International Research Journal of Pure & Applied Chemistry

22(2): 82-89, 2021; Article no.IRJPAC.67559
ISSN: 2231-3443, NLM ID: 101647669

Fate of Citric Acid Addition on Mineral Elements Availability in Calcareous Soils of Jordan Valley

Zohuir A. Al-balawna[1] and Ideisan I. Abu-Abdoun[2*]

[1]Jordan Valley Authority Laboratories, Dair Ulla, Al-Balqa Jordan.
[2]Department of Chemistry, University of Sharjah, Sharjah, United Arab Emirates.

Authors' contributions

This work was carried out in collaboration between both authors. Author ZAA designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. 'Author IIA' managed the analyses of the study and managed the literature searches. Both authors read and approved the final manuscript.

Article Information

DOI: 10.9734/IRJPAC/2021/v22i230389
Editor(s):
(1) Dr. Richard Sawadogo, Research Institute for Health Sciences, Burkina Faso.
Reviewers:
(1) Jibing Xiong, China University of Mining and Technology, China.
(2) Jesus Salvador Luna Alvarez, Universidad Autonoma de Coahuila, Mexico.
Complete Peer review History: http://www.sdiarticle4.com/review-history/67559

Original Research Article

Received 05 February 2021
Accepted 11 April 2021
Published 14 April 2021

ABSTRACT

The variation in physical and chemical properties of calcareous soils in Jordan valley has been changed dramatically due to use large amount of fertilizers in regular manner. Addition of organic acid such as citric acid (CA), can greatly change the pH which can affects plant growth and production, the weakly ionized organic acid present in the calcareous soil mostly in the form of organic matter, can play major rule in soils to raise the availability of mineral nutrients that are essential for crops, by lowering soil density, reducing soil salinity and the effects of suspended particles in soil which may hinder plant growth.

The reduction in the pH of the soil enhance the availability of nutrients such as Fe, Cu, Zn, ions, by converting the metallic insoluble state to ionic form, and thus nutrients are easily available for plants intake, the salinity of the soil did not change by increasing the citric acid concentration, while the pH of the soil decreases.

Data are presented to show the effects of citric acid (CA) concentration, ionic concentration of iron, copper, Zinc and manganese and the decrease in soil PH and soil density.

**Corresponding author: E-mail: abuabdoun@sharjah.ac.ae;*

Keywords: Soil pH; available nutrient; soil salinity; citric acid; soil bulk density.

1. INTRODUCTION

Citric acid or lemon salt is a week organic acid available in many fruits and food products and soft drinks as preservative and flavour enhancer material and as antioxidants and refer to as E330, it is also used to clean the surface of metals, and as water softener. It is a metabolite in plants and has important role in photosynthesis and cellular respiration. Citric acid has three carboxylic acid (COOH) groups which can be deprotonate to form a negatively charged citrate molecule.

The major micronutrients elements for all crops are B, Cu, Fe, Mn, Mo and Zn, other micronutrients needed at low concentrations are essential to the growth of some plants are Ni and Co [1].

Recently The micronutrient deficiencies in crops has increased markedly in Jordan valley due to intensive cropping, loss of top soil by erosion, losses of micronutrients through leaching, liming of acid soils, decreased proportions of farm yard manure compared to chemical fertilizers [2].

The calcareous soils present high levels of free $CaCO_3$ and a high pH value, in addition to large amounts of soluble salts reduced availability of essential mineral nutrients such as Zn, Cu, Mn, Fe, B, and P that are necessary for the growth and development of crops and for quality and quantity of crops yield. Techniques include adding soluble exogenous organic acid such as citric acid (CA), sulphur powder [3-4].

Organic acids are produced by different biosynthetic pathways in plants, and are involved in various metabolic activities such as energy storage, the biosynthesis of amino acids, stomatal functioning, ion balance and the transport of compounds from the vacuole and the mitochondria [5-6].

Acidity has great effects on the nutrient deficiencies, mobilizing some nutrients such as Ca^{2+}, Fe^{3+}, K^{+}, Ca^{2+}, Mg^{2+} and PO_4^{-3} in calcareous soils. Citric acid plays a significant role to decrease bulk density of soil which is indicator of compaction and soil health, it affects infiltration, rooting depth restrictions, available water capacity, soil porosity, plant nutrient availability, and soil microorganism activity, which influence key soil processes and productivity [7].

