Effects of salts on phosphorus adsorption in alkalize Tunisian soil

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Abstract Many previous studies have been conducted in an attempt to determine phosphorus (P) adsorption in soil. Often, these studies cannot be compared, because the reports did not give a satisfactory characterization of the dynamics of soil P in saline conditions. In our experiment, three salts extracts (CaCl₂, NaCl and KCl) with the same concentration (0.01 M) were used to determine the amount of P adsorption in Solonetz soil samples of the semi-arid areas of Kondar region (Tunisia). Also, we focused on the influence of contact time on P-Salts adsorption in the alkalize soil. The analytic data were approached from the following kinetics' models: pseudo first order, pseudo second order and Elovich model. Results obtained showed that salts addition increased significantly the amount of P adsorption with the following order of salts extracts (P-CaCl₂ > P-NaCl > P-KCl > P). The mechanism of phosphate ions adsorption by soil was studied using IR spectroscopy. Infrared spectral characteristics of the amorphous material indicated that the adsorption is due to

exchange phenomena of phosphate ions with surface groups. It was also demonstrated that the addition of CaCl₂ salt caused a shift and an increase of OH, Si-O (Si-O-Si, Si-O-Al) and Al-OH absorption bands which favored the adsorption of P ions. Moreover, the second-order model was shown to be the best fit for describing phosphorus adsorption associated with different salts, as seen from the correlation coefficient R² which ranged from 0.98 to 0.99.

Keywords Phosphorus · Soil · Adsorption · Kinetics · Salts · Infrared spectral

Introduction

Inorganic P is one of the most limiting nutrients in agricultural production and in terrestrial and freshwater ecosystems (Elser et al. 2007). It plays a crucial role in essential physiological processes including photosynthesis, respiration, cell division, cell enlargement and the regulation of enzymes (Abel et al. 2002). The average agricultural soil solution P concentration varies widely among soils. It is about 100–2000 mg P_{total} kg⁻¹ soil representing approximately 350–7000 kg P ha⁻¹ in the surface 25 cm of the soil (Khan et al. 2010), although only a small portion of this phosphorus is immediately available for crop uptake (Morel et al. 2000). P deficiency is critical in highly weathered soils of tropics and subtropics, as well as calcareous/alkaline soils of Mediterranean basin (Hinsinger 2001). However, P is a non-renewable resource (Cordell et al. 2009); the future adsorption of P in soil solution has presented a most important global challenge. To confront this challenge and ensure adequate fertilization of P for optimum plant growing, the knowledge of different processes of P dynamics in soil solution is very interesting in

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assessing the amount of P that can be taken up by plants (Vance et al. 2003; Rengel and Marschner 2005; Harmsen 2007). Adsorption of P is notably controlled by soil solution properties such as pH and concentration and type of dissolved salts (Arai and Sparks 2007). Several factors affect the amount and composition of these salts in soil solution such as high salt content in irrigation water, and some of the fertilizers used in soil contain high levels of potentially harmful salts, such as KCl and NaCl. Cho-ruk and Morrison (2004) found that in salt-affected soil, as the concentration of salts increases, P adsorption declines. Other researches indicate that an increase in salt concentration increases the adsorption and decreases desorption of P. Andersen et al. (2011) suggested that the reduction of the sorption of phosphorus in saline solution soil was the result of the activity of ions' antagonists, which can decrease the activity of phosphate and phosphate transporters of both high and low affinity. The solubility of P increases remains unaffected or decreases depending upon the nature and amounts of salt added. Wang et al. (2010) showed the inverse relationship observed between available P and the chloride content. Bhadha et al. (2012) investigated that increasing level of NaCl decreases the level of P in soil solution. Baker et al. (2013) mentioned that phosphate concentrations in field-grown agronomic crops decreased as salinity (NaCl, CaCl_2) increased. Additionally, increased concentration of Na^+ and Ca^{2+} in soil solution can lead to increased soil ionic strength which may increase P retention (Curtin et al. 1993). Olsen et al. (1960) have shown that most of the soluble salts reacting with soil components contribute less available P and change the soil pH. Some others studies relate the phosphorus adsorption with the kind of soil. In acidic soils, Al–P precipitates as the NaCl concentration increases in the soil. In alkaline soils, high concentrations of Na^+ and increased pH led to increases in the amount of NaHCO_3^- extractable P. With increasing Ca^{2+} concentration, phosphorus (P) can precipitate as soluble Ca–P compounds (Wang et al. 2010). In sodic soils, P may exist as Na–P, which is formed as a result of the presence of soluble sodium salts and which is highly soluble. Curtin et al. (1987) found that when a group of New Zealand soils was Na-saturated, an average 2.6 times more P was available to distilled water (10 consecutive extractions) than from the original soils, where Ca was the dominant exchangeable cation. This effect may have an essential behavior on the adsorption of phosphorus in soils that have become saline or receive saline irrigation water. The vast majority of past investigations found a deleterious effect of dissolved salts on available P. They also found that available P is sensitive to the type of cation brought with chloride. However, we believe that past investigations only furnished a patchy view of the effect of salt concentrations and types, given

