% liming showed adsorption rates at low phosphorus concentrations. This indicates the influence of Fe in acidic soil conditions and Ca in alkaline soil conditions that could resist adsorption at low concentrations. In addition, the application of liming increased Ca which precipitated with P, where at some point reduced the adsorption (Barrow, 2017).

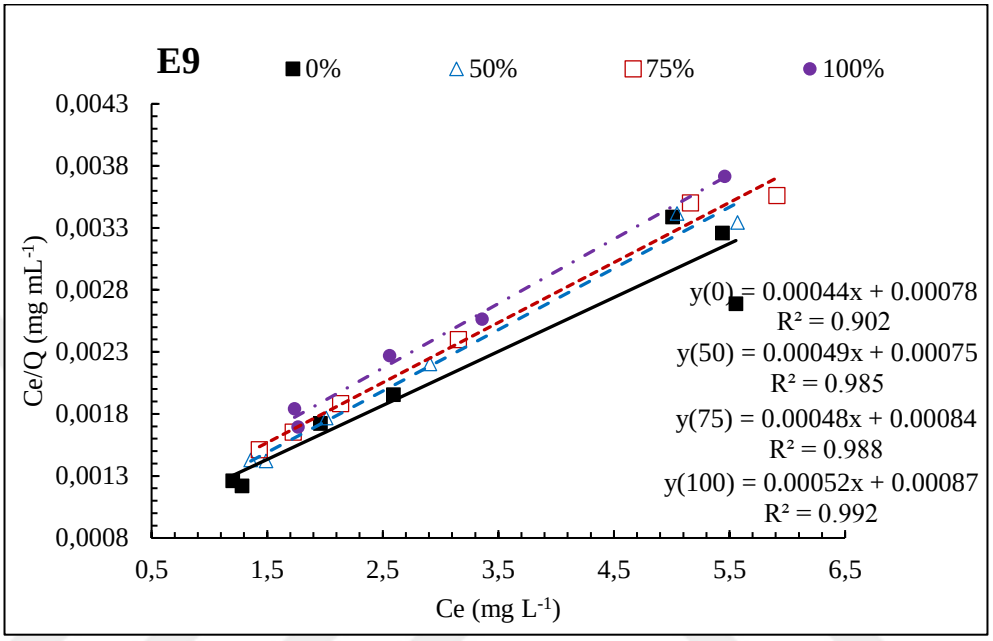

Figure 4.85. Linear Langmuir isotherms of E9 soil treated with differing lime requirements

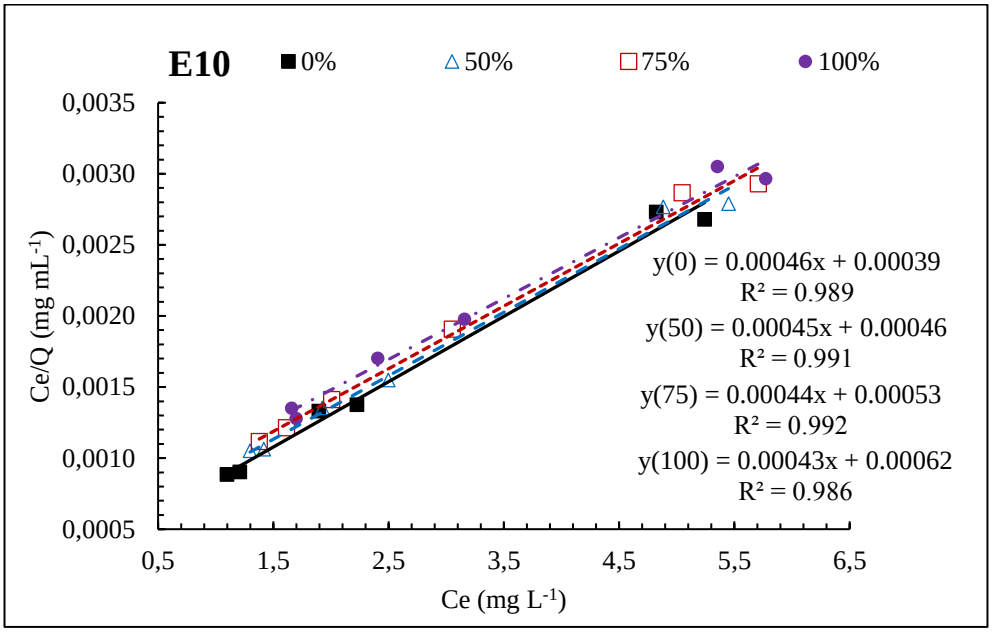

Figure 4.86. Linear Langmuir isotherms of E10 soil treated with differing lime requirements

The maximum adsorption ranged from 1 333 to 1 149 mg kg^{-1} for E9 and 2 564 to 1 613 mg kg^{-1} for E10. In general, Qmax decreased with the use of lime in the soil due to the presence of calcium, which could bind to phosphorus (P) and made it less available for adsorption sites. Lime application could change the soil's pH and surface charge, which in turn affected the electrostatic interactions between phosphorus ions and soil particles. This could lead to phosphorus adsorptions (Asomaning, 2020).

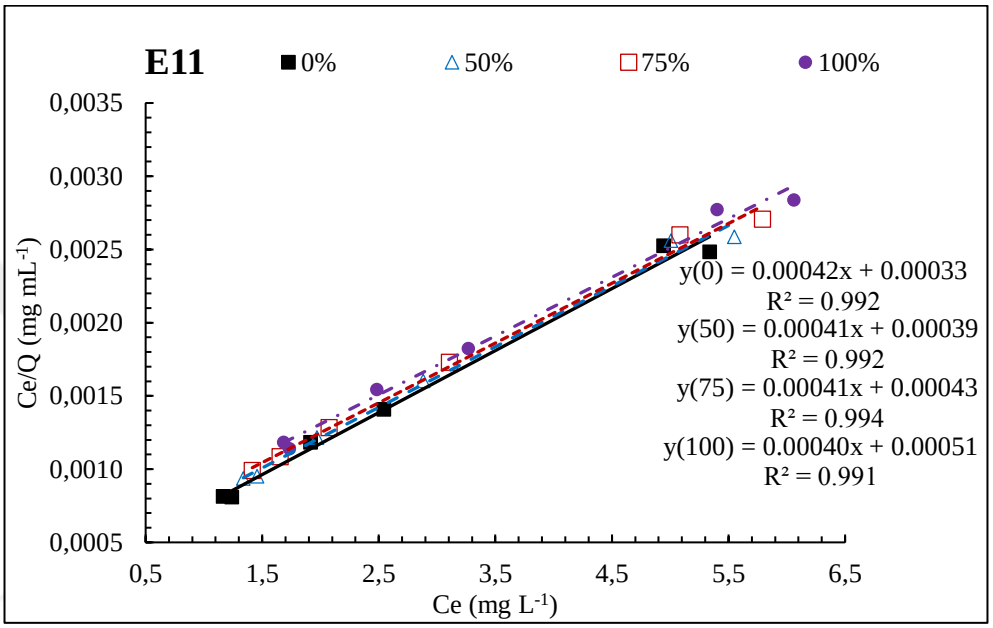

Figure 4.87. Linear Langmuir isotherms of E11 soil treated with differing lime requirements

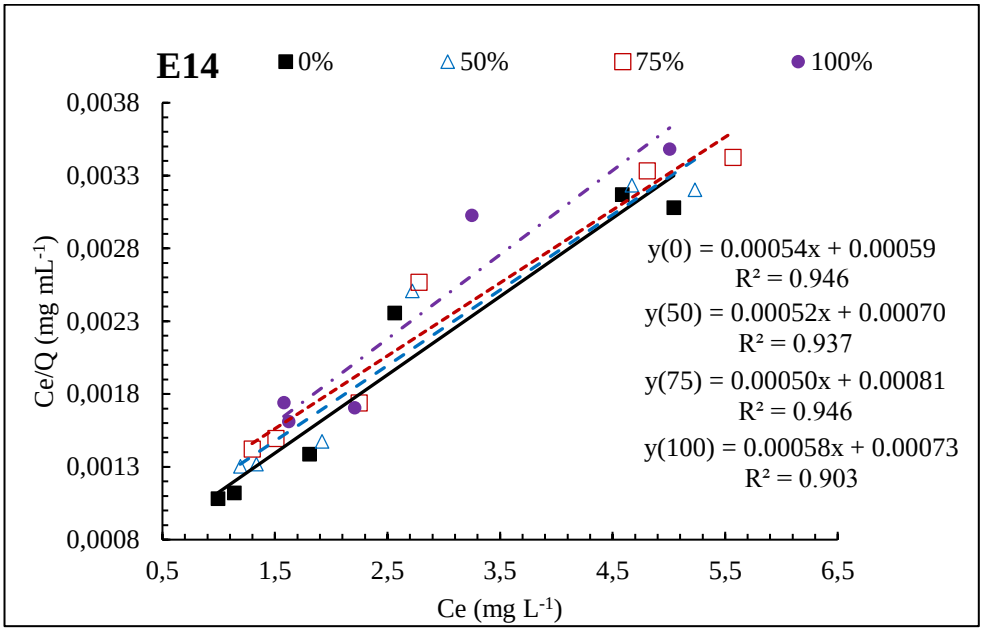

Figure 4.88. Linear Langmuir isotherms of E14 soil treated with differing lime requirements

According to Figure 4.87 and Figure 4.88, the Langmuir isotherm model was a suitable representation for describing the phosphorus adsorption phenomenon on these soils. This result obtained a high R^2 indicating robust relation of the phosphorus adsorption, which varied from 0.991 to 0.993 for E11 and 0.903 to 0.946 for E14. As seen in Figures 4.88 and 4.89, the Kl values of E11 and E14 ranged between 0.786 to 1.275 L mg^{-1} and 1.093 to 1.620 L mg^{-1}. Besides, the maximum adsorptions for E11 ranged from 3 030 to 1 961 mg kg^{-1} and E14 from 1 695 to 1 235 mg kg^{-1}. In general, soils with 0 – 75% lime content exhibited high adsorption rates at low phosphorus concentrations. In soil E14, there was competition with Fe or Ca to invade adsorption sites at phosphorus concentrations between 2.5 – 3 mg L^{-1}. Specifically, in soils with 100% lime content, precipitation was observed at the initial P concentration in both soils. However, in soil E11, the formation of a new adsorption mechanism was apparent, leading to an increase in adsorption, while in E14, there was competition between Ca and P for adsorption. This aligns with the reduction in the maximum adsorption capacity in both soils. When lime dosage increases, calcium ions ($Ca^{2+)}$ from lime reacted with phosphorus, altering the surface charge of the soil. Other ways, calcium also could compete with phosphorus to bind to the adsorption sites on the soil surface. In addition, oxalic acid could form complexes with Ca^{2+} or other compounds, reducing phosphorus adsorption in the soil (Hu et al., 2001; Gisi et al., 2016; Asomaning, 2020; Yigezu et al., 2023).