The increased availability of nutrients results both from the supply of H^+ that acidifies the rhizosphere and soil pore water and from the formation of soluble cation-organic acid complexes, which provides a direct route for absorption in addition to protecting their precipitation. Citric acid is one of the most common organic acids, and in its deprotonated form, makes complexes with elements present in the soil such as Zn, Fe, Mn, and Cu. Hence, it is possible that the addition of CA to calcareous soil could modify the chemical characteristics of the soil pore water and its ionic composition and, consequently, induce changes in the elemental composition and concentrations in leaf tissue and fruit [8].

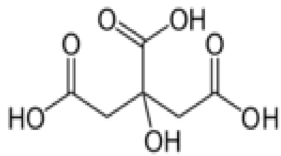
In many groundwater systems, citric acid is among the organic ligands that are continuously produced by microorganisms, root exudation, and decomposition of soil organic matter in the rhizosphere [9]. It has been reported that that citric acid is highly effective in removing uranium, and that the extraction efficiency increases with increasing citric acid concentration [10].

The desorption behavior of heavy metals, Zn(II) and Cu(II), in the contaminated soil using citric acid and citric acid-containing wastewater (CACW) was described [11].

The aim of this study is to determine the effect of CA addition on the chemical and physical characteristics of calcareous soil, and the concentration of anions and cations in soil of the Jordan valley, and to verify the correlation between the concentrations of different elements in the soil solution and water, and to determine the impact of citric acid (CA) on fruit quantity and quality.

2. MATERIALS AND METHODS

Citric acid (CA) is a weak organic acid occurring naturally in many fruits, especially in citrus fruits, also found in animal fluids and tissue, It contains three carboxylic acid groups named; 2-hydroxy-1,2,3-propanetricar-boxylic acid. It has pKa values as follows; pK_{a1} = 3.15; pK_{a2} = 4.77, and pK_{a3} = 6.40. It is is very soluble and used as an additive in many drinks, food and pharmaceutical industries.



Structure of citric acid

This study was carried out at the laboratory of Jordan valley authority which is located at Dair Ulla, Al-Balqa. The climate of the region Jordan valley is very dry, semi-cool, winter extremes, rain in winter precipitation exceeding 30% of the annual total.

2.1 The Site of the Study

Studied soil samples were collected from farm number 115 demand area 22 in Jordan valley which is shown in the given location in Fig. 1.

https://www.google.com/maps/place/32%C2%B013'35.0%22N+35%C2%B036'32.8%22E/@32.226844,35.6114328,17z/data=!4m6!3m5!1s0!7e2!8m2!3d32.2263889!4d35.6091004

Fig. 1. The site location in Jordan Valley

2.2 Preparation of Sample

Samples used in this study were top soils (0−10 cm depth) from the selected location above, then dried in open atmosphere at temperature between 25 - 40ºC, which is typical of the weather conditions at Jordan valley, then the sample was ground well using Agate Mortar and pustule manually, weight out each 500 g sample from the main soil sample into 6 batches in a pockets. Each pockets weighted amount of citric acid was added as shown in Table 1, then 100 ml of distilled water was added to each pocket.

The pocket contents were left to dried at various conditions (20 - 40ºC) for three days. After each period of time, another 100 ml of distilled water was added to each pocket, and the previous irrigation - drying steps were repeated. After these periods samples were dried for three days under the same condition, before grinding and drying each of the soil solid - citric acid of the control experimental analysis, as shown in Table 2.

2.3 Samples Analysis

Analysis of soil-citric acid samples was carried out as follows:

1- Weight out 10.0 g from blank sample to prepare soil extraction (1:5 extract) following the procedure in method of soil analysis [12].

The DTPA (diethylenetriaminepentaacetic acid) micronutrient extraction method is a non-equilibrium extraction for estimating the potential soil availability of Zn, Cu, Mn, and Fe).

