

The impact of oxalic and citric acids on the P sorption prevention and release of Fe, Cu, Zn and Mn metals In metals - calcite system.

Ahmad M. Al-Shabaan¹

ABSTRACT

The efficiency of oxalic acid and of citric acid toward P sorption prevention and metal release in calcite-metals system were examined. A fixed weight of calcite was treated with fixed levels of Fe²⁺, Mn²⁺, Zn²⁺, and Cu²⁺ as chloride for 24 hrs. Then, a fixed level of P and variable rates of either oxalic or citric acid were introduced and reacted for 48 hrs.

The results obtained showed that the final supernatant EC values increased from 3.0 to 7.7 and from 3.0 to 4.7 dS m⁻¹ due to the application from 0.1 to 15.0 mM O.C l⁻¹ (organic carbon) as oxalic and citric acid, respectively. The final pH increased from 8.0 to 10.6 when the system was treated with oxalic acid at 0.1 and 15.0 mM O.C l⁻¹, respectively but remained without change under the effect of citric acid. The values of Ca²⁺ decreased from 27 to 1.7 mg kg⁻¹ when calcium carbonate was attacked by 0.1 and 15.0 mM O.C l⁻¹ of oxalic acid, respectively. In the meantime, Ca²⁺ increased from 41 to 80 mg kg⁻¹ when the calcium carbonate was treated with citric acid. The values of HCO₃⁻ increased from 147 to 1641 mg kg⁻¹ under the effect of oxalic acid and from 122 to 548 mg kg⁻¹ due to the application of citric acid. Oxalic acid prevented 60.5% of added P at 0.1 mM O.C l⁻¹ and then decreased to 14% at 0.5 mM O.C l⁻¹. Citric acid Prevented 71% of added P at the lowest and highest rates. Both acids failed to release any of the sorbed metals.

Key words: Calcite; Organic ligands; Phosphate; Heavy metals; Sorption.

INTRODUCTION

Phosphate and heavy metals sorption and precipitation under calcareous soil conditions have been reported by many investigators (Cole et al., 1953; Clark and Turner, 1954; Kuo and Lotse, 1972; Lahar and Zipori, 1978; McBride, 1979; Al-Shabaan, 1989; Leytem and Westemann, 2003; Zavarin and Doner, 2005). However, phosphate sorption and precipitation in calcareous soils is due mainly to the presence of CaCO₃ and exchangeable Ca to which phosphate anions bind and form various insoluble calcium phosphate products (Al-Shabaan, 1989). On the other hand, chemisorptions and precipitation of Fe, Cu, Zn and Mn carbonates and

hydroxides, under calcareous environments, have been reported by many investigators (McBride, 1979; Norvell and Lindsay, 1982; Elrashid and O'Connor, 1982). Furthermore, organic matter and its derivatives have been reported to improve phosphate solubility by forming strong and stable bonds between the organic reactive functional groups and the cations that are responsible for phosphate precipitation, such as calcium under calcareous conditions or Al and Fe under acidic soil environment (Earl et al., 1979; Al-Shabaan, 1989). Kafkafi et al., (1988) reported that citrate, bicarbonate and oxalate decreased phosphate adsorption to the kaolinite and montmorillonite clays. They concluded that oxalate masked some of the adsorption sites of phosphates. Deb and Datta (1967a and b) studied the influence of many anions, among which were oxalate and citrate, on the sorption of phosphate by soils and observed that phosphate sorption was minimized in the presence of the organic anions. However, they related such results to the chemical and physical nature of these anions, in addition to the phosphate concentration and the pH.

Moreover, metal complexation and or chelation by organic matter components have been considered important mechanisms that modify the natural metal reactions under metal precipitation conditions. Under metal precipitation conditions due to acidic or alkaline soil environments, metals have been reported to stay soluble due to the metal complexation and or chelation with the organic matter functional groups. Thus, such phenomenon has been considered an important factor that may positively affect the solubility and movement of metals in soils (Elsokkary, 1980). Krauskopf (1972) and Lindsay (1979) reported that Zn forms soluble complexes with organic ligands such as EDTA and DTPA.