4.4. Analysis of Variance of Freundlich and Langmuir Isotherms

Table 4.3 shows the impact of the independent variables and their interactions with the Freundlich constant (Kf). The main variables significantly impact the Freundlich constant (Kf), as evident from the significance value of less than 0.05. The interactions among the variables, namely soil and lime, soil and organic acid, lime and organic acid, and their combined effects, all significantly influence phosphorus adsorption. The analysis yielded R^2 value of 1, indicating that the obtained results are statistically acceptable.

Table 4.3. Effect of soil, organic acid and liming on Freundlich constant (Kf)

Variable	Type III Sum of Squares	df	Mean Square	F	Sig.
Soil (S)	5.291	10	0.297	282.04	0.00
Liming (L)	5.776	3	0.962	913.56	0.00
Organic acid (O)	4.969	3	0.641	608.86	0.00
S*L	0.349	30	0.008	7.30	0.00
S*O	2.697	30	0.108	102.28	0.00
L*O	0.859	9	0.056	53.46	0.00
S*L*O	0.52	90	0.005	4.73	0.00
Error	0.433	352	0.001		
Total	2138.497	528			

R Squared = 1.000 (Adjusted R Squared = 1.000)

Based on Table 4.4, the interaction between variables involving soil and lime, soil and organic acid, lime and organic acid, and their combined effects, significantly affect phosphorus adsorption. The primary factors notably influence Freundlich isotherm, in this case, Freundlich exponent (n), as indicated by sig.<0.05. The analysis produced R^2 value of 0.999, suggesting the obtained findings are statistically valid. The interaction between organic acids and liming significantly affected the Freundlich isotherm.

Table 4.4. Effect of soil, organic acid and liming on Freundlich exponent (n)

Variable	Type III Sum of Squares	df	Mean Square	F	Sig.
Soil (S)	12 603	10	1.628	392.46	0.00
Liming (L)	3 162	3	0.336	81.02	0.00
Organic acid (O)	7 804	3	0.764	184.13	0.00
S*L	1 938	30	0.063	15.10	0.00
S*O	5 798	30	0.281	67.72	0.00
L*O	7 826	9	0.454	109.35	0.00
S*L*O	3 576	90	0.052	12.66	0.00
Error	1 272	352	0.004		
Total	2 138 497	528			

R Squared = .999 (Adjusted R Squared = .998)

Organic acids are crucial in altering soil pH and influencing the availability of phosphorus in the soil. On the other hand, liming can increase soil pH, which may neutralize the effects of organic acids. The increase in pH can reduce the solubility of

indigenous phosphorus in the soil, decreasing phosphorus availability for adsorption (Hu et al., 2001; Majumdar et al., 2005; Yang et al., 2019b).

Table 4.5 shows the significant effect of main variables and their interactions to maximum adsorption (Qmax). The regression coefficient (R^2) was 0.999, indicating that the outcome of the analysis was justifiable. The significant value was lower than 0.05, suggesting a significant effect of variables and their interactions with the maximum adsorption (Qmax). Combining organic acids and liming can have complex effects on Langmuir isotherm adsorption. The significant value was lower than 0.05, suggesting a significant effect of variables and their interactions with the maximum adsorption (Qmax). Combining organic acids and liming can have complex effects on Langmuir isotherm adsorption. The presence of organic acids may enhance the adsorption capacity by forming soluble phosphorus complexes. At the same time, liming can alter the adsorption capacity by changing soil pH and nature of adsorption sites (Hu et al., 2001; Adeleke et al., 2017). In addition, there were also notable effects on binding energy. According to the results, the significant value of soil, liming, and organic acid was Sig<0.05, which means a significant impact on binding energy (Kl).

Table 4.5. Effect of soil, organic acid and liming on maximum adsorption (Qmax)

Variable	Type III Sum of Squares	df	Mean Square	F	Sig.
Soil (S)	506230299.89	10	50623029.99	4090.58	0.00
Liming (L)	33471218.05	3	11157072.68	901.54	0.00
Organic acid (O)	5715024.85	3	1905008.28	153.93	0.00
S*L	15703477.30	30	523449.24	42.30	0.00
S*O	42173087.17	30	1405769.57	113.59	0.00
L*O	4764594.59	9	529399.40	42.78	0.00
S*L*O	11537375.64	90	128193.06	10.36	0.00
Error	4356186.00	352	12375.53		
Total	2383006747.00	528			

R Squared = .999 (Adjusted R Squared = .997)

In addition, there were also notable effects on binding energy. According to Table 4.6, the significant value of soil, liming, and organic acid was sig<0.05, which means a significant impact on Langmuir constant. Moreover, the interaction variables were sig<0.05, indicating a notable impact. This result was justified to the R^2 value of 0.993. This significant influence indicates that organic acids and liming play essential roles

in regulating the adsorption behavior of phosphorus in soil. Organic acids can enhance phosphorus availability in the soil solution through complexation, while liming can alter the soil pH and nature of adsorption sites, affecting the adsorption capacity (Andrade et al., 2007; Amin, 2018).

Table 4.6. Effect of soil, organic acid and liming on Langmuir constant (Kl)

Variable	Type III Sum of Squares	df	Mean Square	F	Sig.
Soil (S)	125.23	10	12.52	431.03	0.00
Liming (L)	41.07	3	13.69	471.20	0.00
Organic acid (O)	16.66	3	5.55	191.10	0.00
S*L	11.46	30	0.38	13.14	0.00
S*O	31.45	30	1.05	36.09	0.00
L*O	17.93	9	1.99	68.59	0.00
S*L*O	23.80	90	0.26	9.10	0.00
Error	10.23	352	0.03		
Total	2064.96	528			

R Squared = .993 (Adjusted R Squared = .993)

Tables 4.7 to 4.9 illustrate the differences in effects for each soil type, organic acid, and lime dosage. Table 4.7 indicates distinct variations concerning the Freundlich and Langmuir isotherms among all soil types. Soil type E3 exhibited the lowest level of phosphorus adsorption compared to other soils. This suggested that the phosphorus availability in soil E3 was higher than in the others, measuring 196.8 mg kg^{-1}. Low phosphorus adsorption aligned with the significant adsorption capacity of the soil. Based on the results obtained, the value of Kf for soil E3 was the highest among all soil types.

The highest maximum adsorption is found in soil E3 (Table 4.7). This indicates that the adsorption capacity of soil E3 for phosphorus molecules is greater compared to other soils. However, E3 has the second-lowest affinity energy after E2, which means that phosphorus adsorption is high in soil E3. The lowest maximum adsorption is in soil E7, despite having a high affinity energy for adsorption sites. In this case, the presence of precipitation and ion competition becomes key factors causing the inhibited adsorption rate in soils that have been treated with lime and low-molecular-weight organic acids.

Table 4.7. Main effect of soils on Freundlich and Langmuir isotherm parameters

Soil	Kf (mg kg^{-1})	n	Qmax (mg kg^{-1})	Kl (L mg^{-1})
E1	2.023 d	1.411 d	989.40 j	2.594 a
E2	2.018 d	1.278 f	3065.50 b	1.008 h
E3	2.184 a	1.059	4297.33 a	1.193 g
E4	2.065 c	1.580 a	1736.15 e	1.781 d
E5	2.029 d	1.462 c	1079.25 i	2.337 b
E7	1.891 g	1.502 b	932.79 k	2.272 b
E8	1.953 f	1.417 d	1542.63 f	1.789 d
E9	1.806 h	1.560 a	1178.88 h	2.316 b
E10	1.992 e	1.342 e	1793.42 d	1.581 e
E11	2.125 b	1.166 g	2131.90 c	1.411 f
E14	1.944 f	1.454 c	1330.54 g	1.955 c

Alpha = 0.05

Based on Table 4.8, organic acids exhibited different effects on Freundlich isotherm and Langmuir isotherm. The adsorption capacity and maximum adsorption values showed consistent results, where $CaCl_2$ and citric acid had the highest Freundlich and Langmuir parameter values. According to the results, soils with organic acid applications has limited adsorption rate. Citric acid, as 3 carboxylic groups, could reduce phosphorus adsorption by competing for adsorption sites or forming organic-phosphate complexes.

Table 4.8. Main effect of organic acids on Freundlich and Langmuir isotherm parameters

Organic acid	Kf (mg kg^{-1})	n	Qmax (mg kg^{-1})	Kl (L mg^{-1})
$CaCl_2$	2.067 b	1.525 a	1 947 a	2.042 a
Citric acid	2.128 a	1.200 d	1 675 d	1.912 b
Malic acid	1.907 c	1.453 b	1 787 c	1.848 c
Oxalic acid	1.909 c	1.360 c	1 891 b	1.557 d

Alpha = 0.05

Citric acid could compete with phosphorus for binding to soil surface. When citric acid was present in the soil solution, it could replace phosphorus from the binding sites on the soil surface, reducing the amount of phosphorus adsorbed. On the other hand, citric acid could form organic-phosphate complexes with soluble phosphorus. These complexes can help to protect phosphorus from being bound to the soil surface and increase phosphorus mobility in the soil. As 2-carboxylic groups, malic acid and oxalic acid could form strong complexes with metal ions like iron and aluminum, reducing

the availability of these metals for binding with phosphate ions and indirectly impacting phosphorus adsorption. Additionally, its acidic nature could alter the pH of the solution, affecting the charge on phosphate ions and the surface charge of adsorbent materials, thus influencing adsorption. Also, malic and oxalic acid formed soluble complexes with metal phosphates, potentially increasing phosphorus solubility and mobility, and competed with phosphate ions for adsorption sites on solid surfaces (Feng, 2012; Wang et al., 2016a; Mihoub et al., 2017).

Table 4.9 shows the varying effects of each liming level. The results show that the lowest adsorption capacity and maximum adsorption is found at the 100% liming level. On the other hand, the lowest n and Kl values were observed in the treatment without liming, while the highest values were found at the 100% liming level.

