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PHOSPHORUS SORPTION-DESORPTION IN SOIL AS INFLUENCED BY ORGANIC MATTER, CARBONATES AND Fe-Al OXIDES

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Abstract

Phosphorus (P) reactions in soil are influenced by its chemical components such as organic matter (OM), carbonates, and Fe-Al oxides. This study was aimed to compare the P sorption-desorption processes in two soils in the presence and absence of the aforementioned chemical components. In order to eliminate OM, carbonates, and Fe-Al oxides, the soils were treated with sodium hypochlorite (NaOCl), sodium acetate (NaOAc), and citrate-bicarbonate-dithionate (CBD), respectively. Then, the P sorption-desorption processes were carried out under batch conditions in comparison with the non-treated soils. Results indicated that removal of OM increased the maximum P sorption capacity (Q_{max}) of the soils by 42 and 69 mg kg⁻¹. While, removing of the carbonates decreased the Q_{max} values of the soils by 118 and 67 mg kg⁻¹. Furthermore, the removal of Fe-Al oxides resulted in Q_{max} reduction in the range of 34.3 and 19.2%. The phosphorous desorption sequence in the studied soils was as follows: Fe-Al oxides free > carbonates free > untreated > organic matter free. The standard P requirement (SPR) in the studied soils increased by 15.7 and 28% after OM removal and decreased by 33.3 and 17.03% and 47.9 and 22.6% after removal of carbonates and Fe-Al oxides, respectively. Overall, the results of the present study revealed that the P sorption capacity of the soils decreased in the presence of the OM and increased in the presence of Fe-Al oxides and carbonates. However, the effects of Fe-Al oxides were significantly higher.

Keywords: calcareous soils, isotherm, phosphorus, sodium hypochlorite

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1. Introduction

Phosphorus is an essential nutrient required for all forms of life as well as plant growth and agricultural production (Daly et al., 2015). Low P availability in calcareous soils is one of the main factors limiting the growth of agricultural crops (Engels et al., 2012). The efficiency of P fertilizers for some agricultural crops was found to be about 10-25% (Wang et al., 2011). Soil P availability is governed by important processes such as sorption-desorption reactions, precipitation, and dissolution. These reactions play an important role in supplying P for the plant, determining fertilizer requirement, environmental fate of P, and surface and ground water quality. Various soil components including the organic matter (OM), Fe-Al oxides, calcium

carbonate, and silicate minerals significantly affect the P reactions in the soil (Olsen and Khasawneh, 1980).

The OM can enrich the soil as a P source, and significantly influence the P sorption-desorption processes in the soil through various mechanisms (Yang et al., 2013). Varinderpal et al. (2006) reported that the use of organic fertilizers in Typic Ustochrept soils reduced the P adsorption, maximum buffering capacity and bonding energy, and increased the P concentration in solution. Maluf et al. (2018) also reported that the P adsorption and maximum buffering capacities were reduced with the increasing of humic acid in the soil. However, in some cases, there is a positive correlation between P sorption and soil OM. Yang et al. (2019) expressed that the maximum P adsorption capacity increases after raising the amount of soil OM. These contradictory results associated

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with the effects of OM on the P adsorption-desorption processes led to an unclear understanding of these important processes in the soil (Du et al., 2013; Hiradate and Uchida, 2004).

The amount, nature, and reactivity of the existing carbonate minerals affect to some extent the chemistry of calcareous soils (Hamad et al., 1992). The P reactions in the calcareous soils are affected by the calcium carbonate as the dominant carbonate source. The P reaction with carbonates often involves the adsorption and precipitation processes. Several studies have illustrated that calcium carbonate has an important effect on the P adsorption in the calcareous soils (Freeman and Rowell, 1981; Kuo and Lotse, 1972). Soil P is associated with Fe and Al in the mineral form or specifically adsorbed by Fe and Al oxides through exchanging with hydroxyl groups during the formation of bidentate surface complexes (McDowell and Condron, 2001).

Several studies have investigated the effect of soil components on the P sorption-desorption processes (Gorgin et al., 2011; Maluf et al., 2018). However, most of them have focused on one soil component such as OM or CaCO₃. In addition, some of them have dealt with the artificially created variation in a soil component through the addition of OM and CaCO₃. Mihoub et al. (2016) reported that the P adsorption capacity and bonding energy were increased as the CaCO₃ levels were increased. To better understand the effect of different soil components on the sorption studies, some researchers have implemented the component removal method. Sarkar et al. (2014) observed that the OM removal from the soils increased the boron adsorption, while the Fe and Mn oxides removal significantly reduced the boron sorption in acid soils (pH 4.8). It was observed that the OM removal from a spodic horizon led to a significant increment in the P sorption capacity (Bhatti et al., 1998). The knowledge about the influences of soil chemical components such as OM, carbonates, and Fe-Al oxides on the P sorption-desorption processes is limited to a few studies.

The main purpose of this research was to evaluate and compare the removal effects of OM, carbonates, and Fe-Al oxides on the P sorption-desorption isotherms in two calcareous soils of the Kerman Province, southeast Iran.

