

INFLUENCE OF OXALATE AND CITRATE ON P SORPTION PREVENTION AND THE RELEASE OF THE PRESORBED METALS BY GYPSUM-CALCITE SYSTEMS.

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ABSTRACT

Fixed weight of calcite plus gypsum (1.25g of each) were first reacted with fixed levels (20 ppm of each) of Fe, Cu, Zn and Mn chlorides for 24 hours. Then fixed level of P (20 ppm) only or 0.1, 0.5, 1.0, 5.0, 10.0 and 15.0 mM organic carbon (O.C) L⁻¹ from either oxalic or citric acid were introduced and reacted for 48 hours. The filtrate EC and pH increased under both acids but was greater under oxalic acid systems. The final Calcium was decreasing under oxalic acid treatments where it was 589 and 321 ppm at 0.1 and 15.0 mM O.C L⁻¹, respectively. In contrast, the final Ca was increasing due to citric acid input which was 607 and 780 ppm at 0.1 and 15.0 mM O.C L⁻¹, respectively. Bicarbonate was increasing under both acids, but the increase was greater under citric acid where it increased from 118 to 476 and from 118 to 271 ppm HCO₃⁻ due to 0.1 and 15.0 mM O.C L⁻¹ of citric or oxalic acid, respectively. However, citric acid reduced 60% and 70% of the added P from sorption at 0.1 and 15.0 mM O.C L⁻¹ of it, respectively. But, oxalic acid reduced only 55% and 15% of the added P at 0.1 and 15.0 mM O.C L⁻¹ of it, respectively. Both acids failed to release any of the presorbed metals, but citric acid could release some of Mn in decreasing rates (the highest was 45.5% of the added). Thus, citric acid was more effective than oxalic acid toward P sorption reduction under calcite-gypsum systems.

Keywords: calcareous, gypsiferous, ligand exchange, organic anion sorption, desorption

INTRODUCTION

The problems of phosphate sorption and precipitation under calcareous soil conditions have been reported by several investigators (Cole et al., 1953; Clark and Turner, 1954; Kuo and Lotse, 1972; Griffin and Jurinak, 1973; Al-Shabaan, 1989; Letem and Westemann, 2003).

Phosphate would be strongly bound to the exposed calcite surface sites are precipitates as Ca-phosphates of different stabilities (Al-Shabaan, 1989).

Metal sorption or precipitation have been reported under calcareous soil conditions as well. It has been reported that carbonate surfaces chemisorb heavy metals such as Zn²⁺ (Jurinak and Baurer, 1977) and Mn²⁺ (McBride, 1979). Thus, metal carbonates and hydroxides as insoluble compounds were likely to precipitate under calcareous soil conditions.

However, it has been reported that the organic matter and some of its derivatives were found to be solubilizing agents to both phosphate and metals under their precipitation soil environments. Organic matter with its functional groups or the short chain, low molecular weight organic acids released through the organic matter microbial decomposition were found to

be effective in P compound solubilization or metal complexation or chelation (Elsokkary, 1980).

The phosphate precipitating agents under acidic conditions such as Al and Fe or under alkaline calcareous conditions such as Ca could be captured or competed for by organic ligands such as citrate, oxalate or acetate, etc., which results in phosphate release and increased solubility (Deb and Datta, 1967; Nagarajah et al., 1968; Al-Shabaan, 1989). The degree of such fate successfulness, however, depends on the strength of the chemical bond formed between the precipitating cation agent and the organic anion. The higher the strength of such bond the higher the stability of the product formed and the higher the degree of P solubility successfulness. Such bond strength, however, would be determined by a criterion called the formation constant or stability constant which may determine the specificity of the organic ligand to the cation agent concerned (Lindsay, 1979).

Heavy metal cations, however, were also reported to stay in solution against precipitation under metal soil precipitating conditions provided the presence of organic constituents that capture them within complex or chelate formations (Lindsay, 1979). Kafeafi et al. (1988) reported that citrate, bicarbonate, and oxalate decreased, and acetate and the amino acids increased P adsorption to the kaolinite and montmorillonite clays. They, however, had reported that oxalate masked some of the adsorption sites of phosphates. Deshmukh and Bapat (1972) reported that when phosphate ions come in contact with the free CaCO_3 , they are either adsorbed or precipitated as di- or tri-ca-phosphates. Al-Shabaan (1989) reported that some organic anions and organic constituents reduced P sorption in the order of oxalate > citrate > polytran > soil humate. Furthermore, Al-Shabaan and Al-Bahrani (1995) reported that both oxalate and citrate anions reduced P solubility, but oxalate was more efficient to keep more P in solution compared to that of citrate. Al-Shabaan (paper under publication) compared the effectiveness of oxalate vs. citrate anions toward P sorption prevention and metal release under standard calcite systems, reported that citrate was significantly more effective, under such systems, than that of oxalate towards P sorption prevention, but both totally failed to release any of the presorbed Fe, Cu, Zn and Mn metals. Hence, the system nature and complexity may have affected the organic anions to behave differently.