Table 4.9. Main effect of liming on Freundlich and Langmuir isotherm parameters

Liming	**Kf (mg kg^{-1})**	**n**	**Qmax (mg kg^{-1})**	**Kl (L mg^{-1})**
0%	2.125 a	1.302 d	2 139 a	1.583 c
50%	2.071 b	1.324 c	1 982 b	1.595 c
75%	1.962 c	1.414 b	1 687 c	1.919 b
100%	1.853 d	1.498 a	1 492 d	2.263 a

Alpha = 0.05

As liming increases, the soil pH rises, leading to the solubility of indigenous phosphorus in the soil, resulting in solid phosphorus adsorption at low phosphorus concentrations (Zhang et al., 2014). The increased phosphorus adsorption causes a reduction in the phosphorus adsorption capacity. Liming and phosphorus fertilizer applications have been continuously carried out since the conversion of the land to agriculture. In this context, the average liming requirement needed is 10.55 g kg^{-1}. When the soil pH increases after liming, the calcium and magnesium content from the lime replace hydrogen cations on the soil surface, resulting in the soil surface becoming more negatively charged. This negative charge will attract phosphate ions (PO_4^{3-}) in the soil solution, as they are anionic and have opposite charges. Then, thosphate ions (PO_4^{3-}) on the soil surface interact with the higher negative charge This leads to a more stable and stronger bond between phosphorus and soil (Bolan et al., 2003; Majumdar et al., 2005; Naidu et al., 2006; Asomaning, 2020; Yigezu et al., 2023).

4.5. Correlation of soil properties and Langmuir and Freundlich isotherm' parameters

Table 4.10 presents the correlation analysis results of soil characteristics with Langmuir and Freundlich isotherms under no liming application. The soil without liming showed the highest number of correlations. Soil characteristics that correlated with Langmuir and Freundlich isotherms at 0% liming included potential acid (PA), organic carbon, liming requirement (LR), CEC, phosphorus availability, exchangeable calcium, exchangable magnesium, exchangeable potassium, DTPA-Cu, Total Mn, Total Zn, and Total Ca. Organic carbon positively correlated with the Freundlich exponent (n) values in $CaCl_2$, citric acid, and oxalic acid. Soil organic carbon plays a crucial role in shaping soil's physical and chemical properties, including the soil's ability to bind and retain nutrients such as phosphorus. Increasing soil organic carbon content makes the soil surface more complex with more active binding sites. The presence of more binding sites leads to improved soil capacity to retain and bind phosphorus (Yang et al., 2019b).

There was a positive correlation between exchangeable magnesium and exchangeable potassium. In this case, soils with higher binding energies have a greater affinity for cation ions, including Mg and K. If the soil has high binding energy, more Mg and K ions can be bound to the soil surface, increasing the exchangeable amount of these ions. The soils with a high phosphorus adsorption capacity tend to have more exchangeable Mg and K ions because these ions compete with phosphorus for binding to the soil surface. This finding aligns with the positive correlation observed between CEC and binding energy. CEC refers to the soil's ability to store and bind cation ions such as magnesium (Mg^{2+}) and potassium (K^{+}), so an increase in CEC is correlated with an increase in binding energy as both are related to the interactions of cation ions with the soil surface (Asomaning, 2020). A negative correlation was observed between DTPA-Cu and phosphorus adsorption capacity only in 0% liming treatment. This is because copper (Cu) can compete with phosphorus for binding to soil surface, reducing the phosphorus adsorption capacity and increasing availability in soil solution (Perez-Novo et al., 2009). This phenomenon can be seen in the positive correlation between total Cu and binding energy, indicating competition for adsorption sites between Cu and P.

Table 4.10. Pearson correlation analysis between soil properties and Freundlich and Langmuir isotherms at 0% liming

Parameters	$CaCl_2$				Citric				Malic				Oxalic			
	Kf	**n**	**Qmax**	**Kl**	**Kf**	**n**	**Qmax**	**Kl**	**Kf**	**n**	**Qmax**	**Kl**	**Kf**	**n**	**Qmax**	**Kl**
pH	-0.462	0.096	0.485	-0.433	-0.378	0.013	0.375	-0.072	-0.288	0.140	0.447	-0.406	-0.462	-0.023	0.464	-0.240
PA	0.050	0.135	-0.195	0.462	0.114	-0.001	-0.286	0.383	0.219	-0.186	-0.178	0.102	0.291	-0.055	-0.289	**0.642***
EC	0.010	0.144	-0.150	0.421	0.103	-0.013	-0.238	0.355	0.169	-0.157	-0.155	0.132	0.294	-0.080	-0.225	0.541
OC	0.066	**0.708***	-0.026	-0.073	-0.545	**0.791****	-0.123	0.260	0.099	0.432	0.069	-0.001	-0.308	**0.787****	-0.001	-0.042
$CaCO_3$	-0.154	-0.445	0.314	-0.566	0.038	-0.405	0.378	-0.543	-0.360	0.125	0.395	-0.499	0.095	-0.501	0.398	-0.516
LR	0.131	-0.250	0.581	-0.359	-0.058	-0.067	**0.658***	-0.356	0.253	-0.435	0.484	-0.391	-0.023	-0.112	0.566	-0.256
FC	0.083	0.072	-0.180	0.435	0.157	-0.055	-0.258	0.353	0.211	-0.205	-0.155	0.072	0.350	-0.111	-0.249	0.559
WP	0.165	-0.599	0.275	-0.407	0.402	-0.427	0.431	-0.484	0.159	-0.571	0.231	-0.498	0.379	-0.488	0.365	-0.428
CEC	-0.252	-0.307	**0.697***	-0.494	-0.408	-0.197	**0.615***	-0.308	-0.050	-0.242	0.623*	-0.399	-0.257	-0.362	**0.640***	-0.514
Av.P	-0.295	-0.159	**0.909****	**-0.660***	**-0.616***	-0.033	**0.839****	-0.456	-0.125	-0.056	**0.880****	**-0.645***	-0.383	-0.217	**0.850****	-0.480
Ex.Ca	-0.157	-0.322	**0.610***	-0.400	-0.252	-0.208	0.574	-0.291	0.041	-0.348	0.494	-0.273	-0.164	-0.339	0.564	-0.469
Ex.Mg	-0.171	-0.320	**0.647***	-0.450	-0.386	-0.174	0.572	-0.294	0.026	-0.290	0.580	-0.356	-0.191	-0.348	0.589	-0.507
Ex.K	-0.330	0.021	**0.800****	**-0.602***	**-0.815****	0.129	**0.637***	-0.260	-0.175	0.168	**0.866****	**-0.648***	-0.475	-0.067	**0.728***	-0.405
Ex.Na	-0.175	-0.047	-0.118	0.205	-0.182	-0.063	-0.216	0.163	-0.039	-0.026	-0.158	0.297	-0.232	-0.083	-0.220	0.073
DTPA.Cu	-0.410	-0.154	-0.021	-0.136	0.058	-0.334	0.028	-0.249	**-0.623***	0.448	-0.002	-0.050	-0.335	-0.220	0.002	-0.032
DTPA.Mn	0.138	-0.508	-0.034	-0.129	0.029	-0.309	0.014	-0.311	-0.017	-0.111	0.092	-0.243	0.114	-0.364	-0.029	-0.226
DTPA.Fe	-0.022	-0.076	-0.174	-0.017	0.356	-0.193	-0.138	0.095	-0.130	0.016	-0.234	0.217	0.131	-0.102	-0.071	-0.240
DTPA.Zn	-0.153	-0.204	0.454	-0.234	-0.034	-0.300	0.407	-0.072	-0.174	-0.053	0.451	-0.383	-0.003	-0.328	0.483	-0.193
Tot.Cu	-0.148	-0.027	0.435	-0.308	-0.520	0.132	0.399	-0.375	0.004	0.005	0.477	-0.412	-0.210	-0.063	0.329	-0.043
Tot.Mn	-0.166	0.096	**0.710***	**-0.665***	**-0.733***	0.325	**0.653***	-0.450	0.002	0.060	**0.724***	-0.538	-0.310	0.085	**0.680***	-0.546
Tot.Fe	-0.492	0.228	0.310	-0.328	-0.551	0.216	0.262	-0.402	-0.274	0.301	0.358	-0.454	-0.332	0.006	0.179	0.243
Tot.Zn	-0.402	0.025	**0.765****	**-0.665***	**-0.773****	0.128	**0.674***	-0.494	-0.274	0.258	**0.835****	**-0.710***	-0.455	-0.092	**0.684***	-0.297
Tot.Ca	-0.197	-0.355	**0.729***	-0.571	-0.273	-0.248	**0.698***	-0.401	-0.043	-0.278	**0.635***	-0.418	-0.133	-0.410	**0.711***	-0.596
Tot.Mg	-0.105	0.001	0.489	-0.431	-0.522	0.187	0.406	-0.261	0.122	-0.139	0.481	-0.338	-0.079	-0.071	0.444	-0.420
Tot.Na	0.024	-0.049	-0.073	0.088	-0.217	0.067	-0.204	0.254	0.208	-0.209	-0.053	0.066	-0.106	0.011	-0.137	-0.083

*Correlation is significant at the 0.05 level
**Correlation is significant at the 0.01 level

Table 4.11. Pearson correlation analysis between soil properties and Freundlich and Langmuir isotherms at 50% liming