2. Materials and methods

2.1. Soil sampling and analyses

Two soil samples were collected at 0–30 cm depth from calcareous croplands in Baft and Orzuyeh regions located in Kerman Province, southeastern Iran. After air-drying and grinding, the soil samples were passed through a 2 mm sieve, and their physicochemical properties were determined according to the standard methods, including the soil texture by hydrometer method (Gee and Bauder, 1986), pH in 1:5 soil-water suspension (Thomas, 1996), organic matter (Walkley and Black, 1934),

cation exchange capacity (Rhoads, 1982), calcium carbonate (Allison and Moodie, 1965), active calcium carbonate (Leoppert and Suarez, 1996) and Fe-Al oxides with citrate-bicarbonate-dithionite (Mehra and Jackson, 1960). The soil available P was measured following the method described by Olsen and Sommer (1982).

2.2. Soil treatments

Each soil sample was divided into four sub-samples, based on the removal of OM, carbonates, and Fe-Al oxides, and one sub-sample was used as the control (untreated). Table 1 shows the treatments.

2.3. Phosphorus sorption experiments

In order to investigate the P sorption, 2 g of soil samples (before and after treatment) were placed into 50 ml centrifuge tubes and 25 ml of 0.01 M NaCl solution containing specific concentrations of P within the range of 0–80 mg L⁻¹ were added. Two drops of toluene were added to each tube to prevent microbial growth. The soil suspensions were intermittently shaken by an end-to-end shaker for 24 h at 25°C and centrifuged at 3500 rpm for 5 minutes. To ensure the supernatant clarity, they were passed through Whatman 42 filter papers. The equilibrium P concentration in the solution was determined by the ascorbic acid method using a UV-visible spectrophotometer at 880 nm wavelength (Rice et al., 2017). The amount of adsorbed P was estimated from the difference between its initial and equilibrium concentrations in solution according to the Eq. (1):

$$q = \frac{(C_i - C_e)V}{W} \quad (1)$$

where: q is the amount of P adsorbed per unit weight of the soil (mg kg⁻¹), C_i and C_e (mg L⁻¹) stand for the initial and equilibrium P concentrations, respectively, V (L) is the solution volume and W (kg) is the soil mass.

The Langmuir and Freundlich sorption isotherms were used to describe the P sorption data in this study. The mathematical equations of Langmuir and Freundlich (Eqs. (2) and (3)) models are presented as follows (Sparks, 2003):

$$q = \frac{Q_m K_l C_e}{1 + K_l C_e} \quad (2)$$

$$q = K_f C_e^{1/n} \quad (3)$$

where: q and C_e represent the amount of sorbed P (mg kg⁻¹) and equilibrium P concentration in the solution (mg L⁻¹), respectively. Q_{max} and K_l are the Langmuir constants corresponding to the maximum sorption capacity and sorption affinity of the binding sites. Also, K_f and $1/n$ are the Freundlich empirical constants associated with the sorption capacity and intensity (Moharami and Jalali, 2013).

Table 1. Methods for removal of different soil components

| <i>Treatment</i> | <i>Solution</i> | <i>Reference</i> |
|---------------------|---|------------------------------|
| Organic matter free | sodium hypochlorite (NaOCl) 6% (pH=8.5) | McDowell and Condrion (2001) |
| Carbonates free | sodium acetate (NaOAc) buffer 1 N (pH=5) | Tessier et al. (1979) |
| Fe-Al oxides free | 0.3 M sodium citrate+ 1 M NaHCO ₃ + Na ₂ S ₂ O ₄ powder (CBD) | Mehra and Jackson (1960) |

The standard P requirement (SPR) of soils defined as the amount of sorbed P (mg kg⁻¹) when $C_e = 0.2$ mg P L⁻¹ (Jalali, 2007) was calculated from the fitted Freundlich Eq. (3). The phosphorus maximum buffering capacity (PMBC) was determined based on the Langmuir equation parameters (Q_{max} and K_l) according to Eq. (4) (Maluf et al., 2018):

$$PMBC = Q_{max} \times K_l \quad (4)$$

2.4. Phosphorus desorption experiments

Desorption experiments were carried out following the sorption ones at the highest initial P concentration (80 mg L⁻¹) using the successive extraction method. The soil suspensions were shaken at room temperature (25°C) for 24 h and the supernatants were separated by centrifugation. Then, 25 ml of 0.01 M NaCl were added into the tubes and after 24 h shaking and centrifugation, the equilibrium P concentration in solution was determined. The desorption cycle was repeated seven times for the treated and untreated soils and the P retained by the soil (pre-sorbed P) was determined through the difference between the initial sorbed P and that in desorption equilibrium solution. The P desorption data were fitted to the Freundlich equation as follow (Eq. 5) (Soliemanzadeh and Fekri, 2017):

$$q = K_{desorb} C_e^{1/n_{desorb}} \quad (5)$$

where: K_{desorb} and $1/n_{desorb}$ are Freundlich bounding constants for the desorption coefficient.