Some investigators, however, have studied the behavior and mechanisms of several organic ligands towards phosphate sorption and precipitations under either standard calcite or calcareous soil conditions environments (Al-Shabaan, 1989; Al-Shabaan and Al-Bahrani, 1995). Furthermore, the behavior and the mechanisms of oxalic and citric acids toward P sorption prevention and metal release under standard calcite systems has been studied as well (Al-Shabaan, paper under publication). Hence, it seems reasonable that one may think about the behavior and mechanisms of some organic anions such as oxalate and citrate toward P sorption prevention and the release of the presorbed metals under standard Gypsum-Calcite systems. Hence,, the calcareous (calcite) and gybsiferous (Gypsum) conditions may usually coexist within the arid and semi-arid soil environments.

The present research was designed i) to compare the influence of the standard calcareous (calcite) – gypsiferous (gypsum) systems with the previous studied standard calcite (absolute calcareous) systems toward the behavior and mechanisms that oxalate vs. citrate anion exhibit in the respect of P sorption prevention and metal (Fe, Cu, Zn and Mn) release under such systems.

MATERIALS AND METHODS

- The metal presorption stage.

Standard salt reagents of FeCl₃, CuCl₂, ZnCl₂ and MnCl₂ were used to prepare a stock solution which contained 200 ppm of each metal in a background matrix electrolyte of 0.02M of KCl in one container. Five mls of the stock solution were added to 1.25g of calcite plus 1.25g of gypsum (both were standard reagents) in 50 ml polyethylene tubes. The tubes were closed and held vertically and rotatally shaken on a proper shaker for 24 hours at 140 rpm.

- The stage of P sorption prevention and the release of the presorbed metals.

Several stock solutions of fixed P concentration (20 ppm) prepared from the standard reagent of KH₂PO₄ 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 ml of each treatment stock solution were added to each tube of any three tubes that were devoted to the concerned treatment so that the final total treatment solution volume attained 50 ml so, each treatment was triplicated. Then the tubes were tightly closed and arranged horizontally on a proper holder, shaken on an orbital shaker at 140 rpm for 48 hours, provided the lab temperature and pressure were at standard conditions. The solutions were properly centrifuged and filtered through Watman 42 filter papers and then analyzed for pH and EC, then for HCO₃⁻ by titration due to the method described by Richards, 1969. The Fe, Cu, Zn, Mn and P were determined by an Inductively Coupled Plasma Optical Emission Spectro-Meter instrument (ICP).

Table 1: Shows the mean values of the equilibrium electrical conductivity (EC) as dSm⁻¹, pH, Calcium (Ca), and bicarbonate (HCO₃⁻) concentrations as affected by the increasing concentration added as organic carbon (O.C) as mmole per liter (mM O.C L⁻¹) from the oxalic acid.

O.C mM L ⁻¹	EC dSm ⁻¹	pH	PPM	
			Ca	HCO ₃ ⁻
0.0	5.4	6.8	566	126
0.1	5.1	7.1	589	118
0.5	5.6	8.0	565	122
1.0	6.4	8.2	503	163
5.0	6.6	8.9	503	189
10.0	7.2	9.2	405	244
15.0	8.7	9.5	321	271

Table 2: Shows the mean values of the equilibrium electrical conductivity(dSm^{-1}),pH,Calcium and bicarbonate concentrations as affected by the increasing level of the organic carbon (O.C) added from citric acid as mmole per liter (mM O.C L^{-1}).

O.C mM L^{-1}	EC dSm^{-1}	pH	PPM	
			Ca	HCO^{-3}
0.0	5.4	6.8	566	126
0.1	5.0	7.5	607	118
0.5	5.0	7.5	645	230
1.0	5.0	7.5	637	232
5.0	5.7	7.5	670	234
10.0	5.8	7.7	740	346
15.0	5.9	7.8	780	476

Table 3: Shows the mean values of the equilibrium concentrations of phosphate (P), Fe, Cu, Zn and Mn [as parts per million (ppm)] as affected by the increasing level of the organic carbon (O.C) added from oxalic acid as mmole per liter (mM O.C L^{-1}) under the calcite-gypsum systems.