Parameters	$CaCl_2$				Citric				Malic				Oxalic			
	Kf	**n**	**Qmax**	**Kl**	**Kf**	**n**	**Qmax**	**Kl**	**Kf**	**n**	**Qmax**	**Kl**	**Kf**	**n**	**Qmax**	**Kl**
pH	0.360	-0.430	0.483	-0.433	0.323	-0.367	0.340	-0.030	0.341	-0.302	0.448	-0.474	0.267	-0.287	0.473	-0.303
PA	0.108	-0.058	-0.212	0.546	0.071	0.039	-0.245	0.155	0.095	-0.028	-0.191	0.163	0.168	-0.123	-0.267	**0.703***
EC	0.129	-0.089	-0.167	0.505	0.114	-0.050	-0.201	0.127	0.067	0.036	-0.151	0.124	0.192	-0.159	-0.198	0.559
OC	0.244	-0.057	0.021	-0.298	0.240	0.122	-0.020	0.419	0.152	0.094	0.110	-0.103	0.225	0.032	-0.030	0.020
$CaCO_3$	0.058	-0.233	0.315	-0.481	0.059	-0.380	0.470	**-0.622***	0.097	-0.264	0.425	-0.508	0.045	-0.288	0.374	-0.584
LR	0.584	**-0.614***	0.578	-0.425	0.526	-0.468	0.536	-0.352	**0.721***	**-0.738****	0.422	-0.249	0.556	-0.583	0.580	-0.250
FC	0.135	-0.099	-0.194	0.500	0.116	-0.054	-0.197	0.081	0.104	-0.048	-0.161	0.122	0.208	-0.186	-0.231	**0.618***
WP	0.268	-0.354	0.269	-0.320	0.288	-0.490	0.356	-0.527	0.389	**-0.619***	0.188	-0.378	0.247	-0.402	0.341	-0.303
CEC	0.276	-0.438	**0.672***	-0.426	0.222	-0.367	0.556	-0.348	0.305	-0.423	**0.616***	-0.479	0.180	-0.307	**0.639***	-0.492
Av.P	0.580	**-0.712***	**0.901****	**-0.656***	0.485	-0.525	**0.841****	-0.542	**0.624***	**-0.648***	**0.868****	**-0.665***	0.499	-0.563	**0.857****	-0.519
Ex.Ca	0.250	-0.383	0.583	-0.335	0.215	-0.344	0.463	-0.289	0.284	-0.382	0.476	-0.342	0.167	-0.280	0.571	-0.456
Ex.Mg	0.236	-0.386	**0.622***	-0.383	0.184	-0.310	0.517	-0.332	0.272	-0.404	0.572	-0.432	0.146	-0.267	0.583	-0.452
Ex.K	0.508	**-0.622***	**0.803****	**-0.643***	0.401	-0.382	**0.743****	-0.384	0.520	-0.532	**0.878****	**-0.694***	0.426	-0.456	**0.715***	-0.391
Ex.Na	-0.515	0.459	-0.149	0.336	-0.535	0.496	-0.263	0.216	-0.527	0.396	-0.162	0.218	-0.576	0.579	-0.220	0.147
DTPA.Cu	-0.334	0.220	-0.024	-0.063	-0.326	0.088	0.059	-0.255	-0.344	0.266	0.003	-0.027	-0.341	0.254	0.022	-0.239
DTPA.Mn	-0.375	0.260	-0.037	-0.047	-0.403	0.244	0.128	-0.440	-0.261	-0.091	0.074	-0.110	-0.386	0.273	-0.080	-0.038
DTPA.Fe	-0.107	0.077	-0.172	-0.048	-0.007	-0.194	-0.209	0.205	-0.188	0.227	-0.198	0.084	-0.101	-0.019	-0.068	-0.349
DTPA.Zn	0.541	**-0.655***	0.458	-0.325	0.546	**-0.735****	0.469	-0.366	0.484	-0.442	0.460	-0.384	0.575	**-0.706***	0.503	-0.319
Tot.Cu	0.130	-0.169	0.422	-0.175	0.012	0.101	0.449	-0.415	0.220	-0.307	0.455	-0.356	0.072	-0.022	0.322	0.048
Tot.Mn	0.424	-0.454	**0.715***	**-0.644***	0.349	-0.247	**0.689***	-0.376	0.432	-0.413	**0.742****	**-0.650***	0.330	-0.282	**0.657***	-0.481
Tot.Fe	0.010	-0.018	0.289	-0.022	-0.129	0.275	0.305	-0.333	0.086	-0.106	0.346	-0.434	-0.075	0.179	0.187	0.268
Tot.Zn	0.406	-0.508	**0.762****	-0.587	0.275	-0.238	**0.771****	-0.551	0.463	-0.490	**0.838****	**-0.714***	0.321	-0.330	**0.678***	-0.313
Tot.Ca	0.381	-0.545	**0.707***	-0.513	0.346	-0.530	**0.615***	-0.414	0.412	-0.493	**0.633***	-0.507	0.301	-0.472	**0.715***	**-0.629***
Tot.Mg	0.222	-0.264	0.477	-0.324	0.173	-0.136	0.416	-0.219	0.211	-0.250	0.504	-0.491	0.137	-0.138	0.419	-0.289
Tot.Na	-0.272	0.252	-0.086	0.125	-0.291	0.329	-0.210	0.288	-0.252	0.077	-0.061	0.025	-0.348	0.364	-0.177	0.166

*Correlation is significant at the 0.05 level
**Correlation is significant at the 0.01 level

Table 4.12. Pearson correlation analysis between soil properties and Freundlich and Langmuir isotherms at 75% liming

Parameters	$CaCl_2$				Citric				Malic				Oxalic			
	Kf	**n**	**Qmax**	**Kl**	**Kf**	**n**	**Qmax**	**Kl**	**Kf**	**n**	**Qmax**	**Kl**	**Kf**	**n**	**Qmax**	**Kl**
pH	0.349	-0.428	0.491	-0.475	0.394	-0.456	0.392	-0.070	0.344	-0.377	0.415	-0.366	0.384	-0.423	0.460	-0.189
PA	-0.043	0.120	-0.210	0.584	-0.233	0.413	-0.226	0.267	0.073	-0.049	-0.184	0.105	-0.201	0.333	-0.270	**0.668***
EC	0.017	0.055	-0.166	0.541	-0.158	0.334	-0.199	0.273	0.139	-0.116	-0.148	0.074	-0.128	0.255	-0.208	0.575
OC	0.213	-0.159	0.038	-0.387	0.130	-0.028	0.080	-0.090	0.087	0.002	0.133	-0.237	0.190	-0.141	-0.022	-0.089
$CaCO_3$	0.134	-0.230	0.270	-0.394	0.290	-0.443	0.321	-0.431	0.194	-0.276	0.442	-0.474	0.286	-0.425	0.375	-0.579
LR	0.577	-0.582	0.591	-0.374	0.592	-0.553	**0.611***	-0.557	0.561	-0.562	0.400	-0.325	0.535	-0.509	0.595	-0.367
FC	-0.013	0.086	-0.198	0.549	-0.195	0.372	-0.205	0.211	0.113	-0.092	-0.150	0.043	-0.156	0.283	-0.238	0.592
WP	0.274	-0.337	0.251	-0.274	0.336	-0.406	0.296	-0.423	0.256	-0.292	0.154	-0.222	0.363	-0.400	0.344	-0.275
CEC	0.416	-0.479	**0.692***	-0.464	0.441	-0.500	0.598	-0.258	0.520	-0.596	0.590	-0.425	0.345	-0.389	**0.617***	-0.267
Av.P	**0.645***	**-0.699***	**0.910****	**-0.618***	**0.627***	**-0.631***	**0.880****	**-0.636***	**0.740****	**-0.801****	**0.862****	**-0.735***	0.541	-0.568	**0.848****	-0.502
Ex.Ca	0.396	-0.444	**0.607***	-0.374	0.430	-0.479	0.514	-0.201	0.470	-0.529	0.441	-0.269	0.336	-0.365	0.553	-0.239
Ex.Mg	0.387	-0.437	**0.644***	-0.428	0.399	-0.447	0.562	-0.252	0.492	-0.563	0.550	-0.389	0.303	-0.340	0.562	-0.228
Ex.K	0.541	-0.584	**0.810****	**-0.638***	0.488	-0.479	**0.786****	-0.538	**0.654***	**-0.711***	**0.896****	**-0.823****	0.423	-0.452	**0.702***	-0.371
Ex.Na	-0.405	0.393	-0.117	0.234	-0.444	0.380	-0.215	0.432	-0.341	0.295	-0.175	0.350	-0.513	0.494	-0.242	0.390
DTPA.Cu	-0.348	0.253	-0.054	0.018	-0.222	0.046	-0.055	-0.023	-0.347	0.281	0.010	0.052	-0.239	0.118	0.020	-0.295
DTPA.Mn	-0.346	0.304	-0.056	-0.016	-0.353	0.246	0.036	-0.289	-0.270	0.197	0.108	-0.112	-0.376	0.293	-0.082	-0.053
DTPA.Fe	-0.026	-0.012	-0.183	-0.102	0.164	-0.267	-0.253	0.341	-0.089	0.091	-0.223	0.193	0.189	-0.252	-0.076	-0.163
DTPA.Zn	0.460	-0.492	0.434	-0.238	0.484	-0.454	0.404	-0.303	0.568	-0.600	0.467	-0.539	0.478	-0.475	0.488	-0.317
Tot.Cu	0.159	-0.163	0.433	-0.129	0.013	0.026	0.481	-0.470	0.242	-0.283	0.467	-0.363	-0.039	0.050	0.325	-0.046
Tot.Mn	0.561	-0.585	**0.732***	**-0.668***	0.496	-0.477	**0.746****	-0.598	0.584	**-0.606***	**0.740****	**-0.655***	0.451	-0.468	**0.653***	-0.452
Tot.Fe	-0.002	-0.031	0.293	0.040	-0.172	0.188	0.325	-0.283	0.050	-0.093	0.339	-0.240	-0.177	0.180	0.197	0.146
Tot.Zn	0.438	-0.493	**0.761****	-0.526	0.370	-0.378	**0.785****	**-0.659***	0.532	-0.596	**0.853****	**-0.759****	0.314	-0.356	**0.679***	-0.402
Tot.Ca	0.540	**-0.604***	**0.718***	-0.527	**0.621***	**-0.686***	**0.636***	-0.328	**0.623***	**-0.691***	**0.604***	-0.457	0.532	-0.587	**0.700***	-0.430
Tot.Mg	0.385	-0.394	0.500	-0.391	0.302	-0.276	0.468	-0.252	0.451	-0.480	0.491	-0.411	0.264	-0.261	0.404	-0.105
Tot.Na	-0.207	0.204	-0.052	-0.031	-0.269	0.238	-0.126	0.324	-0.174	0.151	-0.073	0.129	-0.292	0.292	-0.197	0.425

*Correlation is significant at the 0.05 level
**Correlation is significant at the 0.01 level

Table 4.13. Pearson correlation analysis between soil properties and Freundlich and Langmuir isotherms at 100% liming