The percentage of the desorbed P was calculated using the Eq. (6):

$$P_{des} = \frac{q_{ads} - q_{rem}}{q_{ads}} \times 100 \quad (6)$$

where: P_{des} is the percentage of desorbed P, q_{ads} and q_{rem} are the amounts of P adsorbed on the soil surface and that remained in the soil after seven desorption cycles, respectively.

2.5. Statistical analysis

The experimental design was a complete randomized design (CRD) with two factors, and each treatment was replicated three times. Statistical analysis of the data was performed with SPSS 26. Data were subjected to analysis of variance (ANOVA), and the means were compared by the Duncan test for $P \leq$

0.05. The fitness of each equation was evaluated according to its coefficient of determination (R^2) and the standard error of estimate (SE) (Chien and Clayton, 1980) calculated from Eq. (7):

$$SE = \sqrt{\frac{\sum (q - q^*)^2}{n}} \quad (7)$$

where: q and q^* are the measured and calculated amounts of P, respectively, and n is the number of measurements.

The non-linear regression procedure was used for fitting the Langmuir and Freundlich equations to the sorption and desorption data using GraphPad Prism software version 7 (Bhaumik et al., 2014).

3. Results and discussion

3.1. Soil properties

The soils of Orzuiyeh and Baft regions were silt loam and loam textured class, respectively. The soil pH was slightly alkaline for the two investigated soils. The Orzuiyeh soil contained relatively higher amounts of equivalent calcium carbonate (CCE), active calcium carbonate (ACCE), clay, silt, Fe, and Al oxides (Fe_d and Al_d extractable with CBD) compared to Baft area. However, the amounts of OM and sand were higher in Baft soil rather than those in Orzuiyeh (Table 2).

3.2. Phosphorus sorption investigation

The term sorption in the present study refers to the P removal from the solution through the adsorption and precipitation processes (Castro and Torrent, 1998). Sorption isotherms show the relationship between the equilibrium concentration of the sorbate and the sorbed amount onto the sorbent surface at a constant temperature. The P sorption by the untreated and treated soils was plotted in Fig. 1 as a function of equilibrium P concentration in the soil solution. The P sorption increased with the increasing of added P, but its percentage decreased (Fig. 1). This decrement in the sorption percentage could be attributed to the saturation of P sorption sites on the soil surface. This study showed that both the Langmuir ($R^2 = 0.967-0.997$) and Freundlich ($R^2=0.962-0.996$) equations fitted well to the P sorption by the studied soils before and after removal of soil organic matter, carbonates and Fe-and Al-oxides (Table 3). Wolde and Haile (2015) reported that both Langmuir and Freundlich models were able to give a good description of the P

sorption data. Rashmi et al. (2016) found that the Langmuir ($R^2 = 0.96-0.99$) and Freundlich ($R^2=0.95-0.99$) equations fitted well to the P sorption data in four soil orders including Vertisols, Inceptisols, Alfisols, and Ultisols. The maximum P sorption capacities predicted by the Langmuir equation for untreated soils were 668 and 537 mg kg⁻¹ in Orzuiyeh and Baft soils, respectively. The estimated value of Q_{max} is in close agreement with the findings of Jalali and Peikam (2013) and Rashmi et al. (2016). According to these results, the P sorption capacity in Orzuiyeh soil is higher than Baft. This may be due to higher clay and equivalent calcium carbonate content in Orzuiyeh soil compared to Baft (Table 2). Some studies have shown that clay and calcium carbonate

play important roles in fixing P in the soil, so that soils with higher clay content have more P fixation potential than those with less clay (Jalali and Peikam, 2013).

The P sorption in calcareous soils is highly influenced by the adsorption and precipitation reactions on the calcium carbonate surfaces (Freeman and Rowell, 1981). The results showed that P sorption was affected by removing of the soil constituents. Upon the OM removal, the P sorption increased ($p \leq 0.05$) in the studied soils. The increased amounts of Q_{max} obtained from the Langmuir equation after removing OM were about 42 and 69 mg kg⁻¹ in Orzuiyeh and Baft soils, respectively (Table 3).