2- measure the electrical conductivity (EC) ms/cm by using electron conductivity meter (Jenway type). The pH was measured using PH- meter, Metrohm AG..
3- Weight out 25.0 g from blank solution above to extract Cu, Zn, Mn, Fe by using DTPA and measured the extraction by Perkin Elmer AAnalyst 300 Atomic Absorption Spectrometer.
4- To measure soil density, use typical method of irregular solid sample density. Weigh out dry solid soil sample and measure the displaced water volume taken in centimetres per unit of mass in gram (g/m), this is used to measure the bulk density of the reported soil samples in Table 2.

Table 1. Soil samples preparation and citric acid contents, "control experiments"

Pocket No	1	2	3	4	5	6
Weight of soil (g)	500	500	500	500	500	500
Weight of citric acid (g)	0.00	0.50	1.00	1.50	2.00	2.5

3. RESULTS AND DISCUSSION

Plant micronutrients tend to be less available in soils having high pH, and the microbial populations in the soil increases. Addition different quantities of fertilizer will improve the quality of soil and minimizing the effect of sodium, as sodium plays an adverse effect on plants and reduce production, resulting the removing the water content of plant roots and thus weekend the plant, and may cause its death, also increasing of sodium contents in the soil causes closing of the pores of the soil, and finally, the plant died.

Addition of citric acid to calcareous soil, as economic chemical fertilizer, helps in solving many plants problems, such as lowering soil pH, which is an advantage to the soil because the reduction of pH uptake of the trace elements Fe, Cu, Zn, Mn, change them from insoluble metallic form to soluble ionic form, which are important nutrient to plants. It has been reported that increasing cupper ion (Cu^{2+}) concentration in soil can lower the pH and damage the soil pathogen [13].

3.1 Effect of Citric Acid on Soil Salinity

The effects of adding citric acid on lowering soil salinity was carried out**,** the treatments consist of adding different amount of citric acid in grams to each 500 grams of soil as 0.0, 0.5, 1.0, 1.5, 2.0, 2.0 gram, 300 ml of water added during 3 days, after 10 days, the soil salinity were analysed using Electrical conductivities meter, results are reported in Table 2, these results indicate soil samples are stable to citric acid addition to soil.

3.2 Effect of Citric Acid on the Liberalization of Metal Ions

The bioavailability of heavy metal nutrient as a result of different amount of citric acid added to the prepared soil sample leads to rising the concentration of zinc (Zn^{2+}), copper (Cu^{2+}) and Iron(Fe^{+3}) as shown in Fig. 2 and increase the availability of Manganese(Mn^{2+}), copper(Cu^{2+}), zinc(Zn^{2+}) and iron (Fe^{3+}) from insoluble metallic form to soluble ionic form. This is due to lowering of the pH of the soil [11].

3.3 Effect of Citric Acid on Soil Density

Considerable amount of citric acid added to the soil will leads to decrease in soil density as shown in Fig. 2, this is due to carbon dioxide production by chemical reaction of citric acid in soil, thus the new soil density will help the plant root to breathing and good growth of the crops. Results from soil conductivity can be used as an indicator of soil nutrient level.

3.4 Effects of Adding CA on Crops Production and Quality

Adding CA to soil will leads to increasing in corps quality, growth, flowering and yield as shown in Table 3.

3.5 Soil Analysis of Farms in the Area of Study

Table 4. shows Soil salinity, metals contents ppm and pH value of soil in several farms in the area of this study.

Water and soil management practices have facilitated agricultural production on soil marginalized by salinity but an additional gain from these approaches seems problematic [14].

Soil salinity, metals contents and pH were determined for several farms in the area where soil samples collected from Table 4, Soil pH

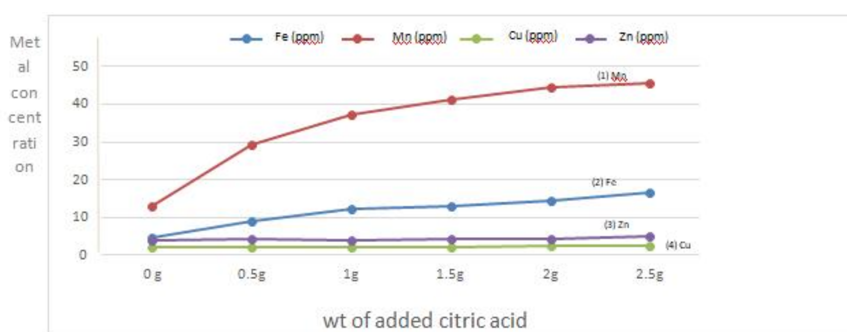


Fig. 2. Effect of citric acid addition on the release of metals cation (Zn, Cu, Fe and Mn) in soil