mM O.C L ⁻¹	PPM				
	P	Fe	Cu	Zn	Mn
0.0	3.0	<0.05	<0.05	<0.05	<0.05
0.1	11.0	<0.05	<0.05	<0.05	<0.05
0.5	1.6	<0.05	<0.05	<0.05	<0.05
1.0	2.2	<0.05	<0.05	<0.05	<0.05
5.0	2.6	<0.05	<0.05	<0.05	<0.05
10.0	3.0	0.05	<0.05	<0.05	<0.05
15.0	3.2	0.05	<0.05	<0.05	<0.05

< = less than

Table 4: Shows the mean values of the equilibrium concentrations of phosphate (P), Fe, Cu, Zn and Mn as parts per million (ppm) as affected by the increasing level of the organic carbon (O.C) added from citric acid as mmole per liter (mM O.C L^{-1}) under the calcite-gypsum systems.

mM O.C L ⁻¹	PPM				
	P	Fe	Cu	Zn	Mn
0.0	3.0	<0.05	<0.05	<0.05	<0.05
0.1	13.6	<0.05	<0.05	<0.05	8.6
0.5	2.2	<0.05	<0.05	0.30	9.1
1.0	9.8	<0.05	<0.05	.040	7.1
5.0	10.2	<0.05	0.20	0.05	6.0
10.0	14.0	<0.05	0.05	0.05	5.2
15.0	14.5	<0.05	0.05	0.2	4.1

< = less than

DISCUSSION

Having studied and discussed the behavior of oxalic acid (oxalate anion) and citric acid (citrate anion) toward phosphate (P) sorption prevention and release of the presorbed Fe, Cu, Zn and Mn metals under standard calcite (calcareous) condition, (paper under publication), the present work would discuss, however, the behavior of both anions toward the same

targets, but under standard Calcite-Gypsum, (calcareous and Gipsiferous) coexisting conditions.

Under such systems, the adsorbent is a mixture of standard reagents of calcite and gypsum (1.25g calcite and 1.25g gypsum in 50 ml of reaction solution). Thus, the chemistry of the solution is expected to be different from the calcite solution alone. In addition, the behavior of oxalate and citrate anions is expected to be different to some extent.

The supportive information could be obtained from the mean values of the solution equilibrium ionic strength, pH, Calcium (Ca) and bicarbonate (HCO^{-3}), equilibrium concentrations.

1 – Electrical conductivity and pH issue:

Tables 1 and 2 show the relationships between the mean values of the equilibrium electrical conductivities, pH, Ca^{2+} and HCO^{-3} concentrations as functions of the increasing levels of organic carbon applied from oxalic and citric acids, respectively. According to the solubility of calcite and gypsum, the solubility of gypsum is much greater than that of calcite (K_s for calcite = 5.03×10^{-9} compared to the K_s for gypsum = 2.44×10^{-5}) (Nakayama, 1971). Under the present mixed adsorbent systems one can expect that the equilibrium concentrations of the concerned ions would be significantly greater than those of the calcite (single adsorbent) systems. This fact was confirmed according to the equilibrium values of the ion concentrations in addition to the electrical conductivities recorded on Tables 1 and 2 compared to those recorded in the previous study. Tables 1 and 2 show that the electrical conductivity increased from 5.1 to 8.7 dSm^{-1} due to 0.1 mM O.C L^{-1} to 15.0 mM O.C L^{-1} of the added oxalic acid, respectively, which corresponded to 5.0 and 5.9 dSm^{-1} due to the same rates of the citric acid, respectively. However, there was a gradual significant increase in the case of oxalate, compared to an almost slight increase in the case of citrate. Tables 1 and 2 also show that there was a significant gradual increase in the equilibrium pH values under the oxalate treatments compared to almost stable pH values under the citrate treatments. From the mentioned Tables, the pH value ranged from 7.1 at 0.1 mM to 9.5 at 15.0 mM O.C L^{-1} of the oxalic acid compared to 7.5 at 0.1 mM to 7.8 at 15.0 mM O.C L^{-1} of the citric acid, respectively. However, the equilibrium pH values under the case of oxalic acid were greater than those of the citric acid. Moreover, the pH values under both acids followed the same trends reported in the previous study (accomplished under calcite only), but the corresponding values were greater under the calcite systems compared to the present Calcite-Gypsum systems under both acids, respectively. It is obvious, that the greater values of the electrical conductivities of the mixed (Calcite-Gypsum) systems were due to greater solubility of the ions under the mixed systems compared to those of single systems. Furthermore, the lower corresponding values of the equilibrium pHs of the mixed adsorbent systems were due to the presence of gypsum which lowered the magnitude of final equilibrium pH compared to that of the single adsorbent systems. In addition, the equilibrium pH values themselves were totally controlled by the presence of calcite even in the mixed adsorbent systems, especially under the case of oxalic acid treatments.