the lack of detailed experimental studies, which should consider concentration gradients for different salt types in the same soil. The aim of this study, therefore, was to (1) assess the P adsorption kinetics in soils from addition of different salts, (2) select the best fit for the data between three equations, and (3) relate the coefficients of these equations to the effects of salt additions.

Materials and methods

Site description

The phosphorus adsorption research was conducted with Solonetz soils samples of the semi-arid areas of Kondar ($36^\circ 08' \text{N}$ $10^\circ 22' \text{E}$) (Mtimet 1999). The climate is moderate in the winter and hot in the summer, with mean annual temperature of 297 K, and mean annual precipitation of 280 mm. The soil (0–25 cm) is clay soil (Calcic-magnesian).

Chemical and physical analysis

Triplicate soil samples were randomly collected at 0–25 cm depth, air-dried, sieved (<2 mm) and stored until analysis. Soil pH was determined in a 1:2 soil: water suspension (Suarez 1999); organic carbon (OC) by the wet oxidation method (Walkley and Black 1934); particle-size distribution by the pipette method (Gee and Bauder 1986) and calcium carbonate equivalent (CCE) by the BaCl_2 extraction method. Mehlich-III (Mehlich 1984) P, Ca, Mg, Fe, Al, Cd, Cu, Mn, were determined by equilibrating 2.5 g of air-dried soil with 25 mL of Mehlich-III extracting solution for 5 min and filtering through Whatman No. 40 filter paper. Concentrations of the various elements in the extracts were determined by inductively coupled plasma optical emission spectrophotometer (CP-OES, Perkins Elmer, Model 4300DV).

Mineralogy analysis

The quantitative mineralogical analysis was extracted from the powder XRD data using an internal standard for each mineral. The clay fraction was quantified, after purification, and based on a pure, standard clay mineral.

Experimental adsorption study

The batch adsorption experiments were carried out in 250 mL Erlenmeyer flasks where 1 g of each soil sample and 100 mL of the P, P–KCl, P–NaCl, P– CaCl_2 with concentration of 100 mg L^{-1} of P (Hamdi et al. 2014) were

prepared with KH_2PO_4 , and 0.01 M of KCl, NaCl and CaCl_2 . The Erlenmeyer flasks were subsequently capped and agitated in an isothermal shaker at 100 rpm and 293 ± 2 K to achieve equilibration at 24 h. A volume of 5 mL of P, P-KCl, P-NaCl, P- CaCl_2 solutions was sampled from Erlenmeyer flasks, centrifuged at 2800(g) for 10 min and the supernatant was immediately analyzed for P using the double-beam UV-Vis spectrophotometer (Shimadzu, Model UV 1601, Japan) at 868 nm (Watanabe and Olsen, 1965). The amount of adsorption at equilibrium, Q_e (mg g^{-1}), was calculated by Eq. (1):

$$Q_e = \frac{(C_i - C_e)}{M} \times V \quad (1)$$

where C_i and C_e (mg L^{-1}) are the liquid-phase concentrations of P at initial and equilibrium, respectively; V is the volume of the solution (L) and M is the mass of dried soil (g). The adsorption tests were performed thrice; the results represent the algebraic average quantities of retained phosphorus.