The competition phenomenon among organic and inorganic anions for the sorption sites and for the free cations has been designated (Kou and Lotse, 1972; Al-Shabaan, 1989). Such competition would result in variable strength of bond formation and stability range

¹ Department of Environment and Natural Agricultural Resources, College of Agriculture and Food Sciences, King Faisal University, P.O. Box 420, Al-Hassa 31982, Saudi Arabia. Received April. 16, 2007, Accepted June 26,2007.

of the product formed between the specific anion and either the surface site or the free cation. The higher the affinity of the sorbed anion to the adsorbent site the higher the stability of the product formed between the anion and the cation concerned. It has been reported, however, that many of the organic anions of the acids of low molecular weight, those of short chains, such as citric, oxalic, tartaric, etc., are so reactive and specifically bound to adsorption sites and free cations in soil environment (Nagarajah et al., 1970).

Calcareous soil conditions prevail under arid and semi-arid environments. Calcite or analogous components generally dominate such systems and present in quantitative amounts thus, would govern the soil solution chemistry. Accordingly, available sorption sites due to the solid surfaces or HCO_3^- , CO_3^{2-} and OH^- free anions in addition to Ca^{2+} would determine the fate of phosphate and the heavy metals such as Fe, Cu, Zn and Mn where they would be precipitated.

The present research was designed to: i) test the effectiveness of the oxalate compared to citrate anion toward P sorption prevention and pre sorbed Fe, Cu, Zn and Mn metals release under standard calcite conditions, and ii) to compare the effect of the present system results to the previous known behavior of oxalate vs. citrate toward P sorption in the previous study accomplished by Al-Shabaan, 1989.

MATERIALS AND METHODS

Metal pre sorption stage.

Standard salt reagents of FeCl_3 , CuCl_2 , ZnCl_2 and MnCl_2 were chosen as source of Fe^{3+} , Cu^{2+} , Zn^{2+} and Mn^{2+} metal cation. Stock solution of 200 mg L^{-1} of each metal was prepared in 0.02 M KCl in one container. KCl was chosen as background electrolyte matrix for all treatments. Five *mls* of the stock solution were added to 2.5g of calcite (powder reagent) which were previously placed in a 50 ml screw cap polyethylene centrifuge tube. Such steps were triplicated for each treatment all over the experiment. The tubes were held vertically against any minor movement on a proper holder with closed caps, and shaken circularly on a proper shaker at 140 rpm for 24 hours. The solutions within the tubes were ready for the next P sorption and metal release stage.

Phosphorus sorption prevention and release:

Several stock solutions of P concentration (20 mg kg^{-1}) were prepared from the standard reagent of KH_2PO_4 in 0.02 M KCl plus an appropriate level of 0.0, 0.1, 0.5, 1.0, 5.0, 10.0 or 15.0 mM l^{-1} of the organic carbon of either oxalic or citric acid standard reagents. Forty-five *mls* of each treatment were added to each tube of any three that were devoted to the concerned treatments so

that the final total treatment solution volume attained 50 *mls*. The tubes tightly closed and arranged horizontally on a proper holder, shaken at 140 rpm for 48 hours. The experiments were conducted under the standard conditions. The solutions were properly centrifuged and filtered through Watman 42 filter papers and then supernatants were collected for analyses. The pH, EC, and HCO_3^- by titration method described by (Richards, 1969). The Fe, Cu, Zn, Mn and P were determined by an Inductively Coupled Plasma Optical Emission Spectrometer instrument.

RESULTS AND DISCUSSION

Effect on electrical conductivity (EC)

The EC must be looked at as a resultant relative proportional factor that is related to the ionic strength of any chemical soil solution system which is an important factor in the sorption desorption studies (Alva et al., 1991). Although, the ionic strengths of the chemical systems under investigation were managed to be controlled by employing a background electrolyte matrix solution of 0.02 M KCl, the equilibrium solutions showed some variable increasing trends in the electrical conductivities, i.e., the ionic strengths. Such increasing trends were suggested to be due to the increasing input of the organic acids, as well as the metal ion salts which corresponded to different treatments. Nevertheless, the importance of the ionic strength comes to the issue due to its effect on the solubility, sorption and desorption of the inorganic and organic ions and ligands in different chemical soil solution systems (He et al., 1997).