However, concerning the issue of the increasing trend of the ionic strengths of the mixed adsorbent systems which corresponded to the increasing level of the acid additions and the influence of such increase on the organic anions and metal sorption, one can expect that the affinity of the organic anions to adsorb on the adsorbent surfaces would be significantly minimized, hence their efficiency to prevent phosphate sorption on such surfaces would be minimized as well. Concerning the equilibrium pH values of the present work, which mostly exceeded 8 under the oxalic systems and exceeded 7.0 under the citric acid systems, it is expected however, that the point of zero charge of the employed adsorbent surfaces has been exceeded as well. Thus, the adsorbent surfaces would possibly mostly be negatively charged. Furthermore, it has been reported, however, that pure calcite is slightly soluble in CO₂ – free distilled water ($pK_s = 8.5$ at 25° C) and the hydration energy of the Ca²⁺ ion is higher than that of the CO₃²⁻ ion so the Ca²⁺ ion will go into solution faster than CO₃²⁻ and thus, a surplus of negative charge will develop on the calcite surface (White, 1981). That was a general rule and may totally apply under certain conditions, however, the standard conditions under which such a rule may definitely take place is where the adsorbent is only calcite which should be present under distilled water systems in addition to the pH of such systems must exceed 9.5+ under which CO₃²⁻ is likely to be free. Nevertheless, with some exceptions to those criteria, the above mentioned rule may help to explain to some extent some of the behaviors of the oxalate and or the citrate anion toward P sorption or metal desorption under the complexed and mixed adsorbent systems under investigations.

The equilibrium calcium and bicarbonate issue:

Although all parameters are related to each other, hence discussing them in segments would highlight the role of each with the connection to the rest. Tables 1 and 2 show the mean values of the equilibrium Ca²⁺ and HCO₃⁻ concentrations as functions of the increasing levels of the organic carbon added from the oxalic and citric acids, respectively. Table 1, under the oxalic acid case, shows that Ca²⁺ was decreasing significantly due to the increasing level of the organic carbon input from the oxalic acid. In contrast, Table 2, under the citric acid case, shows that the equilibrium Ca²⁺ was significantly increasing due to the increasing level of the organic carbon input from citric acid. From Table 1, one can notice that there was 589 ppm of Ca²⁺ at 0.1 mM O.C L⁻¹ of the oxalic acid which significantly and gradually decreased to 321 ppm Ca²⁺ at 15.0 mM O.C L⁻¹ of the same acid. In contrast, Table 2 shows that there was 607 ppm of Ca²⁺ at 0.1 mM O.C L⁻¹ of the citric acid which significantly and gradually increased to 780 ppm Ca²⁺ at 15.0 mM O.C L⁻¹ of the same acid. However, such an opposite behavior trend due to the oxalic vs. citric acid toward the equilibrium Ca²⁺ concentration was confirmed by the previous studies, (A-Shabaan, 1989; Al-Shabaan and Al-Bahrani, 1995 and Al-Shabaan, paper under publication). It was reported that the oxalate anion precipitated calcium from solution in contrast, citrate anion solubilized it. Nevertheless, the only difference that was noticed had to do with the relative magnitude of the amount of corresponding equilibrium Ca²⁺ concentration which were significantly greater

under the present mixed (calcite-gypsum) adsorbent systems compared to those of the single (only calcite) systems of the previous work. Hence, the general trend was analogous in both systems. Such behavior would be considered in the case of P sorption prevention concerning either acids in the following discussion.