Table 2. Analysis result of ions concentrations in soil

Sample No	Wt. CA/ gram	Wt. Soil/ gram	Fe/ (ppm)	Mn/ (ppm)	Cu/ (ppm)	Zn/ (ppm)	EC/ (ms/cm)	PH	Soil density/ (g/cm)
1 blank	0.0 g	500 g	4.53	13.19	2.0	4.07	0.56	13.0	2.00
2	0.5 g	500 g	9.10	29.4	2.1	4.25	0.55	10.0	1.85
3	1.0 g	500 g	12.25	37.35	2.2	4.14	0.57	9.0	1.63
4	1.5 g	500 g	13.00	41.34	2.3	4.18	0.56	8.6	1.42
5	2.0 g	500 g	14.34	44.45	2.4	4.40	0.58	8.0	1.23
6	2.5 g	500 g	16.62	45.50	2.5	5.20	0.57	7.5	1.17

Table 3. Increasing in plant crops and product resulted from CA addition to soil

Plant name	Tempt. OC	CA gram/ 1000 m2	Product without adding CA kg/100 m2	Product with adding CA Kg/1000 M2
Accra	20-30	300	25	40
Accra	20-30	200	20	30
Pepper	20-30	300	110	150
Pepper	20-30	200	100	140

Table 4. Soil salinity, metals contents ppm and pH were determined for several farms in the area

Soil/ location	EC/Cm mmoles	PH	P	k	Ca	Mg	Fe	Zn	Mn	Cu
AA-2	3.5	8.2	21	321	30	40	12	6	3	0.5
AA-3	3.2	8.1	26	230	25	32	10	8	2.8	0.4
KR-4	2.6	8.2	31	409	35	39	14	7	3.2	0.35
KR-5	4.5	8.0	19	270	28	34	9	5	1.8	0.21

Table 5. Analysis of water used for irrigation in this study

Analysis	EC/Cm	PH	Na ppm	Cl	Mg	Ca	K	HCO_3^-	CO_3^{2-}	SO_4^{2-}	NO_3^-
Soil	2.03	8.66	238.0	315	52.2	93.0	31.0	305.0	0	276.2	8.7