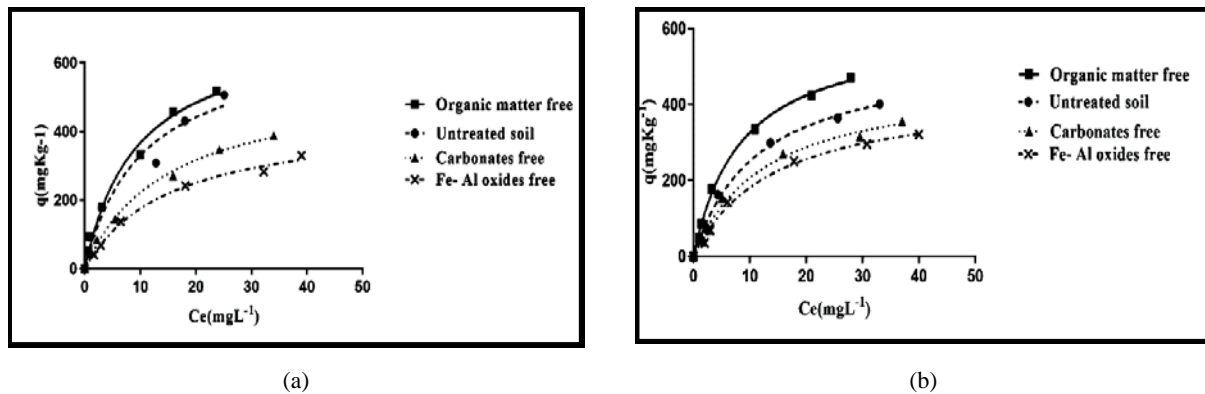


Fig. 1. Phosphorous sorption isotherms fitted to the Langmuir equation in the studied soils: (a) Orzuiyeh and (b) Baft

Table 2. Physical and chemical properties of the studied soils

| Soil properties | Orzuiyeh | Baft |
|--|----------|-------|
| Sand (%) | 14.8 | 44.5 |
| Clay (%) | 22.4 | 11.0 |
| Silt (%) | 62.8 | 44.5 |
| pH | 7.45 | 7.31 |
| EC (dS m ⁻¹) | 3.31 | 0.202 |
| CCE ^a (%) | 18.25 | 10.75 |
| ACCE ^b (%) | 7.68 | 4.48 |
| OM ^c (%) | 1.26 | 2.34 |
| CEC ^d (meq/100g soil) | 13.54 | 13.64 |
| Olsen-P ^e (mgkg ⁻¹) | 8.38 | 14.75 |
| Fe _d ^f (g kg ⁻¹) | 7.78 | 4.54 |
| Al _d ^f (g kg ⁻¹) | 0.653 | 0.215 |

Notes. ^a CCE = calcium carbonate equivalent; ^b ACCE= active calcium carbonate; ^c OM= organic matter; ^d CEC= cation exchange capacity; ^e Olsen P= extractable phosphorus according to method of Olsen; ^f Fe_d and Al_d= Fe and Al oxides extractable with citrate-bicarbonate-dithionite, EC= electrical conductivity

Table 3. Parameters of the P sorption isotherms in untreated and treated soils

| Soil | Treatments | Langmuir | | | | Freundlich | | | |
|----------|---------------------|---------------------------------|----------------------------|-------|-------|----------------------------|--------------------|-------|-------|
| | | Q_{max} (mgkg ⁻¹) | K_i (Lmg ⁻¹) | R^2 | SE | K_f (Lkg ⁻¹) | 1/n | R^2 | SE |
| Orzuiyeh | Untreated | 668 ^b | 0.097 ^c | 0.967 | 0.035 | 85.9 ^b | 0.545 ^a | 0.989 | 0.020 |
| | Organic matter free | 710 ^a | 0.106 ^b | 0.987 | 0.022 | 97.8 ^a | 0.536 ^a | 0.993 | 0.016 |
| | Carbonates free | 550 ^d | 0.067 ^g | 0.994 | 0.011 | 57.6 ^d | 0.549 ^a | 0.996 | 0.009 |
| | Fe-Al oxides free | 439 ^g | 0.066 ^g | 0.994 | 0.009 | 44.8 ^g | 0.546 ^a | 0.984 | 0.016 |
| Baft | Untreated | 537 ^e | 0.087 ^d | 0.994 | 0.012 | 64.0 ^c | 0.536 ^a | 0.973 | 0.026 |
| | Organic matter free | 606 ^c | 0.115 ^a | 0.997 | 0.009 | 86.5 ^b | 0.519 ^b | 0.982 | 0.024 |
| | Carbonates free | 470 ^f | 0.077 ^e | 0.987 | 0.015 | 53.0 ^e | 0.535 ^a | 0.965 | 0.026 |
| | Fe-Al oxides free | 434 ^g | 0.073 ^f | 0.991 | 0.012 | 48.8 ^f | 0.535 ^a | 0.962 | 0.025 |

Note. Significant differences between treatments at $P < 0.05$ levels indicated by different lowercase letters within columns.

The increase in soil P sorption capacity after OM removal could be attributed to the increase in its active sorption sites. The results of the present study are in agreement with those reported by Hiradate and Uchida (2004). They showed that the amounts of adsorbed P increase as OM is removed from an Andisol, indicating that OM occupies the P sorption sites and inhibits P adsorption through competitive sorption. On the other hand, several studies have shown that the effect of OM on increasing or decreasing P sorption depends on the nature of the OM and the soil properties. McDowell and Condon (2001) reported that with the OM removal, the value of P sorption index (PSI) increases and decreases in the arable and grassland soils, respectively. They concluded that, it is unlikely that OM directly binds with P, instead is associating with Al and Fe. The negative charged functional groups in the organic substances such as carboxylic and phenolic groups can compete for P sorption sites and alter the surface charges of Al and Fe oxides causing the P ions to be electrostatically repelled (Liu et al., 1999; Zamuner et al., 2008).