Furthermore, concerning the issue of the equilibrium bicarbonate concentration, Tables 1 and 2 show a gradual significant increase which corresponded to the gradual input of the organic carbon of oxalic or citric acid due to the progressive treatment rates. However, except for the first rate, the values reported for each treatment rate was found to be significantly greater under the case of citric acid compared to those of the oxalic acid. Table 1 shows that there was 118 ppm of HCO_3^- at 0.1 mM O.C L^{-1} of the oxalic acid which gradually and generally significantly increased to 271 ppm HCO_3^- at 15.0 mM O.C L^{-1} of the same acid. However, Table 2 shows that there was 118 ppm of HCO_3^- at 0.1 mM O.C L^{-1} of the citric acid which gradually and significantly increased to 476 ppm of HCO_3^- at 15.0 mM O.C L^{-1} of the same acid. However, the general increasing trend in the equilibrium concentration of HCO_3^- due to the progressive increasing input of the oxalic or citric acid was noticed in the previous studies (Al-Shabaan, 1989; 1995; etc.) and the present work. In contrast, in the previous studies the HCO_3^- values obtained under oxalic acid which corresponded to the same rate of each treatment were significantly greater in the case of the single adsorbent (calcite) systems compared to those of the case of the mixed (calcite-gypsum) adsorbent present study. For the last two rates, there was 980 and 1641 ppm of HCO_3^- at 10.0 and 15.0 mM O.C L^{-1} of the oxalic acid compared to 484 and 584 ppm HCO_3^- at 10.0 and 15.0 mM O.C L^{-1} of oxalic and citric acid, respectively in the previous study. In contrast (Table 1 and 2) and at the same treatment rates, there was 244 and 271 ppm of HCO_3^- compared to 346 and 476 ppm of HCO_3^- under oxalic and citric acid treatments, respectively in the present study. It was justified, however, in the previous study (Al-Shabaan, 1989) that oxalate anion has more affinity to the calcite surfaces and thus, it is likely to exchange for CO_3^{2-} through the phenomenon of ligand exchange and such behavior gave rise to higher concentration of CO_3^{2-} and or HCO_3^- in the equilibrium solution which was confirmed by the gradual disappearance of organic carbon of oxalate from solution. It was reported, however, that oxalate replaced carbonate from calcite and the molar ratio was almost 1:1 (Al-Shabaan, 1989). Nevertheless, such mechanisms would result in a greater amount of HCO_3^- in the equilibrium solution under the case of oxalate compared to that of citrate which was confirmed in all the previous studies which dealt with calcareous or single adsorbent (calcite) systems. Hence, this was not the case under the present study, the mixed (calcite-gypsum) adsorbent systems. Such contradictory findings may be justified based mainly on the different nature of the systems. The complexity of the systems due to the presence of several ions in addition to the presence of two adsorbents. Under the present study, the equilibrium sulfate concentrations (generated from gypsum) and the equilibrium organic carbon were not determined. Thus, the result justification concerning P sorption, metal sorption and release and the above mentioned

faced contradiction would be based on suggestions and possibilities until more future investigations employed which may provide more insight justifications. However, one might suggest that the common ion effect should have had resulted such contradiction. Calcite and gypsum both have calcium as a common ion. Gypsum is significantly more soluble than that of calcite and would release Ca to the solution in greater amounts and such higher amounts of Ca would combine with the released carbonate from calcite and reverse the equilibrium mechanism backward toward the calcite formation. Thus, such mechanism would decrease the equilibrium HCO_3^- concentration which was the case in the present argument.

The efficiency of oxalate toward P sorption prevention and presorbed metal release under calcite-gypsum (mixed adsorbent) systems.

Having discussed the magnitude of the equilibrium pH, electrical conductivity, Ca^{2+} and HCO_3^- values as, supportive parameters, which may affect the efficiencies of the oxalate or citrate anion toward P sorption and metal sorption-desorption, it is time to discuss the actual results concerning those targets from the research data.

Table 3 shows the mean values of the equilibrium concentrations of P, Fe, Cu, Zn and Mn as affected by the increasing level of oxalic acid (as mMO.CL^{-1}) under the mixed adsorbent systems. However, one can notice that the highest P sorption prevention was obtained at $0.1 \text{ mM O.C L}^{-1}$ of the oxalic acid which was when approximately 50% of the added P was recovered. There was a much lower and insignificant recovery of P due to all the next rates. The other P recoveries ranged from 8 to 16% which corresponded to $0.5 \text{ mM O.C L}^{-1}$ to $15.0 \text{ mM O.C L}^{-1}$ of oxalic acid respectively. Such finding is consistent with the results of the previous study of the single adsorbent (calcite) systems which included all other parameters, i.e., the metal chlorides (Al-Shabaan, paper under publication). According to the final equilibrium concentrations of the metals (Fe, Cu, Zn and Mn), one might relate the insignificant oxalate behavior toward P sorption prevention. As was previously stated, oxalate tends to form insoluble salts, either with Ca, Fe, Cu, Zn or Mn. Table 3, however, shows that all Fe, Cu, Zn and Mn were lost from the equilibrium solutions. Accordingly, such metal disappearance was in part probably due to the formation of metal oxalates which would have had created four sinks for a portion of the oxalic acid added. The rest of the oxalate added would, by any means, bind to the adsorbent surfaces. In addition to Ca^{2+} as a fifth target for the oxalate anion, oxalate might bind to the calcite or gypsum surface sites, surface Ca^{2+} and thus, may bind to other Ca or metal cation by the other negative carboxyl group and forming what is called oxalate-bidentate formation.