Figure 1 shows the mean values of the equilibrium electrical conductivities ($dS \text{ m}^{-1}$) as functions of the increasing concentration of the oxalic and citric acids in the calcite Systems. However, EC values were increasing with increasing the additions of the organic carbon from oxalic or citric acid. Nevertheless, such increasing trend was more pronounced in the case of oxalic acid compared to that of the citric acid. The electrical conductivity of the oxalic acid ranged from $3.0 dS \text{ m}^{-1}$ to of $7.7 dS \text{ m}^{-1}$ compared to those of $3.0 dS \text{ m}^{-1}$ to $4.6 dS \text{ m}^{-1}$ of citric acid due to a minimum level of 0.1 to a maximum level of 15.0 mM l^{-1} of the added organic carbon from oxalic or citric acid, respectively.

However, the importance of the electrical conductivity i.e. ionic strength, arises from its influence on the anion ligand and metal sorption – desorption phenomenon. It has been reported that the solution ionic strength modified the adsorption surface charges in addition to the thickness of the diffuse double layer of the adsorbing surfaces. Thus, it may enhance or decrease or has no effect on ligand anion adsorption, (He et al., 1997).

The present research includes oxalate, citrate, in addition to other inorganic anions and metals. It is expected therefore, that the final equilibrium pH (>7.0) values of the systems under investigation accompanied with the ionic strength values concerned may decrease the sorption of the organic anions and hence, may minimize their affinity to be sorbed to the calcite surface sites. Such mechanisms may be considered as one of factors responsible for reducing their efficiency to prevent phosphate precipitation and/or release the sorbed metals.

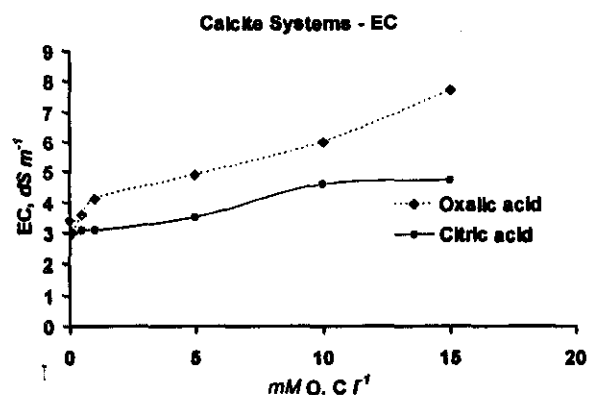


Fig. 1. The mean values of the equilibrium electrical conductivities (EC, $dS m^{-1}$) as functions of increasing concentrations of the organic acids ($mM O.C l^{-1}$) in the Calcite Systems.

Effect on pH

Figure 2 shows the mean values of the equilibrium pH as affected by the increasing concentrations of the oxalic or citric acid in the metals-calcite systems. However, the pH values have been reported to increase significantly in the case of oxalic acid which ranged from 8.0 to 10.6 due to a minimum of 0.1 to a maximum of $15.0 mM l^{-1}$ of the organic carbon added from the oxalic acid, respectively.

Effect on Calcium Concentration

Figure 3 shows greater significant decrease in the released calcium concentration due to the oxalic acid treatments compared to the opposite significant increase that were noticed due to the citric acid treatments. For the oxalic systems, calcium concentrations ranged from $27 mg kg^{-1}$, due to a minimum concentration treatment of $0.1 mM l^{-1}$ of O.C, to a $1.7 mg kg^{-1}$ due to the maximum concentration treatment of $15.0 mM l^{-1}$ of O.C added from the oxalic acid compared to the calcium concentration of $41 mg kg^{-1}$ due to the minimum of $0.1 mM l^{-1}$ of O.C to $80 mg kg^{-1}$ Ca due to the maximum of $15 mM l^{-1}$ of O.C added from citric acid.

Effect on Bicarbonate conditions

Figure 4 showed that a significant increasing trend in the bicarbonate concentration due to increasing

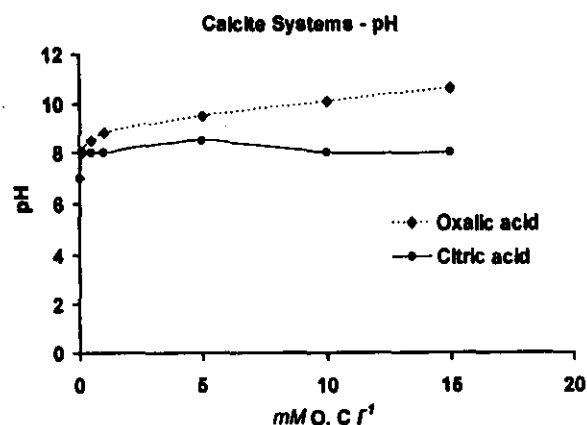


Fig. 2. The mean values of the equilibrium pH as affected by increasing concentrations of the organic acids ($mM O.C l^{-1}$) in the Calcite Systems.