The application of organic residues increased the P content in the soil solution, which could be attributed to the occupation of P adsorption sites on the surfaces of Fe and Al oxides by the organic acids resulting from the decomposition of organic residues (Andrade et al., 2002; Havlin et al., 2005). The sorption isotherms parameters of P for the untreated and Carbonates free soils are presented in Table 3. Removal of carbonates led to the reduction ($p \leq 0.05$) in P sorption by the soil. The decrease amounts in Q_{max} values of Orzuiyeh and Baft soils were obtained as 17.66 and 12.5%, respectively. These results indicate that carbonates play an important role in the P sorption capacity variation in the soil. These results are supported by Jalali and Pikam (2013).

Uygur (2009) indicated considerable reduction in the amount of sorbed P by 33.9-68.3% upon removing the soil carbonates. The calcium carbonate removal from the soil results in a decrement in the surface sorption sites, thus reducing the P sorption capacity. Majidi et al. (2010) reported that the calcium carbonate removal from the soil reduces its boron sorption capacity by 35%. The P reactions in calcareous soils are affected by calcium carbonate as the dominant form of carbonates. Furthermore, P sorption is highly affected by the sorption and precipitation reactions on the calcium carbonate surfaces (Jalali, 2007). The ability of carbonate minerals to adsorb P is due to the presence of $\equiv\text{CaOH}$ and $\equiv\text{CO}_3\text{H}$ functional groups on their external surfaces.

The charge of these surface groups is variable and dependent on the pH and ionic strength of the soluble phase. Carbonate minerals affect the P sorption of the solution through precipitation processes, especially at high P concentrations (Uygur, 2009). The higher decrease in Q_{max} value of Orzuiyeh soil upon removing the carbonates, was possibly due

to the higher content of equivalent calcium carbonate compared to Baft area.

The P sorption isotherms before and after Fe-Al oxides removal are illustrated in Fig 1. The Fe-Al oxides removal caused a significant ($p \leq 0.05$) decrease in the sorption, and the reductions in Q_{max} values were estimated as 34.3 and 19.2% for Orzuiyeh and Baft soils, respectively.

These results further clarified that CBD extractable Fe-Al oxides have an important role in the P sorption capacity by the studied soils. It has been demonstrated that Fe-Al oxides have a high P sorption capacity (Fink et al., 2014; Lair et al., 2009). The role of Fe oxides has been illustrated in a wide variety of calcareous soils (Hamad et al., 1992; Wandruszka, 2006).

At low concentrations, P is initially adsorbed on Fe oxide surfaces through ligand exchange reaction and is later trapped through occlusion (Torrent et al., 1992). McDowell and Condon (2001) reported that the soil treatment with the dithionite-citrate reduces the soil P sorption capacity. P sorption capacity in calcareous soils has a significant relationship with the amount of CBD-extractable Fe (Holford and Mattingly, 1975). The higher decrease in Q_{max} values after Fe-Al oxides removal in Orzuiyeh soil was possibly attributed to the higher Fe-Al oxides contents compared to the Baft soil (Table 2).

Generally, in the present study, according to their P sorption capacities, the studied soils were ordered as: organic matter free > Untreated soil > carbonates free > Fe-Al oxides free.

3.3. Phosphorus desorption investigation

The P desorption isotherm constants and percentage of desorption are presented in Table 4. In untreated soils, after seven successive desorption cycles, the percentage of desorbed P relative to the adsorbed one was calculated as 35.3 and 53.2% in Orzuiyeh and Baft soils, respectively (Table 4). Some studies have shown that P desorption depends on the soil properties and soils with high P sorption capacity have lower P desorption (Gorgin et al., 2011; Prakash et al., 2017). In this study, Orzuiyeh soil indicated higher sorption capacity than Baft, and as a result, less P released in desorption cycles. It is clear that, only a fraction of the sorbed P is only desorbed and a substantial portion has remained in the solid phase after desorption.

The P sorption-desorption isotherms for untreated and treated soils for OM removal are shown in Figs. 2b and 3b. As can be seen, the OM removal led to an increment in the soil P sorption capability. However, in relation to the amount of sorbed P, desorption was lower compared to the untreated soils. The percentages of desorbed P relative to the sorbed one in the studied soils at the first desorption cycle were 14.9 and 18.9%, where desorption decreased by 3 and 10.3% compared to the untreated soils, respectively.