Under such mechanism, oxalate may incorporate phosphate ions by the help of any cation and hence connect the whole bound fraction to the adsorbent surfaces. Accordingly, such mechanisms would remove or significantly decrease the equilibrium free solution existence of either P or metal ions which was confirmed by the present data. However, the ligand exchange phenomenon may by any means take place as well. Oxalate anion, as was reported previously (Al-Shabaan, 1989) replaced CO_3^{2-} from calcite and the replacement ratio was 1:1. Under the present system,

however, any replaced CO_3^{2-} would hydrolyze where it results in OH^- influx in the equilibrium solution and this is the reason behind the increasing pH equilibrium values noticed (Table 1). Hence, some of such CO_3^{2-} or HCO_3^- would be neutralized backwards into the formation of calcite due to the excess of Ca coming from gypsum dissolution and such backward mechanism is suggested to be the main factor that lessens the magnitude of the pH increase to values less than the corresponding figures reported in the single (calcite) adsorbent systems. Although, the increasing ionic strength (i.e., the final equilibrium electrical conductivities) would be expected by any means to minimize the anion sorption to the adsorbent surfaces. However, such a rule seems to be not absolute under all cases, i.e., some organic anions such as oxalate might sorb to adsorption surfaces even at high ionic strength to some extent. Thus, the high ionic strength of the system would then minimize, to some extent, and not inhibit the organic anion sorption to sorbing surfaces.

The odd equilibrium P value which was attained approximately 50% of P sorption prevention and which occurred at 0.1 mM O.C L⁻¹ of the oxalic acid addition and that was the lowest rate employed, needs further insight justification. Furthermore, approximately such P recovery was noticed at the same oxalate rate even in the previous study that dealt with the single (calcite) adsorbent systems. Such finding encourages for more insight investigations.

Nevertheless, the high equilibrium pH values may favor the high metal sorption. Table 3 shows that all the presorbed metals could not be totally released by any of the oxalate levels. Thus, the oxalate anion failed totally to release any of the metals that were presorbed on the calcite-gypsum, mixed adsorbent systems. However, as was stated above and in the previous single (calcite) systems, the metals were expected to either precipitate as metal hydroxides in an environment systems of pH values greater than 7 or precipitate as metal carbonates or precipitate as metal oxalates. In addition, they were probably adsorbed on the negative adsorbent surface sites. All those mechanisms, by any mean, may be the responsible sinks that justify the metal disappearance. Hence, it was mainly the nature of the oxalate anion itself in addition to the system complexity that determined its significant low efficiency to prevent P sorption and its failure to release the presorbed metals.

The efficiency of citrate toward P sorption prevention and presorbed metal release under calcite-gypsum (mixed adsorbent) systems.

Table 2 shows the mean values of the equilibrium electrical conductivity, pH, Ca^{2+} and HCO_3^- concentrations as functions of the increasing rate of the citric acid added. Concerning the case of electrical conductivity which slightly increased from 5.0 to 5.9 dSm⁻¹ at 0.1 mM O.C L⁻¹ to 15.0 mM O.C L⁻¹ of citric acid. Such increase is significantly less compared to that of the oxalic acid which ranged from 5.1 to 8.7 dSm⁻¹ at the same rates of the acid employed. This is probably related to the expected higher concentrations of sulfate and associated ions under the oxalic acid systems. Under the case of citric acid, the pH values were almost stable where it ranged from 7.5 to 7.8 (Table 2). However, the electrical conductivity

and the pH value changes under citric acid cases were almost minimal compared to those under the oxalic acid. Thus, their influence on the P sorption prevention or metal release would be minimal as well. Unlike oxalate, citrate anion would solubilize Ca and increase its final concentration. Table 2 shows that the equilibrium Ca concentration increased gradually and significantly from 607 ppm at 0.1 mM O.C L⁻¹ to 780 ppm at 15.0 mM O.C L⁻¹ of the citric acid applied. In contrast, oxalate decreased the equilibrium Ca concentration from 589 ppm to 321 ppm at the same rates of the citric acid (Table 1). On the other hand, Table 2 shows that citric acid also increased the equilibrium HCO₃⁻ from 118 ppm to 476 ppm due to 0.1 mM O.C L⁻¹ to 15.0 mM O.C L⁻¹ of citric acid, respectively. However, the displaced amount of HCO₃⁻ from calcite by citrate was found to be greater than that of oxalate under the present study (calcite-gypsum systems) compared to the previous study (calcite systems). Such findings may probably show that citrate is more likely to exchange for some HCO₃⁻ from calcite in greater amounts compared to that of oxalate. In contrast, oxalate may exchange for sulfate from gypsum in lesser amounts than citrate but it may exchange for sulfate from gypsum in greater amounts than citrate. Such suggestions were based on the present data under the two adsorbent (calcite-gypsum) systems compared to the previous study (only calcite systems). Al-Shabaan, 1989, also reported that oxalate exchanged for CO₃²⁻ from calcite in significantly greater amounts and the exchange molar ratio was almost 1:1. Such conclusions, however, were recently based on a general suggestion since sulfate determination was omitted under the present study and more insight in future researches are needed to clarify such issue.