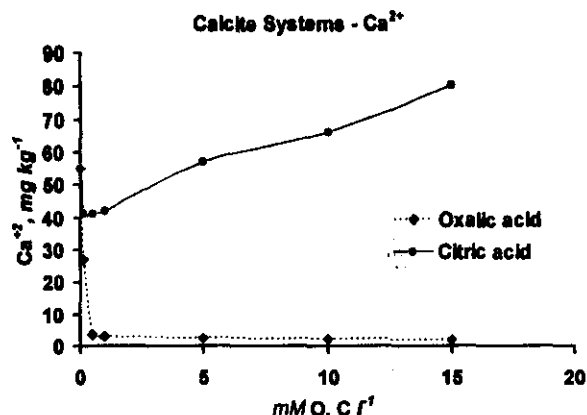


Fig. 3. The relationship between the mean values of the equilibrium calcium concentrations ($Ca^{2+}, mg kg^{-1}$) and the increasing concentrations of the organic acids ($mM O.C l^{-1}$) in the Calcite Systems.

levels of the organic carbon from each acid was observed. Under oxalic acid, at $0.1 mM l^{-1}$ of O.C, the HCO_3^- value was $147 mg kg^{-1}$ which significantly increased to $1641 mg kg^{-1}$ due to the treatment of $15 mM O.C l^{-1}$ from the oxalic acid. On the other hand, under the effect of citric acid, the bicarbonate value was $122 mg kg^{-1}$ at $mM l^{-1}$ of O.C concentration and bicarbonate value was increased significantly to $548 mg kg^{-1}$ due to $15 mM l^{-1}$ of added from citric acid. However, the corresponding values of the bicarbonate concentrations were greater in the case of the oxalic acid compared to those of the citric acid.

Influence of oxalate on prevention of phosphate sorption

The oxalic acid ($pk_1 = 1.23$ and $pk_2 = 4.19$) is expected to be fully dissociated under the pH values of the present study. However, the phosphate – organic anion reaction has been reported to be strongly

dependent on the form of the organic anion, which in turn is dependent on the pH. The organic anion forms are fully dissociated at pH above 6.5 ($\text{pH} > \text{pK}_a$), and therefore their capacity for releasing phosphate could be generally significantly minimized or negligible (Hingston et al., 1972).

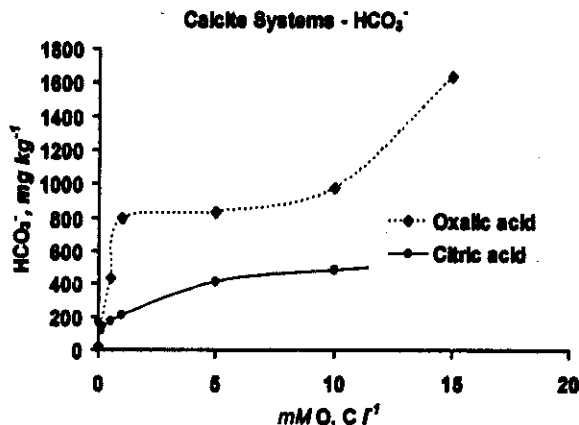


Fig. 4. The relationship between the equilibrium concentrations of bicarbonate (HCO_3^- , mg kg^{-1}) and the increasing concentrations of the organic acids (mM l^{-1}) in the Calcite Systems.

Figure 5 shows that the maximum amount of the phosphate sorption prevention was reported at 0.1 mM l^{-1} of the oxalic acid. There was 12.1 mg kg^{-1} of P in the solution which corresponded to 60.5% of phosphate sorption prevention.