Table 4. Parameters of the Freundlich P desorption isotherm and percentage of desorption in the studied soils

| Soil | Treatments | Freundlich | | | | P desorption% |
|----------|---------------------|-----------------------------|--------------------|-------|-------|-------------------|
| | | K_{desorb} (Lkg^{-1}) | $1/n_{desorb}$ | R^2 | SE | |
| Orzuiyeh | Untreated | 370 ^b | 0.055 ^g | 0.61 | 0.039 | 35.3 ^e |
| | Organic matter free | 423 ^a | 0.027 ^h | 0.55 | 0.030 | 25.3 ^f |
| | Carbonate free | 218 ^d | 0.146 ^d | 0.90 | 0.02 | 50.8 ^d |
| | Fe-Al oxides free | 163 ^e | 0.167 ^c | 0.78 | 0.026 | 56.7 ^c |
| Baft | Untreated | 219 ^d | 0.136 ^e | 0.806 | 0.034 | 53.2 ^d |
| | Organic matter free | 337 ^c | 0.062 ^f | 0.686 | 0.034 | 36.5 ^e |
| | Carbonate free | 152 ^f | 0.212 ^b | 0.866 | 0.029 | 63.8 ^b |
| | Fe-Al oxides free | 119 ^g | 0.247 ^a | 0.878 | 0.038 | 68.8 ^a |

Note. Significant differences between treatments at $P < 0.05$ levels indicated by different lowercase letters within columns

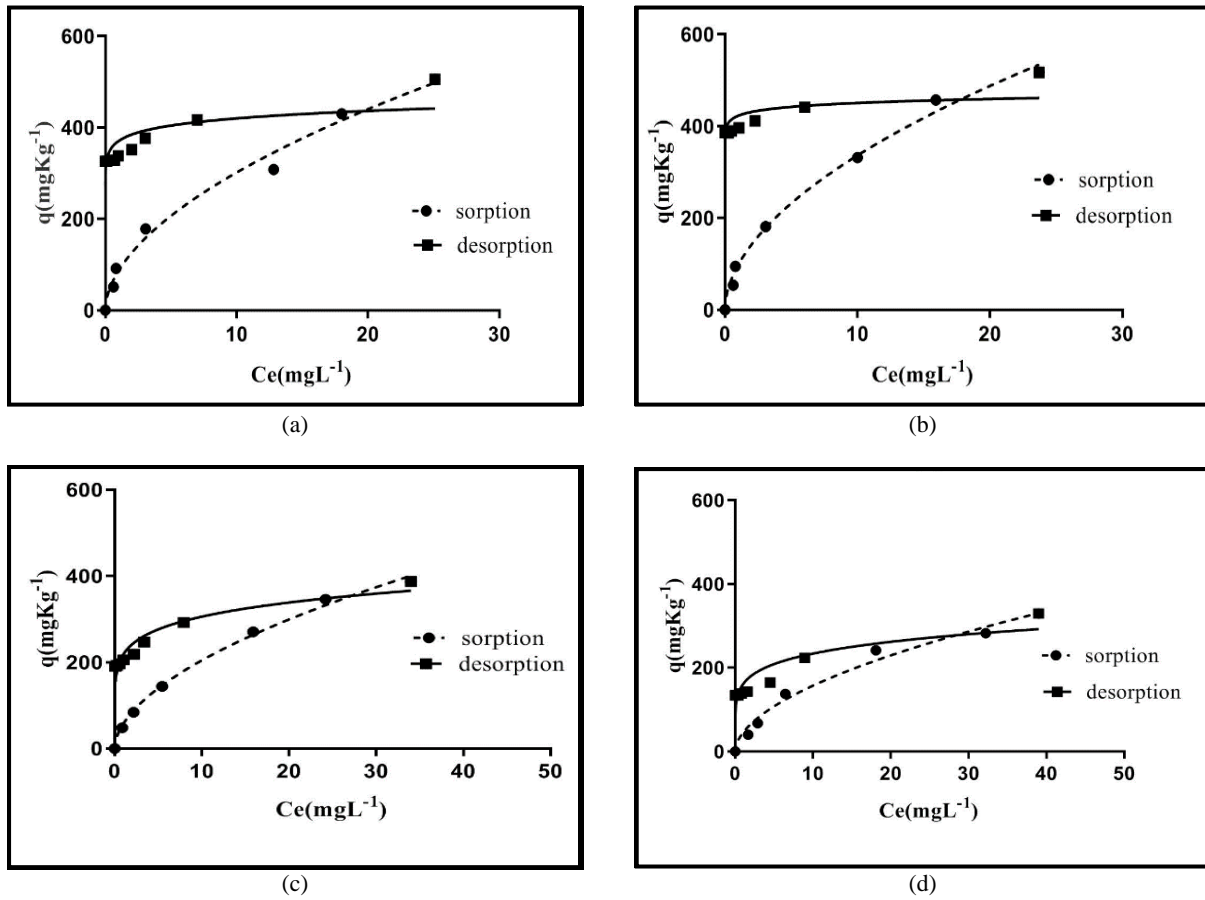
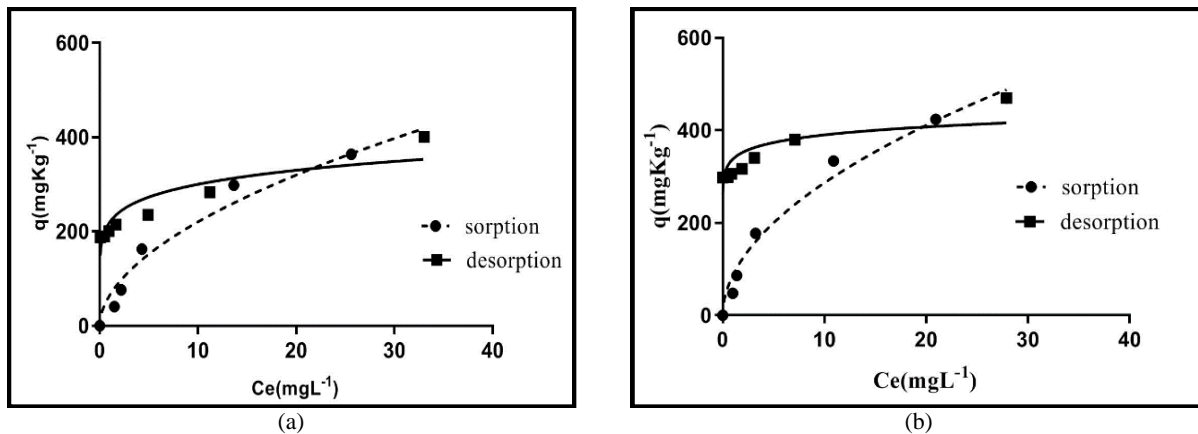