Parameters	$CaCl_2$				Citric				Malic				Oxalic			
	Kf	**n**	**Qmax**	**Kl**	**Kf**	**n**	**Qmax**	**Kl**	**Kf**	**n**	**Qmax**	**Kl**	**Kf**	**n**	**Qmax**	**Kl**
pH	0.351	-0.466	0.476	-0.392	0.351	-0.466	0.437	-0.337	00.398	-0.467	0.474	-0.460	0.388	-0.505	0.382	0.000
PA	0.039	0.064	-0.202	0.534	0.039	0.064	-0.276	0.432	0.008	0.064	-0.195	0.154	-0.005	0.141	-0.302	0.595
EC	0.106	-0.007	-0.158	0.487	0.106	-0.007	-0.237	0.394	0.073	-0.005	-0.151	0.114	0.061	0.072	-0.329	**0.635***
OC	0.138	0.192	0.026	-0.310	0.138	0.192	0.126	-0.096	0.090	-0.003	0.053	-0.275	0.150	0.034	-0.081	0.116
$CaCO_3$	0.193	-0.481	0.291	-0.440	0.193	-0.481	0.307	-0.339	0.263	-0.413	0.334	-0.345	0.252	-0.497	0.343	-0.498
LR	0.556	-0.488	0.579	-0.380	0.556	-0.488	0.585	-0.297	0.548	-0.509	0.554	-0.425	0.532	-0.458	**0.712***	-0.440
FC	0.084	0.001	-0.187	0.490	0.084	0.001	-0.273	0.465	0.059	0.009	-0.171	0.095	0.043	0.084	-0.299	0.585
WP	0.267	-0.405	0.244	-0.274	0.267	-0.405	0.251	-0.195	0.348	-0.383	0.265	-0.311	0.310	-0.400	0.509	-0.480
CEC	0.422	-0.542	**0.699***	-0.539	0.422	-0.542	0.554	-0.251	0.448	-0.483	0.644*	-0.384	0.408	-0.489	0.539	-0.164
Av.P	**0.678***	**-0.733***	**0.917****	**-0.672***	**0.678***	**-0.733***	**0.818****	-0.376	**0.687***	**-0.718***	**0.891****	**-0.682***	**0.664***	**-0.707***	**0.782****	-0.346
Ex.Ca	0.383	-0.465	**0.607***	-0.437	0.383	-0.465	0.489	-0.244	0.401	-0.412	0.545	-0.279	0.362	-0.405	0.491	-0.166
Ex.Mg	0.385	-0.473	**0.653***	-0.520	0.385	-0.473	0.509	-0.206	0.404	-0.422	0.594	-0.331	0.365	-0.419	0.501	-0.164
Ex.K	0.585	**-0.618***	**0.827****	**-0.700***	0.585	**-0.618***	**0.706***	-0.248	0.590	**-0.625***	**0.815****	**-0.693***	0.579	**-0.624***	**0.615***	-0.174
Ex.Na	-0.439	0.354	-0.110	0.179	-0.439	0.354	-0.241	0.197	-0.439	0.437	-0.181	0.428	-0.466	0.413	-0.226	0.215
DTPA.Cu	-0.300	-0.034	-0.051	0.078	-0.300	-0.034	-0.044	-0.140	-0.250	0.094	-0.029	0.076	-0.257	-0.019	0.031	-0.287
DTPA.Mn	-0.329	0.133	-0.026	-0.119	-0.329	0.133	-0.117	0.198	-0.281	0.225	-0.025	0.085	-0.314	0.168	0.148	-0.430
DTPA.Fe	-0.044	-0.063	-0.194	-0.047	-0.044	-0.063	-0.138	-0.150	-0.013	-0.046	-0.184	0.085	-0.007	-0.091	-0.234	0.117
DTPA.Zn	0.587	**-0.714***	0.443	-0.255	0.587	**-0.714***	0.339	0.024	**0.607***	**-0.655***	0.473	-0.555	0.582	**-0.647***	0.293	0.104
Tot.Cu	0.161	-0.130	0.446	-0.209	0.161	-0.130	0.394	-0.137	0.153	-0.139	0.425	-0.210	0.142	-0.120	0.443	-0.317
Tot.Mn	0.520	-0.410	**0.735****	**-0.717***	0.520	-0.410	**0.721***	-0.441	0.516	-0.497	**0.719***	-0.577	0.522	-0.477	0.600	-0.371
Tot.Fe	-0.004	-0.024	0.294	0.040	-0.004	-0.024	0.326	-0.330	0.015	-0.053	0.299	-0.106	0.018	-0.070	0.323	-0.243
Tot.Zn	0.473	-0.531	**0.775****	-0.574	0.473	-0.531	**0.727***	-0.402	0.485	-0.542	**0.776****	**-0.603***	0.482	-0.556	**0.678***	-0.405
Tot.Ca	0.546	**-0.663***	**0.721***	-0.594	0.546	**-0.663***	**0.631***	-0.386	0.573	**-0.617***	**0.678***	-0.444	0.540	**-0.620***	0.586	-0.251
Tot.Mg	0.349	-0.262	0.507	-0.479	0.349	-0.262	0.444	-0.238	0.353	-0.319	0.475	-0.315	0.343	-0.290	0.321	-0.077
Tot.Na	-0.266	0.272	-0.046	-0.077	-0.266	0.272	-0.180	0.236	-0.247	0.281	-0.099	0.178	-0.272	0.276	-0.111	0.225

*Correlation is significant at the 0.05 level
**Correlation is significant at the 0.01 level

Table 4.11, Table 4.12, and Table 4.13 present the correlation analysis results of soil characteristics with Langmuir and Freundlich isotherms under liming application. Soil characteristics that correlated with Langmuir and Freundlich isotherms at liming 50 – 100% are potential acid, $CaCO_3$, electrical conductivity (EC), liming requirement, field capacity, wilting point, CEC, phosphorus availability, exchangable magnesium, exchangable potassium, DTPA-Zn, total Mn, total Zn, and total Ca.

There was a positive correlation between lime requirement and Freundlich and Langmuir adsorption isotherms at 50% and 100% liming. The positive correlation between lime requirement and maximum phosphorus adsorption indicates that the higher the lime requirement of the soil, the higher the capacity of the soil to bind and store phosphorus. This means that the lime application can improve the soil's ability to retain and strengthen phosphorus adsorption so that phosphorus can be more effectively retained and available to plants (Penn & James, 2019). However, the negative correlation between lime requirement and Freundlich exponent (n) value shows an opposite relationship, indicating that increasing lime requirement may reduce the nonlinear effect of phosphorus adsorption at low concentrations.

In addition, there was a positive correlation between exchangeable cations and cation exchange capacity with maximum adsorption at all liming levels. Soils with high CEC have empty exchange spaces that can hold cation ions ad more cation ions can be bound on the soil surface, which means that the amount of these ions that can compete with phosphorus for binding on the soil surface also increases. As a result, soils with high CEC, which have higher Ca, Mg, and K contents, tend to have a higher phosphorus adsorption capacity (Asomaning, 2020). In the liming treatment, DTPA-Zn was negatively correlated with phosphorus adsorption properties. When the DTPA-Zn content in the soil increases, there is likely to be an increase in the availability of Zn in the soil solution. This may compete with phosphorus for binding to soil surface sites available for adsorption.

Total Mn, Zn, and Ca in all liming treatments were correlated with phosphorus adsorption. Specifically, the total concentrations of these microelements were negatively correlated with phosphorus adsorption properties but positively correlated with phosphorus capacity, maximum adsorption, and binding energy, indicating a

mechanism by which metal ions such as Mn, Zn, and Ca compete with phosphorus for adsorption on soil surface sites, reducing phosphorus adsorption capacity. On the other hand, an increase in the content of these metals may increase in soil surface charge or form compounds that facilitate phosphorus adsorption (Riemsdijk et al., 1987).

Available phosphorus was the variable with the highest correlation value with phosphorus adsorption in soils without and with liming. Available phosphorus was negatively correlated with adsorption properties but positively correlated with maximum adsorption, binding energy, and adsorption capacity. This indicates that the higher the phosphorus availability in the soil solution, the less phosphorus is bound by the soil surface. This could be because high phosphorus availability makes phosphorus more soluble in the soil solution and not firmly bound by the soil surface. The positive correlation between available phosphorus and phosphorus adsorption parameters indicates the influence of the solubility of native phosphorus in the soil (Zhang et al., 2014). When native phosphorus is soluble in soil solution, phosphate ions (PO_4^{3-}) can interact with negatively charged soil surfaces, such as clay minerals and iron and aluminum oxides. The negative charge on the soil surface will attract anionic phosphate ions, thus increasing the adsorption capacity of the soil to hold and bind phosphorus. In addition, when phosphorus availability increases in the dissolved form in the soil solution, plants can more easily take up phosphorus through the root absorption process. Along with the increase in phosphorus availability to plants, plants' demand for phosphorus also increases, which may result in increased interaction between phosphorus and the soil surface to fulfill plants' phosphorus needs (Devau et al., 2009; Ch'ng et al., 2014; Hasan et al., 2016; Mihoub et al., 2017; Fu & Wan, 2021).

5. CONCLUSION AND RECOMMENDATIONS

The findings from this study demonstrate the successfully application of Langmuir and Freundlich isotherms to validate the sorption data in response to soil type, lime dosage, and organic acids. Specifically, the presence of low molecular weight organic acids and the varying levels of lime were observed to impact the sorption behavior of the soils significantly. Freundlich parameter increases and adsorption capacity decreases as the liming level increases. On the other hand, the results of Langmuir isotherm analysis present a quite different pattern. In general, with increasing liming level, the binding energy decreased and the adsorption maximum value increased. The dissolution of aluminum (Al) and iron (Fe) phosphates was present in the soil, which is directly influenced by the neutralization rate. This increased pH can trigger the dissolution of various phosphorus-containing compounds. particularly aluminum and iron phosphates. As a result. more phosphorus is released into the soil solution, increasing the equilibrium concentration of phosphorus. However, Langmuir isotherm shows results that indicate the presence of base saturation, in this case, Ca^{2+} in the soil. which can reduce phosphorus adsorption.

Liming and application of low molecular weight organic acids play an effective role in reducing phosphorus adsorption in certain soils in the Black Sea region. Comparison between three different types of organic acids shows that citric acid causes a continuous decrease on adsorption with increasing liming. On the other hand. malic acid decreased phosphorus adsorption at 50% liming and oxalic acid decreased phosphorus adsorption at 100% liming. The number of the functional group was likely the primary reason for such behavior. The specific effects of these organic acids were observed under low phosphorus loads, which suggests that their influence on phosphorus availability is more pronounced under conditions where phosphorus is limited.