The minimum phosphate sorption prevention was obtained at 0.5 mM l^{-1} , which was 2.8 mg kg^{-1} of P and corresponds to 14% of P sorption prevention. However, values from 3.1 to 3.7 mg kg^{-1} of P which corresponded to 16 to 18.5% of P sorption prevention at 1.0 mM l^{-1} and 15.0 mM l^{-1} of the oxalic acid added, respectively. Furthermore such findings may confirm that oxalate efficiency is dependent on the pH in order to prevent P sorption. However, oxalate anion has been reported to be more effective, as mentioned above, toward P sorption prevention and its effectiveness increased significantly with its level. Al-Shabaan (1989) reported that there was a significant increase in the equilibrium P concentration due to the increase in oxalate addition to the calcite system. He reported that there was 83.9% of the added P in solution due to the maximum level of oxalate added. Nevertheless, the systems under the present study are different from Al-Shabaan's systems, which were very simplified calcite systems and contained no metals. The complex nature of the present research, in addition, the oxalate anion would modify the results and complicate the issue. Although both systems showed a significant increase in the final

equilibrium, of carbonate or bicarbonate concentration which were suggested to hydrolyze and give rise to the pH. This fact was confirmed in Figure 2. But, the final equilibrium P did not follow a similar trend. In addition, the oxalate anion precipitated calcium from the solution and reduced its amount gradually as its level increased. This trend was reported in the previous work and was confirmed in the present study, as well, where its final equilibrium concentration decreased gradually and were found to be 27 mg kg^{-1} and 1.7 mg kg^{-1} in the solution at $0.1 \text{ mM O.C l}^{-1}$ and $15.0 \text{ mM O.C l}^{-1}$ added from oxalic acid respectively, compared to 55 mg kg^{-1} of the control.

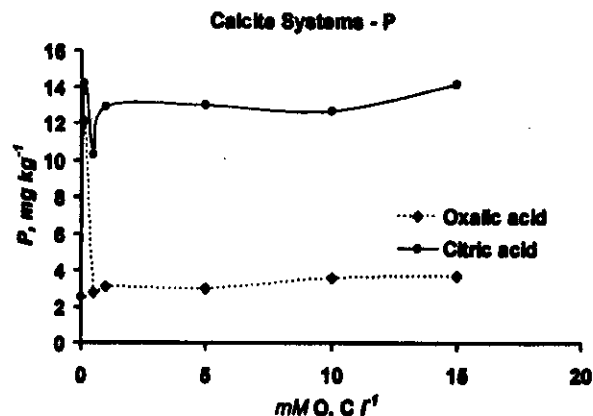


Fig. 5. The mean values of the relationships between the equilibrium phosphate concentrations and the increasing concentrations of the organic acids in the Calcite Systems.

In order to justify such a difference, one may look at the nature of the oxalate anion itself in addition to the complex nature of the present systems. The oxalate anion would fully dissociate under our systems ($\text{pH} > \text{pK}_a$ of the oxalic acid) and becomes divalent negatively charged anion. However, such a nature would enable the anion to react with either positively charged sorption sites on the calcite surfaces or bind to the soluble metal ions in the solution in addition to the calcium ion. The divalent negatively charged oxalate anion is expected to employ its two negative edges in different orientations. It may act as a bridge between the calcite positively charged calcium, on one side, and bind to one of the solution metals on the other side which, at the same time, bind to the solution phosphate and such mechanism would result in the formation of a chain of calcite - oxalate - metal - phosphate type of interaction. However, such a mechanism has been suggested to create P sorption sites on calcite surfaces (Leytem and Westemann, 2003). It is clear that such a mechanism would include metals and reduce their concentrations in the system solution as well. The oxalate anion is expected to partially cover some of the

phosphate sorption sites on the calcite surfaces, but such coverage efficiency would be more effective in the absence of the metals where they would be expected to compete with the positively charged sites on the calcite surfaces and such competition would significantly minimize their amount which were devoted for the surface coverage and, hence create more vacancy for more P sorption on the calcite surfaces. Such mechanisms may explain the general lower oxalate efficiency to prevent P sorption in the present study compared to the previously mentioned study (Al-Shabaan, 1989).

Influence of oxalate on release of metal sorbed by calcite.

The metals (Fe, Cu, Zn and Mn) were given the chance to react with calcite first. The oxalic acid and P were introduced to the calcite systems after the metal sorption took place. Under such conditions, the efficiency of the oxalate anion to release the presorbed metals would be studied. However, all metals were not detected. In fact, the ICP instrument could not detect any value greater than 0.05 mg kg^{-1} which meant that they were precipitated or strongly sorbed at all levels of the oxalic acid additions. Such a finding would prove that the oxalate anion totally failed to release any of the presorbed metals under investigation.