Fig. 2. Phosphorus sorption-desorption isotherms fitted to the Freundlich equation in Orzuiyeh soil: (a) Untreated soil, (b) organic matter free, (c) carbonates free, and (d) Fe-Al oxides free.



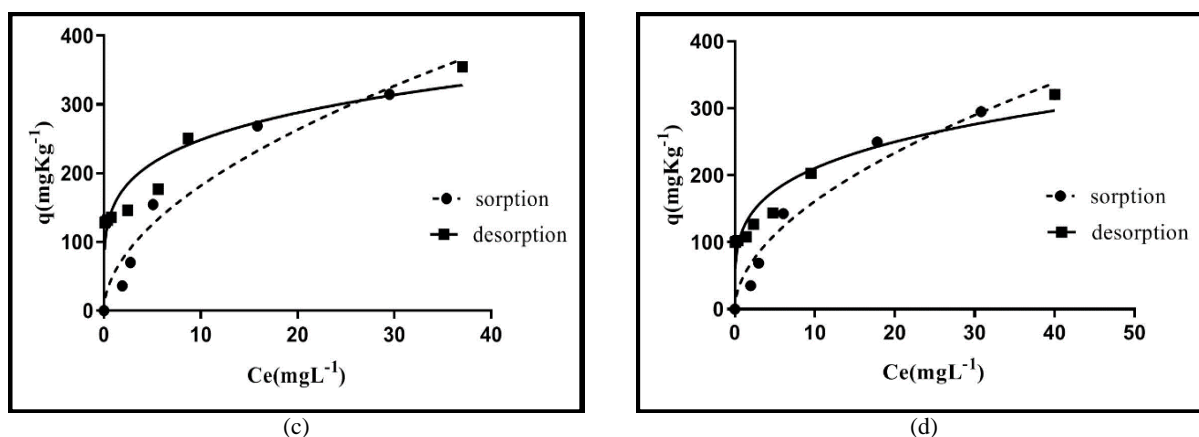


Fig. 3. Phosphorus sorption-desorption isotherms fitted to the Freundlich equation in Baft soil: (a) untreated soil, (b) organic matter free, (c) carbonates free, and (d) Fe-Al oxides free

Generally, after seven successive desorption cycles, the percentages of desorbed relative to the sorbed P in Orzuiyeh and Baft soils were respectively estimated as 25.3 and 36.5%, where the desorption rate decreased by 10 and 16.7% compared to untreated soils, respectively. Additionally, the soils with higher OM content have higher P desorption capacities (Prakash et al., 2017). The OM removal from the soil causes P to be more sorbed on Fe-Al oxide surfaces with high energy and leads to a decrease in the P desorption from the soil.

After soil treatment with NaOAC buffer solution to remove carbonates, the percentages of desorbed P relative to the absorbed one after seven successive desorption cycles were obtained as 50.81 and 63.8% in Orzuiyeh and Baft soils, respectively, indicating that the rate of desorption increased by 15.41 and 10.6% compared to the untreated soils. This result highlighted that the presence of carbonate minerals in the soil significantly increases the P retention by the soil through adsorption and precipitation processes. Soils with higher CaCO_3 contents have lower P desorption capacities (Prakash et al., 2017).

Figs. 2d and 3d exhibit that the P sorption on CBD treated soils to Fe-Al oxides removal are more reversible than that of untreated ones. Fe-Al oxides removal reduced the soil P sorption capacity. P desorption decreases with an increment in the amount of Fe-Al oxides in a soil (McDowell and Condron, 2001). Therefore, for the amount of sorbed P, more P was desorbed from Fe-Al oxides removed soils compared to the other treated ones (Fig. 2). The percentage of desorbed P after seven successive desorption cycles in the Orzuiyeh soil was evaluated as 56.7%. This indicates that the removal of Fe-Al oxides by CBD in this soil increased the desorbed P by 21.3%. Removing the Fe-Al oxides in the Baft soil, increased the percentage of desorbed P after seven successive desorption cycles from 53.2 to 68.8% (Table 4). As a result, according to their desorption rates the studied soils were ordered as: Fe-Al oxides free > carbonates free > untreated soil > organic matter free.