Adsorption kinetic study

Various kinetic models have been used by various researchers, where the pseudo-first-order, pseudo-second-order models and Elovich equation were studied.

Pseudo-first-order model

Rate equation of Lagergren is generally described by Eq. (2):

$$\frac{dQ}{dt} = K_1(Q_e - Q) \quad (2)$$

where K_1 is the pseudo-first-order constant. After integration, by applying the conditions, $Q_t = 0$ at $t = 0$ and $Q_t = Q_t$ at $t = t$, Eq. (2) becomes:

$$\log(Q_e - Q) = \log Q_e - \frac{k_1 t}{2.303} \quad (3)$$

where k is a constant and Q_e is the amount of P adsorbed at equilibrium in mg g^{-1} and constant k and Q_e can be calculated from the plot of $\log(Q_e - Q)$ versus time (t).

Pseudo-second-order model

The pseudo-second-order kinetic model is expressed as follows:

$$\frac{dQ}{dt} = k_2(Q_e - Q)^2 \quad (4)$$

Integrating the equation for the boundary conditions $t = 0$ to $t = t$ and $Q = 0$ to $Q = Q$ gives:

$$\frac{t}{Q} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (5)$$

where k_2 is the second-order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$), by plotting of $\frac{t}{Q}$ versus t is a linear relationship. Values of k_2 and Q_e were calculated from the intercept and slope of the plots of $\frac{t}{Q}$ versus t .

The Elovich equation

The Elovich is one of the useful models, it can be expressed as:

$$\frac{dQ}{dt} = \alpha \exp(-\beta Q t) \quad (6)$$

where α is the initial adsorption rate ($\text{mg g}^{-1} \text{min}^{-1}$) and β is the desorption constant (g mg^{-1}). To simplify the Elovich equation, assume $\alpha\beta t \gg 1$ and by applying boundary conditions $Q_t = 0$ at $t = 0$ and $Q_t = Q_t$ at $t = t$, Eq. (6) gives:

$$Q_t = \left(\frac{1}{\beta}\right) \ln(t + t_0) - \left(\frac{1}{\beta}\right) \ln t_0 \quad (7)$$

where $t_0 = \frac{1}{\alpha\beta}$. If t is much larger than t_0 , Eq. 7 can be simplified as:

$$\left(\frac{1}{\beta}\right) \ln(\alpha\beta) + \left(\frac{1}{\beta}\right) \ln(t) \quad (8)$$

A plot between Q_t versus $\ln(t)$ yields a linear relationship with a slope of $\left(\frac{1}{\beta}\right)$ and an intercept of $\left(\frac{1}{\beta}\right) \ln(\alpha\beta)$. The term $\left(\frac{1}{\beta}\right)$ indicates the number of sites available for adsorption.

Statistics

The statistical analyses were implemented with XLSTAT (2012). The analysis of variance ANOVA and post hoc multiple comparisons Tukey's test ($P < 0.01$) were used to examine the effects of salt extracts' addition on the variation of chemical composition in different solutions.

Fourier transform infrared spectroscopy analysis

Soil samples were dried and finely ground (< 2 mm) overnight before the spectroscopic analysis. Diffuse reflectance (MIR) spectral measurement of the soil samples was performed using a spectrophotometry double-beam analysis (FT-IR) (Camspec M550) at λ_{max} of 660 nm. Fourier transform infrared spectrometry (PerkinElmer

Spectrum two) was used to analyze the functional groups in the adsorbent. The transmission spectrum was acquired with 4 cm^{-1} resolution and the spectrum was corrected for a KBr background. For BET specific surface area estimation, a porosimeter accelerated surface area and porosimetry system (ASAP 2010) was used.