Once again, to account for such results, one would probably look at the nature of the oxalate anion itself, in addition to the systems complexity under investigation. The probable oxalate salts formed with Fe^{3+} , Cu^{2+} , Zn^{2+} and Mn^{2+} would be insoluble and thus precipitate from solution. Another sink would be the sorption site for the calcite surfaces on the carbonate negative charges. Furthermore, the formation of Fe^{3+} , Cu^{2+} , Zn^{2+} and Mn^{2+} hydroxides which are almost insoluble and are likely to form under high pH systems. The formation of Fe^{3+} , Cu^{2+} , Zn^{2+} and Mn^{2+} insoluble carbonates is likely to be an additional sink (McBride, 1979). In addition to incorporating the metal ion in the oxalate - metal - phosphate bridging formation that would even create another sink to the lost metal cations from the solution.

Influence of citrate on phosphate and metals sorbed by calcite.

Citric acid was introduced with phosphate at once to the presorbed metals on calcite surfaces. From Figure 5, it is noticed that a significant increase in the P concentration at the lowest level of the citric acid added which remained approximately without any change until the maximum level of the added citric acid, except at the 0.5 mM l^{-1} which attained the lowest P concentration. There was 71% of the added P in solution due to the addition of 0.1 mM l^{-1} of the citric acid and this amount of soluble P was obtained at the highest

level of the acid, as well, which was 15.0 mM l^{-1} . However, such results generally would show that citrate anion was more effective than the oxalate anion in the P sorption prevention under the present systems. Citrate prevented approximately 52% of P at the lowest level and 71% of P from sorption at the highest level of the citrate added, compared to approximately 60% of P at the lowest level and 14% at 0.1 mM l^{-1} of the added oxalic acid which did not differ from the rest of the treatments. Such a finding is in contrast to the previous study (Al-Shabaan, 1989) where the oxalate anion was more effective than that of citrate anion toward the P sorption prevention. Citric acid would be fully dissociated under the present research systems. The tri-negatively charged citrate anion would probably behave in such a different manner compared to that of oxalate. The citrate salts are soluble compared to those of oxalate ones. It was reported that calcium citrate concentration was increased in the solution due to the progressive increase of its addition to the calcite systems. Al-Shabaan (1989) reported that in contrast to the oxalate anion, citrate increased the total soluble calcium 300% compared to the control whereas oxalate precipitated it. In the present study, (Figure 3) there was 41 mg kg^{-1} of calcium in the solution at 0.1 mM l^{-1} of the citric acid which increased significantly to 80 mg kg^{-1} at 15.0 mM l^{-1} of the citric acid. In contrast, there was only 27 mg kg^{-1} of calcium in the solution at 0.1 mM l^{-1} of the oxalic acid which significantly decreased to 1.7 mg kg^{-1} at 15.0 mM l^{-1} of oxalic acid. Furthermore, citrate has significantly less affinity to adsorb on the calcite surfaces compared to the oxalate anion (Al-Shabaan, 1989). Figure 4 shows the amount of bicarbonate brought to the solution due to increasing added citrate compared to that of oxalate. The efficiency of citrate to exchange for bicarbonate is significantly less than that of oxalate (Figure 4). There was 147 mg kg^{-1} of bicarbonate in the solution due to 0.1 mM l^{-1} of added oxalate which significantly increased and reached to 1641 mg kg^{-1} at 15.0 mM l^{-1} of added oxalic acid. On the other hand, there was only 122 mg kg^{-1} of bicarbonate in the solution due to 0.1 mM l^{-1} of citric acid which increased, but the maximum level did not exceed 548 mg kg^{-1} at 15.0 mM l^{-1} of added citric acid. Such results were in agreement with the previous study, but the behavior of oxalate and citrate anions toward P sorption was found to be the opposite under the present study conditions compared to the previous study (Al-Shabaan, 1989). However, from the data provided in the present study, a possible solution to such a contradiction may be attained. The pH values of oxalate were generally greater than those of citrate. Figure 2 shows that the oxalate pH values ranged from 8.0 to 10.6 and were increasing significantly, whereas those of