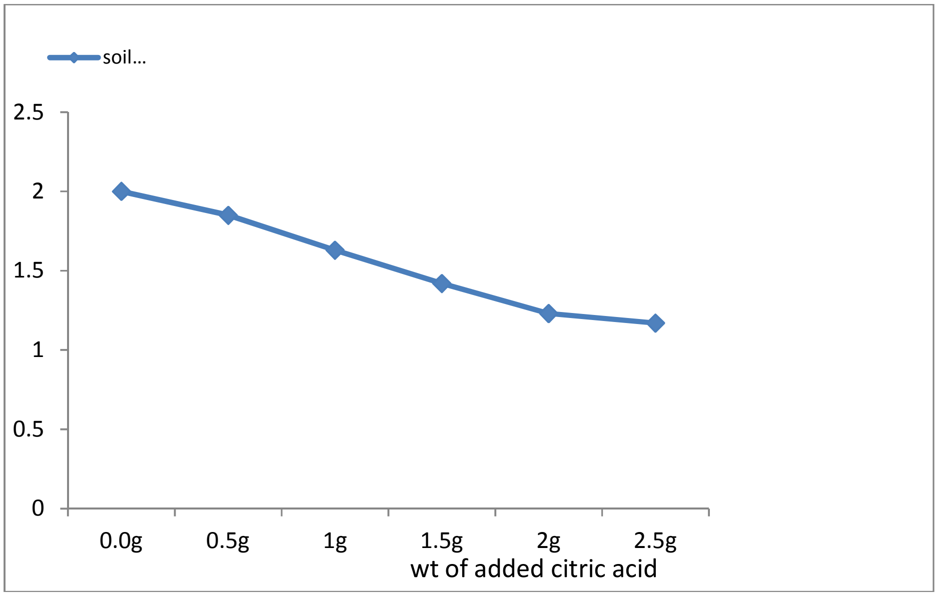


Fig. 3. Effect of citric acid addition on soil density

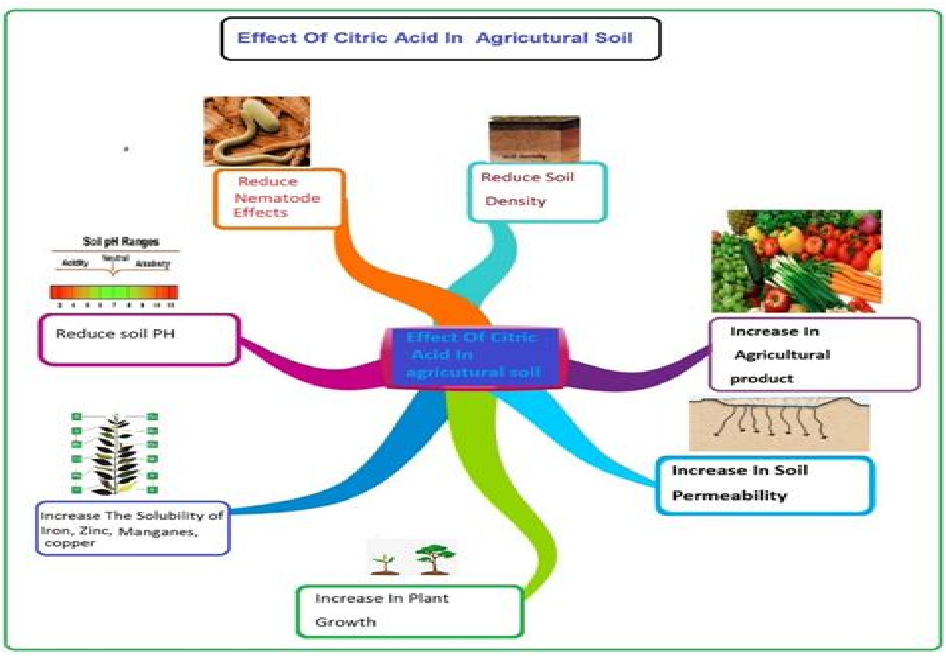


Fig. 4. Effect adding citric acid addition on soil and plants

values were alkaline and ranged between 8.0 to 8.3, salinity varies between 2.6 - 4.5. metals variation is reported in ppm. It is clear that the variation in metal availability with change in the soil acidity or CA concentration.

Studies shows that some nutrient deficiencies have major negative consequences for crop production, resulting in yields reduction and a poor quality of food and feed. Also, inappropriate use of fertilizer may lead to pollution of terrestrial and aquatic environments around plants. Thus while fertilizer production itself is highly energy demanding, contributing to climate change may result in unwanted direction [15].

3.6 Analysis of Water Used for Irrigation

The water quality parameters used for irrigation is reported in Table 5. This study was carried out to assess the suitability of water sources for irrigation in Jordan Valley. The area is fairly flat, with an average slope of less than 2%. Monitoring irrigation water quality is very important to the sustainability of crop production and productivity [16]

Fig. 4 summarized the enhancement of soil and crops as a result of adding citric acid to soil.

4. CONCLUSION

Addition of citric acid to calcareous soil does not increase the salinity as compared to the fertilizers, it increases the availability of nutrients such as Manganese (Mn), Copper (Cu), Zinc (Zn), and Iron (Fe), these nutrients are more significant for plant growth and crops production amounts. Citric acid addition moisturize the soil by reducing soil salinity and pH, also enhance chemical reactions for lime and oxides in the soil, which leads to reduce soil density and enhance the availability of the essential nutrients for plant growth and production. The addition of citric acid raised the fruit production per plant. Thus it is recommended to apply CA to the nutrient solution as part of the nutritional management of several plants.

While this study was conducted in Jordan Valley to assess the suitability of various water sources for irrigation another farming industry will benefit greatly from the results.