Results and discussion

Soil characteristics and adsorption mechanism investigation

Initial soil physicochemical characteristic were showed in the Table 1. The soil of the experiment has high quantities of clays. The value of pH is 8.66 indicated that is an alkalize soil. Soil analyses gave values of 24 meq/100 g (CEC), 3.6% organic matter (OM), and nutrients 3.4 (P), 680 (K), 17,784 (Ca), 11 (Mg), 143 (Fe), and 12(Al) (mg kg^{-1} soil). Exchangeable calcium concentration was high, where phosphate anions will be fixed, and the dominant form of phosphorus is maybe P-Ca characterized by low lability (McKenzie et al. 2003; Shen et al. 2011). Moreover, as indicated earlier, mineral analysis on Table 2 indicates a preponderance of clays. According to many others studies; the clays had a high affinity to adsorb the phosphate (Bratieres et al. 2008; Chang et al. 2010). The adsorption of phosphate anion is maybe performed by silanol functional groups on the clay surface specially on the calcite surface at alkalize solution ($\text{pH} = 8.66$) (Hanudin et al. 2014; Cartes et al. 2015) which was observed on IR spectra of our soil in 797.6 cm^{-1} . The principal adsorption mechanism is ligand anionic exchange involving the formation of inner sphere surface complexes (Hanudin et al. 2014). In fact, clays are generally associated with (hydro) oxides (Jing et al. 2010). These latter film coatings on the surface of the minerals soil (Martins et al. 2008). This film involves the formation of a variable charge and a strong ability to bind phosphate, in exchange against hydroxyl ions (Nacry et al. 2005; Goldberg et al.

2008). Also, it is reasonable to speculate that the phosphorus is adsorbed on the surface of soil by hydrogen bond. To develop this hypothesis, a physicochemical characterization of soil before and after adsorption was made using FTIR analysis.

Contact time effect

The sorption of P as a function of contact time is shown in Fig. 1. It can be revealed that the P adsorption rate was rapid for the first 12 h and decreased over time. Equilibrium P adsorption was established after approximately 24 h at an initial concentration of 100 mg L^{-1} . It can be suggested that the presence of three phases in adsorption of P may be explained as follow: the first phase is characterized by a high rate of adsorption, then the rate reduces linearly (second phase) until the slow adsorption phase starts. The same results were revealed by Hamdi et al. (2014). The fast adsorption rate at the initial stage may be explained by an increased availability in the number of active binding sites on the soil surface. The adsorption rapidly occurs and normally controlled by the diffusion process from the bulk to the surface. In the later stage the adsorption is likely an attachment-controlled process such as the penetration of P ion into the pores of soil micro-aggregates and P ion saturation of the adsorbent surface prevent P ion adsorption for each increase of P application (Hemmannuella et al. 2011).

Salt effect on P adsorption

The effect of salts on the retention of phosphate ions was also presented by the Fig. 1. It can be shown that all three types of salt additions could increase the P adsorption in the soil solution to compare with the control sample. However, P adsorption can be varied according to the type of salts (Mihiri et al. 2016). After addition of 0.01M of all salts, it has been occur an increase of measured P adsorption which reached 2.6%, 4.31%, and 8.39% in the case of P-KCl, P-NaCl and P-CaCl₂, respectively. The results emphasize the complex relationship between salinity and P adsorption in the soil.