citrate were around 8.0 which remained generally unchanged at this value. Such a finding results in a greater amount of hydroxyl anion in the equilibrium solution under the oxalic acid systems compared to those under the citric acid systems. Furthermore, it is obvious, from Figure 4, that the bicarbonate exchanged for or brought to the equilibrium solution was significantly greater in the case of oxalic acid compared to that of citric acid. There was almost approximately two to three folds (433 to 1641 mg kg^{-1}) of solution bicarbonate in the case of oxalic acids times that of the citric acid (177 to 548 mg kg^{-1}). Furthermore, the Fe, Cu, Zn and Mn metal cations were lost from the equilibrium solution and only $<0.05 \text{ mg kg}^{-1}$ was detected from each. Compared to the case of oxalate the possible mechanisms through which the metals were removed from the solution, which was dominated by precipitation with either OH^- and or HCO_3^- and oxalate anions in addition to sorption on the calcite surfaces, the citrate anion systems would be expected to act in different ways. Both oxalate and citrate systems totally lost their soluble metals, hence the citrate system had significantly less hydroxyl and bicarbonate anions which were possibly great sinks for metals, thus one would look for other sufficient sinks that fulfill and justify such disappearances. Nevertheless, a possible suggestion, that fulfills and justifies metal cations removal from the solution under the citrate systems may, be related to a possible greater affinity of the metals to be adsorbed to the negative sites on the calcite surface. Although some of the metals would be possibly precipitated as hydroxides and carbonates, which would be suggested to be significantly less than that under the oxalic acid situations, the greater amounts of the metal cations under the citric acid situation are suggested to be significantly sorbed on the calcite surfaces. Such surface metal sorption would be bound by one positive charge of the metal and it would bridge to the citrate anion through the other positive edge. The other deprotonated carboxyl groups of the citric acid would orient themselves to the bulk solution. However, such negatively charged carboxyl groups would be suggested to be either totally free or bind to some calcium to a significantly lower level. Such a suggestion would incorporate most of the metals and hold them sorbed on the calcite surfaces. In addition, it would mask the active calcite surfaces, chemically and physically, with citrate ions. Moreover, citrate with its outer free negative charges would repel the phosphate anions and give rise to the resultant significant equilibrium P concentrations which were noted. Nevertheless, such possible suggested mechanisms may give some interpretation to the higher final equilibrium concentration of P as well as to the removal of metal

ions from the final equilibrium solution under the case of citric acid systems.

ACKNOWLEDGEMENTS

I would like to deeply thank my friend, Professor Abdulaziz M. Al-Bahrani for his assistance concerning computer work and other aspects. I also wish to thank Mr. Mondhir R. Al-Kwaity, an undergraduate student from our department for some lab work in a special study. Special thanks must also be extended to the staff of the Chemical Analysis Laboratory of Saudi Aramco at Al Uthmania Plant, especially to Mr. M. H. Al-Abdullah for the metal analysis by their ICP instrument.

REFERENCES

- Al-Shabaan, A.M. 1989. The effect of organic solutes on the sorption of orthophosphate by calcite and calcareous soils. Ph.D. Dissertation, Ohio State Univ., Columbus, Ohio. Pp. 46-59.
- Al-Shabaan, A.M. and A.M. Al-Bahrani. 1995. The effect of citric and oxalic acids on phosphorus and some macronutrients of the Hoagland's solution shaken with calcareous soils. *Annals Agric. Sol., Ain Shams Univ., Cairo*, 40(2), 933-942.
- Alva, A.K. ; M.E. Sumner and W.P. Miller. 1991. Relationship between ionic strength and electrical conductivity for soil solutions. *Soil Sci.* 152:239-243.
- Clark, J. S., and R. C. Turner. 1955. Reactions between solid calcium carbonate and orthophosphate solutions. *Can. J. Chem.* 33:665-671.
- Cole, C.V., S. R. Olsen, and C. O. Scott. 1953. The nature of phosphate sorption by calcium carbonate. *Soil Sci. Soc. Am. Proc.* 17:352-356.
- Deb, D.L., and N. P. Datta. 1967a. Effect of associating anions of phosphorus retention in soils: I. Under variable phosphorus concentration. *Plant and Soil* 26:303-316.
- Deb, D.L., and N. P. Datta. 1967B. Effect of associating on phosphorus retention in soil: II. Under variable anion concentration. *Plant and Soil* 26:432-444.
- Earl, K.D., J.K. Syers, and J.R. McLaughlin. 1979. Origin of the effect of citrate, tartrate and acetate on P sorption by soils and synthetic gels. *Soil Sci. Soc. Am. J.* 43:674-678.
- Elrashid, M.A., and G.A. O'Connor. 1982. Influence of solution composition on sorption of zinc by soils. *Soil Sci. Soc. Am. J.*, 46:1153-1157.
- Elsokkary, I.H. 1980. Reactions of labeled $^{65}\text{ZnCl}_2$, $^{65}\text{ZnEDTA}$ and $^{65}\text{ZnDTPA}$ with different clay-systems and some alluvial Egyptian soils. *Plant and Soil* 54:383-393.
- He, L.M., L.W. Zelazny, V.C. Baligar, K.D. Ritchey, and D.C. Martens. 1997. Ion strength effects on sulfate and phosphate adsorption on Y-alumina and kaolinite: triple-layer model. *Soil Sci. Soc. Am. J.* 61:784-793.
- Kafkafi, U., B. Bar-Yosef, Rivka Rosenberg, and G. Sposito. 1988. Phosphorus adsorption by kaolinite and montmorillonite: II. Organic anion competition. *Soil Sci. Soc. Am. J.* 52:1585-1589.
- Kafkafi, U., A.M. Posner, and J.P. Quirk. 1967. Desorption of phosphate from kaolinite. *Soil Sci. Soc. Amer. Proc.* 31:348-353.