ACKNOWLEDGMENT

Support to this work from Jordan valley authority laboratories, Dair Ulla, -Al-Balqa, Jordan, and the Department of Chemistry, University of Sharjah (UOS) is gratefully acknowledged.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Fabián Pérez-Labrada, Adalberto Benavides-Mendoza, Luis Alonso Valdez-Aguilar, Valentín Robledo-Torres. Citric acid in the nutrient solution increases the mineral absorption in potted tomato grown in calcareous soil. Pak J Bot. 2016; 48(1):67-74.
2. Ammari TG, Tahhan RS. Soil salinity changes in the Jordan Valley potentially threaten sustainable Irrigated Agriculture Pedosphere. 2013;23(3):376-384.
3. Al-Bahrany AM, Al-Shabaan AM. The effect of oxalic and citric acids on the plant absorption of phosphate and other nutrients from fertilizer added to calcareous soil. Ann Agric Sci Cairo. 1995; 40:943-951.
4. Zohuir A Al-Balawna, Ideisan I Abu-Abdoun. The effect of sulphur powder addition on the chemical and physical properties of soil in Jordan Valley. J. of Agric and Envir. Sci. 2019;8(2):1-9.
5. Recep Vatansever, Ibrahim Ilker Ozyigit, Ertugrul Filiz. Essential and beneficial trace elements in plants, and their transport in a Review. Appli Biochem and Biotech. 2017;181:464-482.
6. Thomas Christian de Bang, Søren Husted, Kristian Holst Laursen, Daniel Pergament Persson, Jan Kofod Schjoerring. The molecular–physiological functions of mineral macronutrients and their consequences for deficiency symptoms in plants. New Phytologist. 2021;229 (5):2379-3036.
7. Alessio Siciliano, Carlo Limonti, Giulia Maria Curcio, Raaele Molinari. Advances in struvite precipitation technologies for nutrients removal and recovery from aqueous waste and wastewater. Sustainability. 2020;36(12):7538 -7574.
8. Junhao Qin, Osim Enya, Chuxia Lin. Dynamics of Fe, Mn, and Al liberated from contaminated soil by low-molecular-weight organic acids and their effects on the release of soil-borne trace elements. Appl. Sci. 2018;8:2444-2455.
9. Sposito G. The chemistry of soils, Oxford University Press, Oxford, U.K.); 1989.
10. Cetin Kantar, Bruce D Honeyman. Citric acid enhanced remediation of soils contaminated with uranium by soil flushing and soil washing. J. Environ. Eng. 2006; 132(2):247-255.
11. Fan Gu, Yu Zhang, Qiang Tang, Cong Lu, Ting Zhou. Contaminated soil using citric acid and citric acid-containing wastewater. Intern. J. of Civil. Eng. 2018;16:1607-1619.
12. Lindsay WL, Norvell WA. Development of a DTPA Soil Test for Zinc, Iron, Manganese and Copper. Soil Sci Soc of Amer J. 1978;42:421-428.

13. Ademola O Olaniran, Adhika Balgobind, Balakrishna Pillay. Bioavailability of heavy metals in soil: impact on microbial biodegradation of organic compounds and possible improvement strategies. Int. J. Mol. Sci. 2013;14(5):10197-10228.
14. Zahir ZA, Munir A, Asghar HN, Arshad M, Shaharoona B. Effectiveness of rhizobacteria containing ACC-deaminase for growth promotion of peas (*Pisum sativum*) under drought conditions. J. Microbiol. Biotechnol. 2008;18(5):958 - 963.
15. Sharpley A, Jarvie H, Flaten D, Kleinman P. Celebrating the 350th Anniversary of phosphorus discovery: A conundrum of deficiency and excess. J. of Environ. Qual. 2018;47:774 -777.
16. Davie Kadyampakeni, Richard Appoh, Jennie Barron, Enoch Boakye - Acheampong. Analysis of water quality of selected irrigation water sources in Northern Ghana. Wat. Sci. & Techno. Wat. Sup. Water Sup. 2018;18(4): 1308-1317.

Peer-review history:
The peer review history for this paper can be accessed here:
http://www.sdiarticle4.com/review-history/67559