Table 1 Soils' physicochemical properties

pH	OM (%)	CEC meq/(100 of soil)	Chemical content (mg/kg)							Physical content (%)		
			P	Ca	Al	Fe	K	Mg	Mn	Clay	Sand	Silt
8.6	3.6	24	3.4	17784	12	143	680	11	22	58.6	28.6	12.8

Table 2 Soil mineralogical composition

	Kaolinite	Quartz	Calcite	Smectite	Illite	Chlorite
Abundance of mineralogy	+	+++	+++	+	–	–
+++ Abundant, ++ moderately abundant, + poorly abundant

Fig. 1 Effect of contact time in adsorption of P associated with addition of KCl, NaCl and CaCl_2 (0.01 M) salts by the alkalize soil

Curtin et al. (1993) revealed that addition of salt increases the soil ionic strength. With increase in soil ionic strength, phosphate activity reduced, and P adsorption tended to increase; hence P adsorption decreased (Von Wandruszka 2006a, b). On the other hand, the increase of the P sorbed in the alkaline conditions in the presence of different salts may be due to the higher soil pH (Shaheen et al. 2009). Sorption processes are time-dependent, pH-controlled, and process rates decrease with time (Bolan et al. 1986). Garoma (1996) reported that at $\text{pH} > 7$, phosphorus in soil solution exists mainly in the form of HPO_4^{2-} . This divalent ion with two nucleophilic centers and the potential to act as a bidentate ligand may have greater affinity for the adsorbent surfaces. Additionally, Morgan (1997) and Mostafa (1999) also revealed that under alkaline conditions in the presence of free calcium carbonate, sorption of $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ on calcite could occur by replacing water, HCO_3^- or OH^- ions present on the calcite particles.

It has been observed that the CaCl_2 addition was the most effective in increasing the concentration of P adsorption in the soil solution followed by NaCl and KCl salts. However, this classification of salts to enhance P adsorption can be associated with the degree applied of valence and affinity of following cations (Ca^{2+} , Na^+ and K^+). One possible reason for this is that divalent cations increase the P sorption because they can fit into cavities of adsorbed phosphate ions. Similar results were indicated by Bhadha et al. (2012). Also Bolster and Sistani (2009) revealed that important differences between soils and CaCl_2 versus KCl solutions can also be attributed to factors such as organic matter content and pH. Several studies showed that these results can be explained respectively by the medium and high solubility of K-phosphate and Na-phosphate (Bhadha et al. 2012; Rogers et al. 2005). Furthermore, the increase of P sorption after addition of Ca-salts can be explained by the low solubility of Ca-phosphates (Mahmood et al. 2000). Curtin et al. (1993) signaled

that P adsorption increases with increasing Na^+ adsorption ratio (SAR) in the soil. However, when the soil solution contains high Na^+ concentrations, this ion can be replaced by exchangeable Ca^{2+} ion on the particle surface allowing the dissolution of P (Dudal and Gérard 2004).

Kinetic results interpretation

The pseudo-first-order plot of P adsorption in the different solutions on addition of different salts is illustrated in Fig. 2. From the plot the pseudo-first-order rate constant k_1 and the adsorption capacity Q_e were computed from the slope and intercept of the plot and presented in Table 3. It can be seen that the values of the pseudo-first-order rate constant varied with chemical modification and the following decreasing arrangement was determined: $\text{P-CaCl}_2 > \text{P-NaCl} > \text{P-KCl} > \text{P}$. Moreover, Fig. 3 depicts the plot of $\frac{t}{Q_t}$ versus contact time for the pseudo-second-order equation for adsorption of P. From the plot, the values of the pseudo-second-order rate constant k_2 and the sorption capacity Q_e computed from the slope and intercept are presented in Table 3. It can be seen that the values of k_2 and Q_e were enhanced with the addition of salts and the following decreasing arrangement was determined $\text{P-CaCl}_2 > \text{P-NaCl} > \text{P-KCl} > \text{P}$. The Elovich equation plot for P adsorption is shown in Fig. 4. Table 3 shows the constants of the Elovich equation, α is the initial adsorption rate, and β is the desorption capacity that are obtained from the slope and intercept of the Elovich plot. As observable from the data (Table 3), the values of α and β indicate a general trend of variation (increase in case of α and decrease in case of β) with the addition of the following salts, KCl, NaCl and CaCl_2 . It can be concluded that the adsorption phenomenon is more rapid in the case of Ca-P according to the α term value of the Elovich equation. The decrease from P-CaCl_2 to P-KCl may be due to the modification of soil surface functions as demonstrated in the following paragraph.