Table 4 shows the mean values of the equilibrium concentrations of P, Fe, Cu, Zn and Mn as functions of the increasing rate of the citric acid added as mM O.C L⁻¹. One can notice that the equilibrium P concentration attained its highest recovery at the highest rates of citric acid application which were 14.0 and 14.5 ppm (70 to 72.5%) at 10.0 mM O.C L⁻¹ and 15.0 mM O.C L⁻¹ of citric added, respectively. However, the lowest rate which was 0.1 mM O.C L⁻¹ of the citric acid recovered 13.6 ppm of final P (68% of the added), while the minimum recovery was obtained at 0.5 mM O.C L⁻¹ of the same acid. Furthermore, the recovery level increased to 9.8 and 10.2 (49 and 51% of the added) due to 1.0 and 5.0 mM O.C L⁻¹ of the acid applied. Nevertheless, the behavior of citric acid toward P sorption prevention is significantly much greater than that of the oxalic acid which was significantly less efficient in this case. Accordingly, such a finding would contradict the previous study of Al-Shabaan, 1989, which showed that the oxalate anion was more efficient than that of citrate toward the P sorption prevention. However, the previous system contained only calcite and metals were not incorporated in it, i.e., it was a very simplified system. On the other hand, in another recent study (under publication), Al-Shabaan reported the same trends of oxalic and citric acids towards P sorption prevention provided such systems contained only calcite, but employed the same metals in them. Hence, the system complexity due to the additional reactants would be expected to change the anions in concern. However, both acids resulted in approximately greater than 50% of P recovery of the present study which was

drastically decreased to a minimal point of each which was at 0.5 mM O.C L⁻¹ of each. Furthermore, after this rate, the P recovery was very small and did not exceed 16% at 15.0 mM O.C L⁻¹ under the case of the oxalic acid, whereas the P recovery increased significantly from the same rate and reached 72.5% of the added P at 15.0 mM O.C L⁻¹ of the citric acid. However, similar to such behavior was noticed under some studies, Traina (1986) in his work on the effect of ionic strength and Ca ions on citrate-orthophosphate interaction in an acidic, montmorillonitic soil suspension, reported that an addition of citric acid at low concentration (<0.1 mol m⁻³) produced a drop in residual orthophosphate solubility and then the orthophosphate solubility gradually returned to its value as the citric acid concentration was increased to 0.6 mol m⁻³. The author, however, attributed such phenomenon to the increased quantity of exchanged AL³⁺ through the addition of organic acid at low concentration which hydrolyzed and combined to the H₂PO₄⁻ to form AL(OH)₂ H₂PO₄. In addition, such phenomenon was reported with other acids such as tartaric and formic at low concentration of them (Traina, 1985). The same author reported that such a finding may occur due to either the above mechanism or by increasing the ionic strength of solution or by introducing a cation such as Ca. However, under the present study, it is likely that the formation of a compound such as Ca₂(OH)₂HPO₄ takes place at approximately 0.5 mM O.C L⁻¹ of oxalic acid and citric acid, respectively where the minimum P recovery was obtained. Furthermore, in general, the formation of M_x (OH) HPO₄ may take place as well with the other metals (M_x) that were present under the present system conditions. Hence, the presence of an excess of OH ions, especially under the oxalic acid systems, in addition to the presence of HOP²⁻₄ (not H₂PO₄⁻) under the pH of the present system makes it almost possible for the concerned compounds to form and result in the show up of the minimal points of the P sorption prevention under the case of either oxalic or citric acid systems. In addition, some investigators suggest the formation of what is called bidentate phenomenon which may be probably responsible for the above mentioned phenomenon. Parfitt et. al., 1977, suggested that at low concentrations of the oxalic acid, the oxalate anion was incorporated in a bidentate formation where it oriented one negative side of the carboxyl group to adsorb to the Fe of the goethite surfaces whereas the other negative side was bound to another Fe, (Fe-OOCOO-Fe). Such a suggestion may possibly hold in our systems where oxalate or even possibly citrate could orient themselves, under low concentrations of them, through such a way that let one negative side to be adsorbed to calcite or even gypsum calcium and the other negative side (or sides in the case of citrate) to bind to any metal in solution which in turn binds to a phosphate group. Accordingly, such mechanism generally may explain, in addition to other mechanisms, the disappearance of metals employed from solution in addition to the interpretation of P sorption prevention decline at the acid rate concerned.

It was suggested, however, that the superiority of citrate over oxalate to prevent P sorption prevention under the present study may be attributed to some mechanisms through which citrate tended to bind to the sorption surfaces by one end and possibly let the other two negatively charged

carboxyls free which repelled phosphate anions and gave rise to greater P solubility. Under such a suggestion, metals were suggested to have a greater affinity to surface sorption.