REFERENCES

Adeleke, R., Nwangburuka, C., & Oboirien, B. (2017). Origins, roles and fate of organic acids in soils: A review. *South African Journal of Botany, 108*, 393-406. https://doi.org/10.1016/j.sajb.2016.09.002

Akrawi, H. S. Y., Al-Obaidi, M. A., & Abdulrahman, Ch. H. (2021). Evaluation of Langmuir and Freundlich Isotherm Equation for Zinc Adsorption in Some Calcareous Soil of Erbil Province North of Iraq. *International Collaborative Conference of Modern Agriculture Technologies.* March 24 – 25, Iraq, 012017.

Amin, A. E. A. Z. (2018). Influence of some organic acids on availability and adsorption of phosphorus as well as corn growth in a clay soil. *Alexandria Journal of Soil and Water Science*s, *2*(2), 134-149. https://doi.org/10.21608/ajsws.2018.225471

Anderson, N. P., Hart, J. M., Sullivan, D. M., Christensen, N. W., Horneck, D. A., & Pirelli, G. J. (2013). Applying lime to raise soil ph for crop production (Western Oregon). Oregon State University. Retrieved August 01, 2023, from https://catalog.extension.oregonstate.edu/sites/catalog/files/project/pdf/em9057.pdf.

Andrade, F. V., Mendonça, E. S., Silva, I. R., & Mateus, R. F. (2007). Dry-matter production and phosphorus accumulation by maize plants in response to the addition of organic acids in Oxisols. *Communications in Soil Science and Plant Analysis, 38*(19-20), 2733-2745. https://doi.org/10.1080/00103620701662976

Asomaning, S. K. (2020). Processes and factors affecting phosphorus sorption in soils. In *Sorption in 2020s*. (pp. 1-15)

Atalay, I. (1983). A general survey of the vegetation of north-eastern anatolia. Ege Coğrafya Dergisi. Retrieved August 01, 2023, from https://dergipark.org.tr/en/pub/ecd/issue/4893/67113.

Ball, J. (1999). Understanding and correcting soil acidity. Noble Research Institute. Retrieved November 21, 2021, from https://www.noble.org/regenerative-agriculture/soil/understanding-and-correcting-soil-acidity/.

Barrow, N. J. (1984). Modelling the effects of pH on phosphate sorption by soils. *Journal of Soil Science, 35*(2), 283-297. https://doi.org/10.1111/j.1365-2389.1984.tb00283.x

Barrow, N. J. (2017). The effects of pH on phosphate uptake from the soil. Plant and Soil. Retrieved November 21, 2021, from https://www.jstor.org/stable/44245097.

Bender-Özenç, D., & Yazıcı, Ş. (2022). Trabzon İli Beşikdüzü İlçesinde farklı arazi kullanımı altındaki toprakların özellikleri ve verimlilik durumunun belirlenmesi. *Akademik Ziraat Dergisi*, *11*(2), 341-352. https://doi.org/10.29278/azd.1106440

Bolan, N. S., Naidu, R., Mahimairaja, S., & Baskaran, S. (1994). Influence of low-molecular-weight organic acids on the solubilization of phosphates. *Biology and Fertility of Soils, 18*(4), 311-319. https://doi.org/10.1007/BF00570634

Bolan, N., Domi, C. A., & Denis, C. (2003). Soil acidification and liming interactions with nutrient and heavy metal transformation and bioavailability. *Advances in Agronomy, 78*(2001), 215-272. https://doi.org/10.1016/S0065-2113(02)78006-1

Bolster, C. H., & Hornberger, G. M. (2007). On the use of linearized Langmuir equations. *Soil Science Society of America Journal, 71*(6), 1796-1806. https://doi.org/10.2136/sssaj2006.0304

Brady, N. C., & Ray, W. R. (2017). *The Nature and Properties of Soils.* United States of America, Pearson Education.

Bulmer, D., Kar, G., Hamilton, J. Siciliano, S., & Peak, D. (2018). Extent and mechanism of interaction between phosphate and citrate in a calcareous soil. *Soil Science Society of America Journal, 82*(2), 315-322. https://doi.org/10.2136/sssaj2017.08.0289

Ch'ng, H. Y., Ahmed, O. H., & Majid, N. M. Ab. (2014). Improving phosphorus availability in an acid soil using organic amendments produced from agroindustrial wastes. *The Scientific World Journal, 2014*(506356), 1-6. https://doi.org/10.1155/2014/506356

Çolak, H. E., & Memişoğlu, T. (2018). Trabzon ilinde tarımsal arazi kullanımındaki zamansal değişimin CBS ile belirlenmesi. *Afyon Kocatepe Üniversitesi Fen ve Mühendislik Bilimleri Dergisi, 18*(3), 946-958. https://doi.org/10.5194/isprs-annals-IV-4-W4-167-2017

Daly, K., David, S., Stan, L., & David, P. W. (2015). Phosphorus sorption, supply potential and availability in soils with contrasting parent material and soil chemical properties. *European Journal of Soil Science, 66*(4), 792-801. https://doi.org/10.1111/ejss.12260

Dunne, K. S., Holden, N. M., O'Rourke, S. M., Fenelon, A., & Daly, K. (2020). Prediction of phosphorus sorption indices and isotherm parameters in agricultural soils using mid-infrared spectroscopy. *Geoderma, 358*, 113981. https://doi.org/10.1016/j.geoderma.2019.113981

Devau, N., Cadre, E. L., Hinsinger, P., Jaillard, B., & Gérard, F. (2009). Soil pH controls the environmental availability of phosphorus: Experimental and mechanistic modelling approaches. *Applied Geochemistry, 24*(11), 2163-2174. https://doi.org/10.1016/j.apgeochem.2009.09.020

Dunn, L. E. (1943). Lime requirement determination of soils by means of titration curves. Wolters Kluwer Health. Retrieved July 21, 2023, from https://journals.lww.com/soilsci/citation/1943/11000/lime_requirement_determination_of_soils_by_means.3.aspx#ContentAccessOptions.

Ejigu, W., Yihenew, G. S., Eyasu, E., & Eyayu, M. (2023). Effect of lime rates and method of application on soil properties of acidic Luvisols and wheat (Triticum aestivum, L.) yields in northwest Ethiopia. *Heliyon*, *9*(3), e13988. https://doi.org/10.1016/j.heliyon.2023.e13988

Errassifi, F.. Menbaoui, A. Autefage, H., Benaziz, L., Ouizat, S., Santran, V., Sarda, S., Lebugle, A., Combes, C., Barroug, A., Sfihi, H., & Rey, C. (2010). Adsorption onto nanocrystalline apatitic calcium phosphates applications to growth factors and drugs delivery. *8th Pacific Rim Conference on Ceramics and Glass Technology (PACRIM-8)*, May 31 – June 31, Canada, 577364.

Eslamian, F., Qi, Z., & Qian, C. (2021). Lime amendments to enhance soil phosphorus adsorption capacity and to reduce phosphate desorption. *Water Air and Soil Pollution*, *232*(2), 66. https://doi.org/10.1007/s11270-021-05024-3

Feng, C., Yan, L., Song, D., & Guan, L. Z. (2012). The effects of soft leaching with low molecular weight organic acids on soil P release characteristics. *Advanced materials research*, *518-523*(1), 2900-2905. https://doi.org/10.4028/www.scientific.net/AMR.518-523.2900

Fox, T. R. (1995). The influence of low-molecular-weight organic acids on properties and processes in forest soils. In *Carbon Fonns and Functions in Forest Soils*. (pp. 43-62)

Fox, T. R., & Comerford, N. B. (1990). Low-molecular-weight organic acids in selected forest soils of the southeastern USA. *Soil Science Society of America Journal*, *54*(4), 1139-1144. https://doi.org/10.2136/sssaj1990.03615995005400040037x

Fu, W., & Wan, Y. 2021. Study on the Effects of Low Molecular Organic Acids on the Availability and Morphology of Phosphorus in Calcite Soils. *IOP Conference Series: Earth and Environmental Science*. January 22-25, China, 012029.

Ghasemi, J., & Asadpour, S. (2007). Thermodynamics' study of the adsorption process of methylene blue on activated carbon at different ıonic strengths. *The Journal of Chemical Thermodynamics*, *39*(6), 967-971. https://doi.org/10.1016/j.jct.2006.10.018

Gaviglio, K., Shields, S., & Mondala, A. (2018). Synergistic runoff particulate-bound phosphorus extraction by oxalate and citrate ligands in a mixed aqueous extractant system. *Clean - Soil, Air, Water*, *47*(1), 1700499. https://doi.org/10.1002/clen.201700499

Gee, G., & Bauder, J. W. (1989). Particle-size analysis. In *Methods of Soil Analysis, Part 1. Physical and Mineralogical Methods.* (pp. 383-411)

Gisi, S. D., Giusy, L., Mariangela, G., & Michele, N. (2016). Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: A review.

Sustainable Materials and Technologies, 9, 10-4, https://doi.org/10.1016/j.susmat.2016.06.002

Gökçe, C. (2019). *Assessment of Soil Properties in Terms of Sustainable Soil Management in Hazelnut Orchards Located on Central Black Sea Region*. (Yüksek Lisans Tezi, Ondokuz Mayis Üniversitesi Fen Bilimleri Enstitüsü)

Goh, T. B., Arnaud, R. S., & Mermut, A. R. (1993). Carbonates. In *Soil Sampling and Methods of Analysis* (pp. 177-199)

Gunary, D. (2006). A new adsorption isotherm for phosphate in soil. *European Journal of Soil Science, 21*(1), 72-77. https://doi.org/10.1111/j.1365-2389.1970.tb01153.x

Gypser, S., Schütze, E., & Freese, D. (2019). Crystallization of single and binary iron- and aluminum hydroxides affect phosphorus desorption. *Journal of Plant Nutrition and Soil Science, 182*(5), 741-750. https://doi.org/10.1002/jpln.201700543

Hardjowigeno, S. (2003). *Ilmu Tanah*. Jakarta, Akademika Pressindo.