الملخص العربي

تأثير كل من حامض الأوكساليك و حامض الستريك على حماية الفوسفور و تحرير كل من كاتيون الحديد و النحاس و الزنك و المنجنيز من الأدمصاص في نظم نموذجيه من الجير .

احمد بن معنوق الشبعان

قيمة ال pH لم تتأثر بالإضافات المتزايدة من حامض الستريك . أما أيون الكالسيوم فقد انخفض تركيزه من ٢٧,٠ إلى ١,٧ مليجرام لكل كيلو جرام عندما فوعل الجير بـ ٠,١ و ١٥ مليمول كربون/ل من حامض الأوكساليك على التوالي . وعلى النقيض من ذلك فإن أيون الكالسيوم قد ازداد تركيزه من ٤١,٠ إلى ٨٠,٠ مجم/كجم عندما فوعل الجير بحامض الستريك عند نفس التركيزات . وقد وجد أن أيون البيكربونات قد ازدادت من ١٤٧,٠ إلى ١٦٤١,٠ مجم/كجم تحت تأثير حامض الأوكساليك و ازدادت من ١٢٢,٠ إلى ٥٤٨,٠ مجم/كجم تحت تأثير حامض الستريك عند نفس التركيزات المذكورة . لقد تمكن حامض الأوكساليك من حماية مامقداره ٦٠,٥ % من الفوسفور المضاف عند تركيز ٠,١٠ مليمول /ك.ع من الحمض ثم انخفض إلى مامقداره ١٤% عند تركيز ٠,٥ مليمول/كربون من الحمض نفسه . لقد تمكن حامض الستريك من حماية ٧١% من الفوسفور المضاف عند التركيزين الأعلى و الأدنى من الحمض . ومن جانب آخر لم يتمكن كل من الحامضين من تحرير أي من كاتيونات المعادن المدمصة .

لقد تمت دراسة تأثير كل من حامض الأوكساليك و حامض الستريك على حماية الفوسفور من الأدمصاص و كذلك على تحرير كاتيونات المعادن الثقيلة من الأدمصاص في نظم قياسية من الجير .

وفي هذه النظم تمت مفاعلة وزن ثابت (٢,٥ جم) من الجير مع تركيزات ثابتة (٢٠ جزء في المليون) من كل من كاتيون الحديد و النحاس و الزنك و المنجنيز في صورة كلوريدات و لمدة ٢٤ ساعة . ثم تلا هذه المرحلة إضافة تركيز ثابت من الفوسفور (٢٠ جزء في المليون) بالترافق مع تركيزات متزايدة من كل من حامض الأوكساليك أو حامض الستريك كل على حده و فوعلت مع محتويات المرحلة الأولى ولمدة ٤٨ ساعة .

وقد أوضحت نتائج الدراسة الى زيادة قيمة التوصيل الكهربائي في الراشح من ٣,٠ إلى ٧,٧ مليمول/سم عند تركيز ٠,١ و ١٥,٠ مليمول من الكربون العضوي في اللتر المضافة من كل من حامض الأوكساليك و حامض الستريك على التوالي . و كذلك فإن قيمة ال pH قد ازدادت من ٨,٠ إلى ١٠,٦ عند تركيز ٠,١ و ١٥ مليمول كربون /ل من حامض الأوكساليك على التوالي بيد أن