Fig. 2 Pseudo-first-order modeling (100 mg P L^{-1} , 22°C , soil mass = 1 g and 0.01 M of KCl, NaCl and CaCl_2)

Table 3 Modeling parameters

Q_{exp} (mg g ⁻¹)	Pseudo-first order			Pseudo-second order			Elovich		
	R_2	Q_{e1}	K_1 (mn ⁻¹)	R_2	i_{e2}	K_2 (mg g ⁻¹ mn ⁻¹)	R_2	α (mg g ⁻¹ mn ⁻¹)	β (g mg ⁻¹)
P 7,09	0.97	6.84	0.041	0.99	7.17	0.032×10^{-2}	0.99	0.06	3.98
P-KCl 7,28	0.98	6.24	0.042	0.99	7.3	0.029×10^{-2}	0.99	0.06	3.85
P-NaCl 7,41	0.98	6.29	0.043	0.99	7.9	0.003×10^{-1}	0.98	0.062	3.61
P-CaCl ₂ 7,74	0.96	6.87	0.045	0.98	7.6	0.033×10^{-2}	0.98	0.066	3.71

Fig. 3 Pseudo-second-order modeling (100 mg P L⁻¹, 22 °C, soil mass = 1 g and 0.01 M of NaCl, KCl and CaCl₂) **Fig. 4** Elovich kinetic model (100 mg P L⁻¹, 22 °C, soil mass = 1 g and 0.01 M of KCl, NaCl and CaCl₂)

Coefficient of determination analysis

For an appropriate description of the mechanism of P adsorption associated with different salts addition, it was necessary that different kinetic models be tested to determine their extent of fitness to the experimental sorption data. The coefficient of determination R^2 was chosen as the error function for the kinetic model analysis. This is because linear regression implicitly minimizes the sum of the squares of the errors to determine the equation parameters. As observable from the data (Table 3) of the

Fig. 5 Infrared spectral characteristics of soil (a), soil-P (b), soil-P-CaCl₂ (c)

linear coefficient of determination R^2 values of the different kinetic models used to evaluate the P adsorption, it shows that the pseudo-second order kinetic equation had the highest R^2 values. Thus, this kinetic model was taken as the best fit equation for the description of the mechanism of P adsorption. Also, the calculated Q_e values obtained from the second-order kinetic model agree with the experimental Q_e values for all the cases. These suggest that the P adsorption onto soil of Kondar region follows the second order kinetic model.

Infrared spectral characteristics

Figure 5 shows the infrared spectral characteristics of soil samples of Kondar. The peak assignments in the spectra represented OH stretching vibration (3697.48; 3621.46; 3435.66 cm⁻¹) (Li et al. 2015; Saikia et al. 2010), C-H stretching (2925.08 cm⁻¹) (Li et al. 2015), HOH deformation of the adsorbed water (2514.8348; 1798.7848; 1643 cm⁻¹) (Saikia et al. 2010; Hanudin et al. 2014), carbonate stretching vibration (1453.95; 872.47 and 713.02 cm⁻¹) (Li et al. 2015; Madejova et al. 2001), P-O