Harrold, S. A., & Tabatabai, M. A. (2006). Release of inorganic phosphorus from soils by low- molecular- weight organic acids, *Communications in Soil Science and Plant Analysis, 37*(9-10), 1233-1245. https://doi.org/10.1080/00103620600623558

Hasan, Md. M., Hasan, Md. M., Teixeira da Silva, J. A., & Li, X. (2016). Regulation of phosphorus uptake and utilization: transitioning from current knowledge to practical strategies. *Cellular and Molecular Biology Letters, 21*(7), 1-19. https://doi.org/10.1186%2Fs11658-016-0008-y

Haynes, R. J., & Mokolobate, M. S. (2001). Amelioration of Al toxicity and P deficiency in acid soils by addition of organic residues: A critical review of the phenomenon and the mechanisms involved. *Nutrient Cycling in Agroecosystems, 59*(1), 47-63. https://doi.org/10.1023/A:1009823600950

Hendershot, W. H., Lalande, H., & Duquette, M. (2007). Soil reaction and exchangeable acidity. In *Soil Sampling and Methods of Analysis*. (pp 173-178).

Hu, H. Q., He, J. Z., Li, X. Y., & Liu, F. (2001). Effect of several organic acids on phosphate adsorption by variable charge soils of central China. *Enviroment International, 26*(5-6), 353-358. https://doi.org/10.1016/S0160-4120(01)00012-5

Hu, H., Liao, L., & Wang, X. (2002). Effect of low molecular weight organic acids on inorganic phosphorus transformation in red soil and its acidity. *Ying Yong Sheng Tai Xue Bao, 13*(7), 867-70. https://pubmed.ncbi.nlm.nih.gov/12385221/

Hughes, S. L., Reynolds, B., Bell, S. A., & Gardner, C. (2000). Simple phosphorus saturation index to estimate risk of dissolves P in runoff from arable soils. *Soil Use and Management, 16*(3), 206-21. https://doi.org/10.1111/j.1475-2743.2000.tb00194.x

Ince, F. (1975). Urfa, Diyarbakır, Erzurum ve Rize bölgelerinde kireç taşı ve bazalt ana kayalardan oluşan toprakların morpholojik, fiziksel ve kimyasal özellikleri üzerine araştırmalar. *Atatürk Üniversitesi Ziraat Fakültesi Dergisi, 6*(3), 35-48.

Jiang, H., Li, T., Han, X., Yang, X., & He, Z. (2012). Effects of pH and low molecular weight organic acids on competitive adsorption and desorption of cadmium and lead in paddy soils. *Environmental Monitoring and Assessment, 184*(11), 6325-6335. https://doi.org/10.1007/s10661-011-2422-y

Jiao, Y., Whalen, J. K., & Hendershot, W. H. (2007). Phosphate sorption and release in a sandy-loam soil as ınfluenced by fertilizer sources. *Soil Science Society of America Journal, 71*(1), 118-124. https://doi.org/10.2136/sssaj2006.0028

Johnson, S. E., & Loeppert, R. H. (2006). Role of organic acids in phosphate mobilization from ıron oxide. *Soil Science Society of America Journal, 70*(1), 222-234. https://doi.org/10.2136/sssaj2005.0012

Kabata-Pendias, A. (2011). *Trace Elements in Soils and Plants*. Boca Raton, CRC Press.

Kacar, B., Przemeck, E., Özgümüş, A., Turan, C., Katkat, A. V., & Kayıkçıoğlu, İ. (1987). *Mikroelement Gübrelerin Çay Bitkisi Üzerine Etkileri*. *International Tea Symposium*. June 26-28, Rize, 97-106.

Kahraman, M. (2016). *The Determination of Soil Productivity and Plant Nutrition Correlations on Ordu-Center District Hazelnut Gardens*. (Yüksek Lisans Tezi, Ordu Üniversitesi Fen Bilimleri Enstitüsü)

Khademi, Z. J. D. L., Malakouti, M. J., & Asadi, F. (2010). Organic acids differ in enhancing phosphorus uptake by Triticum aestivum L. effects of rhizosphere concentration and counterion. *Plant and Soil, 334*(1-2), 151-159. https://doi.org/10.1007/s11104-009-0215-7

Klute, A. (1986). Water retention: Laboratory methods. In *Methods of Soil Analysis, Part 1. Physical and Mineralogical Methods*. (pp. 635-662)

Kpomblekou, A. K., & Tabatabai, M. A. (2003). Effect of low-molecular weight organic acids on phosphorus release and phytoavailabilty of phosphorus in phosphate rocks added to soils. *Agriculture, Ecosystems and Environment, 100*(2-3), 275-284. https://doi.org/10.1016/S0167-8809(03)00185-3

Kuo, S. (1996). Phosphorus. In *Methods of Soil Analysis Part 3- Chemical Methods*. (pp. 869-919)

Lee, Y. B., & Kim, P. J. (2007). Reduction of phosphate adsorption by ıon competition with silicate in soil. *Korean Journal of Enviromental Agricultre, 26*(4), 286-293. https://doi.org/10.5338/KJEA.2007.26.4.286

Lindsay, W. L., & Norvell, W. A. (1978). Development of a DTPA soil test for zinc, iron, manganese and copper. *Soil Science Society of America, 42*(3), 421-428. https://doi.org/10.2136/sssaj1978.03615995004200030009x

Lindsay, W. L. (2001). *Chemical Equilibria in Soils*. USA, The Blackburn Press.

Liu, S. (2015). Cooperative adsorption on solid surfaces. *Journal of Colloid and Interface Science, 450*(2), 224-238. https://doi.org/10.1016/j.jcis.2015.03.013

Majumdar, B., Kailash, K., Venkatesh, M. S., & Patiram. (2005). Effect of liming on phosphorus adsorption and desorption behaviour of acidic Alfisols and Entisol of Meghalay. Indian Journals. Retrieved August 1, 2023, from https://www.indianjournals.com/ijor.aspx?target=ijor:jisss&volume=53&issue=2&article=007.

Mendes, G. O., Murta, H. M., Valadares, R. V., Silveira, W. B., Silva, I. R., & Costa, M. D. (2020). Oxalic acid is more efficient than sulfuric acid for rock phosphate solubilization. *Minerals Engineering, 155*, 106458. https://doi.org/10.1016/j.mineng.2020.106458

Mihoub, A., Daddi-Bouhoun, M., Naeem, A., & Saker, M. L. (2017). Low-molecular weight organic acids improve plant availability of phosphorus in different textured calcareous soils. *Archives of Agronomy and Soil Science, 63*(7), 1023-1034. https://doi.org/10.1080/03650340.2016.1249477

Moradi, N., Sadaghiani, M. R., Sepehr, E., & Mandoulakani, B. A. (2012). Effects of low-molecular-weight organic acids on phosphorus sorption characteristics in some calcareous soils. *Turkish Journal of Agriculture and Forestry, 36*(4), 459-468. https://doi.org/10.3906/tar-1106-38

Murphy, J., & Riley, J. P. (1962). A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta, 27*, 31-36. https://doi.org/10.1016/S0003-2670(00)88444-5

Myers, D. (1999). *Surfaces, Interfaces, and Colloids Principles and Applications*. New York, John Wiley & Sons, Inc.

Naidu, R., Syers, J. K., Russ, T., & Kirkman, J. H. (2006). Effect of liming and added phosphate on charge characteristics of acid soils. *European Journal of Soil Science, 41*(1), 157-164. https://doi.org/10.1111/j.1365-2389.1990.tb00053.x

Nelson, D. W., & Sommers, L. E. (1996). Total carbon, organic carbon, and organic matter. In *Methods of Soil Analysis, Part 3. Chemical Methods*. (pp. 961-1010)

Neswati, R., Azizah, N., Lopulisa, C., & Abdullah, S. (2018). Effect of humic subtances produced from lignite and straw compost on phosphor availability in

oxisols. *International Journal of Soil Science*, *13*(1), 42-49. https://doi.org/10.3923/ijss.2018.42.49

Okman, C., & Öztürk, F. (1987). Çay Bitkisinin İklim İsteklerine Göre Ekonomik Gelişme Bölgesi. *International Tea Symposium*. June 26-28, Rize, 9-16.

Oral, A. (2013). *Düşük Molekül Ağirlikli Organik Asitlerin Arpada Fosfor Alimina Etkisi*. (Yüksek Lisans Tezi, Isparta Uygulamalı Bilimler Üniversitesi Lisansüstü Eğitim Enstitusü)

Özcan, H., Dengiz, O., & Erşahin, S. (2018). Alisols-Acrisols. In *The Soils of Turkey*. (pp. 207-216)

Özey, R. (2002). *Türkiye Coğrafyası ve Jeopolitiği*. Istanbul, Aktif Yayınevi.

Özkutlu, F., Akkaya, Ö. H., Ete, Ö., Şahin, Ö., & Korkmaz, K. (2015). Rize ilindeki bazı çay bahçelerinin toprak ve yaprak analizi ile besin element düzeylerinin belirlenmesi. *Harran Tarım ve Gıda Bilimleri Dergisi*, *19*(2), 94-103.

Özyazıcı, G. Özyazıcı, M. A., Özdemir, O., & Sürücü, A. (2010). Some physical and chemical properties of tea grown soils in Rize and Artvin provinces. *Anadolu Journal Agriculture Science*, *25*(2), 94-99.

Özyazıcı, M. A., Aydoğan, M., Bayraklı, B., & Dengiz, O. (2013). Doğu Karadeniz bölgesi kırmızı-sarı podzolic toprakların temel karakteristik özellikleri ve verimlilik durumu. *Anadolu Tarım Bilim Dergisi*, *28*(1), 24-32. https://doi.org/10.7161/anajas.2013.281.24

Paul, C. S., Mercl, F., Szakova, J., Tejnecky, V., & Tlustos, P. (2021). The role of lowmolecular weight organic acids in the release of phosphorus from sewage sludge-based biochar. *All life*, *14*(1), 599-609. https://doi.org/10.1080/26895293.2021.1932611

Penn, C. J., & James J. C. (2019). A critical review on soil chemical processes that control how soil pH affects phosphorus availability to plants. *MDPI Journal Agriculture*, *9*(6), 120. https://doi.org/10.3390/agriculture9060120

Perassi, I., & Borgnino, L. (2014). Adsorption and surface precipitation of phosphate onto $CaCO_3$–montmorillonite: Effect of pH, ionic strength and competition with humic acid. *Geoderma*, *232-234*, 600-608. https://doi.org/10.1016/j.geoderma.2014.06.017

Perez-Novo, C., Alipio B., Jose, E. L., & David, F. (2009). The effect of phosphate on the sorption of copper by acid soils. *Geoderma*, *150*(1-2). 166-170. https://doi.org/10.1016/j.geoderma.2009.02.001