Table 4 also shows the final equilibrium concentrations of the presorbed metals due to the increasing rate of the citric acid added. From the same Table, one can notice that all metals disappeared from the solution except Mn. Manganese, generally was decreasing and the maximum amount released of it was 9.1 ppm (45.5% of the added) which was attained at 0.5 mM O.C L⁻¹ of the citric acid, whereas the lowest recovery was obtained at the highest rate of the acid which was 4.1 ppm (20.5% of the added) at 15.0 mM O.C L⁻¹ of the acid. The mechanisms by which most of the presorbed metals (except Mn) in this case were not released even partially at any rate of the citric acid was attributed to the complexity of the systems under investigation, as well as to the nature of citrate ion itself as was suggested in some of the previous studies (Al-Shabaan, paper under publication). It was suggested, however, that all metals may have had precipitated as hydroxides or carbonates (or oxalates under oxalic acid conditions). Another mechanism that might contribute to such results is the adsorption on the adsorption sites of the adsorbent surfaces through which citrate may bind to one end of the sorbed metal ion and bind to another free metal ion in solution and so on. The failure behind the citrate inefficiency to release all but some of the Mn metal may be possibly attributed to the greater affinity of Fe, Cu and Zn metals than that of Mn to the sorption surfaces or possibly to the OH or HCO₃⁻ and or CO₃²⁻, especially in the presence of gypsum accompanied by the presence of citrate which was not the case under the previous studies which contained only calcite or those under oxalic acid systems in all cases. It seems, under some circumstances, however, that citrate would win to some extent the race of competition among the rest of the anions, but only with Mn through releasing some of sorbed amounts and bring it to solution, possibly as Mn – citrate complexes which was confirmed by the data obtained.

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تأثير كل من أنيون الأوكسالات وأنيون السترات على الحيلولة دون إدمصاص الفوسفور و كذلك تحرير المعادن المدمصة في نظم قياسية من خليط من الجبس و الجير .

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لقد تمت مفاعلة وزن ثابت من خليط من كل من الجير و الجبس (1.25 جم من كل من هما) مع تركيزات ثابتة (20 جزء في المليون) من كل من كاتيون معدن الحديد و النحاس و الزنك و المنجنيز على صورة كلوريدات و لمدة 24 ساعة في المرحلة الأولى . ثم تلا ذلك إضافة تركيز ثابت من الفوسفور (20 جزء في المليون) يرافقه تركيزات متزايدة من الكربون العضوي (ك.ع) ثم تم مفاعلة الخليط لمدة 48 ساعة . وفي الراشح لوحظ ازدياد قيمة كل من التوصيل الكهربائي و رقم ال PH مع زيادة تركيز الأحماض ولكن هذه الزيادة كانت اكبر في حالة حمض الأوكساليك . أما الكالسيوم فقد تناقص تركيزه بزيادة تركيز حمض الأوكساليك حيث كان 589 و 321 جزء في المليون (ج.م) عند تركيز 0.1 و 15.0 مليمول / لتر من ك.ع / لتر على التوالي . وعلى النقيض من ذلك فقد تزايد تركيز الكالسيوم مع تزايد إضافة حمض السترات وقد كان 607 و 780 ج.م عند 0.1 و 15 مليمول كربون عضوي / اللتر على التوالي . ومن جهة أخرى فقد تزايد تركيز البايكربونات بتأثير كلا الحمضين ولكن التزايد كان أكبر تحت حمض الستريك حيث ازداد من 118 إلى 476 وكذلك من 118 إلى 271 ج.م من البايكربونات نتجت عن إضافة 0.1 و 15 مليمول / لتر ك.ع من كل من حمض الستريك و الأوكساليك على التوالي . ومن جهة أخرى فقد حال حمض الستريك دون أدمصاص 60% و 70% من الفوسفور المضاف عند تركيزات 0.1 و 15.0 مليمول / لتر ك.ع منه على التوالي . أما حمض الأوكساليك فقد حال دون أدمصاص 55% و 15% فقط من الفوسفور المضاف عند تركيزات 0.1 و 15.0 مليمول / لتر ك.ع منه على التوالي . ومن جهة أخرى لم يتمكن كلا الحمضين من تحرير المعادن المدمصة و لكن حمض الستريك تمكن من تحرير نزر يسير من المنجنيز بمعدل متناقص . و بالجملة فقد تقرر بأن حمض الستريك كان أكثر فاعليه في الحيلولة دون أدمصاص الفوسفور بالمقارنة مع حمض الأوكساليك في النظم القياسية المدروسة من الجير و الجبس .