3.4. Phosphorus Maximum Buffering Capacity (PMBC) and Standard Phosphorus Requirement (SPR)

PMBC is an important index for evaluating the soil P fixing capacity calculated using the parameters of the Langmuir equation. It is an indirect index of soil P availability as it is indicative of soil resistance to the P transfer from the solid phase to the solution (Maluf et al., 2018). The estimated PMBC values in treated and untreated studied soils were in the range of 28.9-75.3 L kg^{-1} (Table 5). As can be seen from Table 5, the OM removal from the soil increased ($p \leq 0.05$) PMBC values in both studied soils by 16.2 and 49.2%, respectively. Some studies have shown that increasing OM in the soil reduces the P sorption (Prakash et al., 2017) and PMBC (Maluf et al., 2018). Jalali and Ranjbar (2011) reported that the addition of organic residues improved the P availability of the calcareous soils. PMBC values significantly decreased in the soils after carbonates removal. This decrease is likely attributed to the reducing effect of carbonate accompanying cations (Ca or Mg) on P sorption capacity and PMBC as a consequence (Maluf et al., 2018).

The removal of Fe-Al oxides resulted in PMBC reduction ($p \leq 0.05$). These results further clarified that Fe-Al oxides play an important role in the P sorption capacity. Upon the Fe-Al oxides removal, the P sorption capacity and bonding energy decreased which resulted in PMBC reduction as a consequence. Previous investigations have highlighted the correlation between iron oxides and P buffering capacity (Solis and Torrent, 1989). Fink et al. (2014) found that the PMBC index is mainly influenced by soil pH, particle size distribution, clay mineralogy, the amount and type of Fe and Al oxides, and types of soil crystalline oxides. SPR is defined as a P concentration in the soil solution that is not limiting plant growth and various amounts are mentioned for it in the different sources. Havlin et al. (2005) suggested that the range of 0.005-0.3 mg P L^{-1} of soil solution is suitable for growing different crops. In this study, the concentration of 0.2 mg L^{-1} was used to calculate the

SPR using the Freundlich equation (Jalali, 2007). The SPR has been estimated as 35.7 and 27 mg kg⁻¹ in the untreated soils, respectively (Table 5). The SPR value for Orzuiyeh soil was higher than that of Baft due to the clay and calcium carbonate equivalent contents. Jalali (2007) reported that the range of SPR values in Hamadan surface soils is between 4 and 102 mg kg⁻¹. Organic matter removal significantly increased the P requirement by 15.7 and 28% in Orzuiyeh and Baft soils, respectively.

Some studies have further shown that soils with higher P sorption capacities have higher SPR values (Rashmi et al., 2016). The OM removal led to an increase in the P sorption capacity of the studied soils. The carbonates removal from the studied soils reduced their requirement for P by 33.3 and 17.03%, respectively. The SPR index decreased after Fe-Al oxides removal by 47.9 and 22.6% in Orzuiyeh and Baft soils, respectively. In general, the sequence of soils based on their SPR in the present study was as: organic matter free > untreated soil > carbonates free > Fe-Al oxides free.

Table 5. PMBC and SPR values in control and treated soils

| Soil | Treatments | SPR | PMBC |
|----------|---------------------|--------------------|-------------------|
| Orzuiyeh | Untreated | 35.7 ^b | 64.8 ^c |
| | Organic matter free | 41.3 ^a | 75.3 ^a |
| | Carbonates free | 23.8 ^d | 36.8 ^e |
| | Fe-Al oxides free | 18.6 ^f | 28.9 ^f |
| Baft | Untreated | 27.0 ^c | 46.7 ^d |
| | Organic matter free | 37.5 ^b | 69.7 ^b |
| | Carbonates free | 22.4 ^{de} | 36.2 ^e |
| | Fe-Al oxides free | 20.9 ^{ef} | 31.7 ^f |

Note. Significant differences between treatments at $P < 0.05$ levels indicated by different lowercase letters within columns

4. Conclusions

The present study investigated the effect of soil chemical constituents on the P sorption and desorption processes in the soil. The removal of OM from the studied soils led to increase in P sorption due to the activation of sorption sites in Fe-Al oxides and hydroxides and newly formed ones on the mineral surfaces. But, the amount of desorbed relative to the sorbed P was decreased. Removing the carbonate minerals from the soils reduced the P sorption due to the reduction in sorption sites.

However, P desorption increased after the carbonates removal. Although Fe-Al oxides are identified to act as the P sorption sites in acidic soils, but their removal from the calcareous soils decreased their P sorption. The results of this study indicated that the P sorption capacity decreased in presence of organic matter, while it increased in the presence of Fe and Al oxides as well as carbonates. The effects of Fe and Al oxides were greater as compared to the carbonates.

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