Perminova, I. V., Frimmel, F. H., Kudryaystev, A. V., Kulikova, N. A., Abbt-Braun, G., Hesse, S., & Petrosyan, V. S. (2003). Molecular weight characteristics of humic substances from different environments as determined by size exclusion chromatography and their statistical evaluation. *Environmental Science and Technology, 37*(11), 2477-2485. https://doi.org/10.1021/es0258069

Riemsdijk, W. H., Lexmond, T. M., Enfield, C. G., & Zee, S. E. A. T. M. (1987). Phosphorus and heavy metals: Accumulation and consequences. In *Animal Manure on Grassland and Fodder Crops Fertilizer or Waste?*. (pp. 213-227)

Sarımehmet, M., & Muftoğlu, N. M. (1993). Doğu Karadeniz bölgesi çay tarım topraklarının organik madde durumu. ResearchGate. Retrieved July 29, 2023, from https://www.researchgate.net/publication/310445749_Dogu_Karadeniz_Bolgesi_cay_tarim_topraklarinin_organik_madde_durumu/citations

Schmitt, D., Paulo, H. P., & Carlos, A. C. (2017). Chemical distribution of phosphorus in soils used during the development of sorption ısotherms. *Soil Science Society of Amerika Journal, 81*(1), 84-93. https://doi.org/10.2136/sssaj2016.07.0220

Schmitt, D. E., Gatiboni, L. C., Orsoletta, D. J. D., & Brunetto, G. (2018). Formation of ternary organic acids-Fe-P complexes on the growth of wheat (Triticum aestivum). *Revista Brasileira de Engenharia Agrícola e Ambiental*, *22*(10), 702-706. https://doi.org/10.1590/1807-1929/agriambi.v22n10p702-706

Shafqat, M. N., & Pierzynski, G. M. (2014). The Freundlich adsorption isotherm constants and prediction of phosphorus bioavailability as affected by different phosphorus sources in two Kansas soils. *Chemosphere, 99*, 72-80. https://doi.org/10.1016/j.chemosphere.2013.10.009

Sheldrick, B. H., & Wang, C. (1993). Particle size distribution. In *Soil Sampling and Methods of Analysis*. (pp. 499-511)

Simonsson, M., Östlund, A., Rendjall, L., & Sigtryggsson, C. (2018). Pools and solubility of soil phosphorus as affected by liming in long-term agricultural field experiments. *Geoderma, 315*, 208-219. https://doi.org/10.1016/j.geoderma.2017.11.019

Stevenson, F. J. (1994). *Humus chemistry: Genesis, Composition, Reactions*. New York, Wiley.

Ström, L., Owen, A. G., Godbold, D. L., & Jones, D. L. (2002). Organic acid mediated P mobilization in the rhizosphere and uptake by maize roots. *Soil Biology and Biochemistry, 34*(5), 703-710. https://doi.org/10.1016/S0038-0717(01)00235-8

Sui, Y., & Thompson, M. L. (2000). Phosphorus sorption, desorption, and buffering capacity in a biosolids-amended Mollisol. *Soil Science Society of America Journal, 64*(1), 164-169. https://doi.org/10.2136/sssaj2000.641164x

Summer, M. E., & Miller, W. P. (1996). Cation exchange capacity and exchange coefficients. In *Methods of Soil Analysis, Part 3. Chemical Methods*. (pp. 1201-1229)

Taşkın, M. B., Balcı, M., Soba, M. R., Kaya, E. C., Özer, P., Tanyel, G., Kabaoğlu, A., Turan, M. A., & Taban, S. (2015). Doğu Karadeniz bölgesinde çay tarımı yapılan toprakların ve çay bitkisinin azot, fosfor, potasyum, kalsiyum, magnezyum ve kükürt durumları. *Toprak Su Dergisi*, *4*(2), 30-40. https://doi.org/10.21657/tsd.05240

Thomas, G. W. (1996). Soil pH and soil acidity. In *Methods of Soil Analysis. Part 3. Chemical Methods.* (pp. 475-490)

Tuyisenge, J. C. (2021). *Kireçlemenin Asit Topraklarda Inorganik Fosfor Fraksiyonları Üzerine Etkisi*. (Yüksek Lisans Tezi, Isparta Uygulamalı Bilimler Üniversitesi Lisansüstü Eğitim Enstitüsü)

Usta, S. (1995). *Toprak Kimyası.* Ankara, Ankara Üniversitesi.

Uygur, V., & Karabatak, I. (2009). The effect of organic amendments on mineral phosphate fractions in calcareous soils. *Journal of Plant Nutrition and Soil Science*, *172*(3), 336-345. https://doi.org/10.1002/jpln.200700326

Uygur, V., Durgun, B., & Senol, H. (2017a). Chemical fractions of phosphorus: The effect of soil orders, soil properties, and land use. *Communications in Soil Science and Plant Analysis*, *48*(11), 1319-1335. https://doi.org/10.1080/00103624.2017.1341919

Uygur, V., Durgun, B., & Sukuşu, E. (2017b). Profile-Based Available Phosphorus Fractions in Different Soil Ordos. *International Congress of Agriculture and Environment*. November 16-18, Antalya. 53.

Uygur, V., Karaduman, M. A., Keçeci, M., Sukuşu, E., & Müjdeci, M. (2017c). Competitive adsorption of heavy metals in different soils. ResearchGate. Retrieved November 11, 2021, from https://www.researchgate.net/publication/325538527_Competitive_adsorption_of_heavy_metals_in_different_soils#fullTextFileContent

Uygur, V., Durgun, B., Sukuşu, E., Müjdeci, M., & Alaboz, P. (2018). Evaluation of Heavy Metal Pollution in Atabey Plain Induced Plant Cover Related Input Managements. *V. International Multidisciplinary Congress of Eurasia*, July 24-26, Barcelona, 202-203.

Ünal, H. (1967). *Rize Çay Topraklarının Anzim Aktiviteleri ve bu Aktivitelerle Önemli Toprak Özellikleri Arasındaki İlgiler*. Ankara, Ankara Üniversitesi Basımevi.

Qayyum, M. F., Ashraf, I., Abis, M., & Steffens, D. (2015). Effect of biochar, lime, and compost application on phosphorus adsorption in a Ferralsol. *Journal of Plant Nutrition and Soil Science*, *178*(4), 576-581. https://doi.org/10.1002/jpln.201400552

Wang, Y., Chen, X., Whalen, J. K., Cao, Y., Quan, Z., Lu, C., & Shi, Y. (2015). Kinetics of inorganic and organic phosphorus release influenced by low molecular weight organic acids in calcareous, neutral and acidic soils. *Journal of Plant Nutrition and Soil Science, 178*(4), 555-566. https://doi.org/10.1002/jpln.201500047

Wang, Y., Whalen, J. K., Chen, X., Cao, Y., Huang, B., Lu, C., & Shi, Y. (2016a). Mechanisms for altering phosphorus sorption characteristics induced by low molecular weight organic acids. *Canadian Journal of Soil Science, 96*(3), 289-298. https://doi.org/10.1139/cjss-2015-0068

Wang, Y. Z., Hu, B. Q., & Yan, Y. (2016b). Effects of low molecular weight organic acids on phosphorus adsorption characteristics in a black clay soil in northeast China. In *Fresenius Environmental Bulletin.* (pp. 517-524).

Wei, S., Wenfeng, T., Fan, L., & Wei, Z. (2014). Surface properties and phosphate adsorption of binary systems containing goethite and kaolinite. *Geoderma, 213*, 478-484. https://doi.org/10.1016/j.geoderma.2013.09.001

Wen, X., Yin, W., Pengfei, C., Dong, L., Siqi, M., Chenrui, Z., Tongxu, L., & Liang, T. (2020). Surface charge properties of variable charge soils influenced by environmental factors. *Applied Clay Science, 189*, 105522. https://doi.org/10.1016/j.clay.2020.105522

Wong, M. T. F., Gibbs, P., Nortcliff, S., & Swift, R. S. (2000). Measurement of the acid neutralizing capacity of agroforestry tree prunings added to tropical soils. *Journal of Agricultural Science, 134*(3), 269-276. https://doi.org/10.1017/S0021859699007388

Yang, X., Chen, X., Guo, E., & Yang, X. (2019a). Path analysis of phosphorus activation capacity as induced by low-molecular-weight organic acids in a black soil of Northeast China. *Journal of Soils and Sediments, 19*(2), 840-847. https://doi.org/10.1007/s11368-018-2034-z

Yang, X. Chen, X., & Yang, X. (2019b). Effect of organic matter on phosphorus adsorption and desorption in a black soil from Northeast China. *Soil and Tillage Research, 187*, 85-91. https://doi.org/10.1016/j.still.2018.11.016

Yigezu, E., Fanuel, L., & Alemayehu, K. (2023). Effects of liming and different land use types on phosphorus sorption characteristics in acidic agricultural soil of Sodo Zuria Woreda, Southern Ethiopia. *Heliyon, 9*(3), 14124. https://doi.org/10.1016/j.heliyon.2023.e14124

Zhang, M., Li, C., Li, Y. C., & Harris, W. G. (2014). Phosphate minerals and solubility in native and agricultural calcareous soils. *Geoderma, 232-234*, 164-171. https://doi.org/10.1016/j.geoderma.2014.05.015

Zhang, H., Li, Q., Zhang, X., Chen, W., Ni, J., Yang, L., & Wei, R. (2020). Insight into the mechanism of low molecular weight organic acids-mediated release of phosphorus and potassium from biochars. *Science of The Total Environment, 742*, 140416. https://doi.org/10.1016/j.scitotenv.2020.140416

Zhang, J. X. Gao, L., & Pang, Z. D. (2021). Effect of low-molecular-weight organic acids on phosphorus soil activation: A laboratory study of the soils from Wangbeng section of the Huaihe River Basin, China. *Plant, Soil and Environment, 67*(11), 660-667. https://doi.org/10.17221/379/2021-PSE

Zhu, H., Bing, H., Wu, Y., Sun, H., & Zhou, J. (2021). Low molecular weight organic acids regulate soil phosphorus availability in the soils of subalpine forests, eastern Tibetan Plateau. *CATENA, 203*, 105328. https://doi.org/10.1016/j.catena.2021.105328

Zhu, H., Bing, H., & Wu, Y. (2022). Citric acid promotes the mobilization of phosphorus under the lower concentration of low molecular weight organic acids in acidic forest soil. *Adsorption Science and Technology, 2022*, 5071907. https://doi.org/10.1155/2022/5071907

CURRICULUM VITAE