stretching (1032 cm^{-1}), O–P–O bending (535.6 cm^{-1}) (Large et al. 2011; Wang et al. 2016). The bond Si–O–Al (1005 cm^{-1}) (Saikia et al. 2010; Hanudin et al. 2014), The bond Al₂-hydroxide (913.36 cm^{-1}), Si–O stretching of quartz (797.6 cm^{-1}) (Li et al. 2015; Saikia et al. 2010) and Si–O–Si deformation (469.62 cm^{-1}) (Madejova et al. 2001; Saikia et al. 2010). Reaction with P ions resulted in a shift in these absorption bands. The shift of the peaks assigned to OH stretching vibration was derived to OH belonging to aluminol groups replaced by P ions, through ligand exchange. Strengthening on the peaks absorption bands indicated that stretching vibration intensity of OH increased due to adsorption of the anions. The shift assigned to C–H stretching, and the increase of the intensity at this peak is due to the interaction between C–H groups and phosphate ions. The peak of the absorption band assigned to water bending was shifted to higher frequency, from 2514.84 to 2514.93 cm^{-1} . This can be attributed to water adsorbed by the material was replaced by the phosphate anion. While strengthening the intensity at the peak of the absorption band indicates the addition of water carried by the anion–anion exchanger. Regarding the peak assigned to Si–O–Al, the wave number tends to shift toward the higher, from 1005 to 1009.6 cm^{-1} , likely this is due to the contribution of the vibrating group P=O stretching of phosphate ions. The same thing happens at the peaks of Si–O–Si and Si–O, in this case, absorption bands were shifted to lower wave numbers. In contrast, the peak of the absorption band assigned to Al–OH tends the frequency shift towards lower, i.e., from 913.36 to 911.8 . This is probably caused by the reaction of Al-hydroxide complex formation with the ligand anion exchanger (phosphate anion). The strengthening intensity of the absorption band assigned to P–O and O–P–O bending indicates the addition of phosphate ions (from 36.06 to 53.39% and from 39.44 to 62.21% , respectively).

The addition of CaCl₂ salt causes also a shift in these absorption bands. The peak assigned to OH stretching vibration was shifted to a lower wave number (from 3435.66 to 3427.99 cm^{-1}). Reinforcement at absorption band showed an increase in the intensity of stretching vibration of OH groups carried by the anion–anion exchanger. The peak assigned to water bending was shifted to a higher wave number. This was probably because part of water adsorbed by amorphous mineral was replaced by the phosphate anion. Reinforcement at the peaks located at 1032 and 533.91 cm^{-1} showed an increase in the intensity of P–O and O–P–O bending.

Conclusion

In this paper, an attempt has been made to use different salts addition (CaCl₂, NaCl, KCl) to predict the behavior of P adsorption in alkalize soil of the Kondar region. On the

basis of the results, it appears that P adsorption was rapid initially and gradually diminished to attain equilibrium after which there was no significant change in adsorption rates. The decline in the reaction rate may be caused by the formation of calcium phosphate coatings on the soil surface and the decline in the available surface area for adsorption. Moreover, it has been found that by addition of salts in solution, P adsorption significantly increased. Applications of three different kinetic equations to the data show that the rate of P adsorption was best predicted by the pseudo-second-order kinetic model. Infrared spectral characteristics of the amorphous material indicated that the reaction of amorphous clay with CaCl₂ salt caused a shift and an increase of OH, Si–O (Si–O–Si, Si–O–Al) and Al–OH absorption bands.

The results further showed that cation species (Na⁺, K⁺ and Ca²⁺) played a vital role in the fate of P in saline environments and will contribute to a more efficient management of P in relation to other ions.

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Compliance with ethical standards

Conflict of interest The present paper is an original work with no conflict of interest of any kind.

References

- Abel S, Ticconi CA, Delatorre CA (2002) Phosphate sensing in higher plants. *Physiol Plant* 115:1–8. doi:[10.1034/j.1399-3054.2002.1150101.x](https://doi.org/10.1034/j.1399-3054.2002.1150101.x)
- Andersen DS, Helmers MJ, Burns RT (2011) Phosphorus sorption capacity of six Iowa soils before and after five years of use as vegetative treatment areas. *Am Soc Agri Biol Eng. Michigan* <http://www.asabe.org>. Accessed 7–10 August 2011
- Arai Y, Sparks DL (2007) Phosphate reaction dynamics in soils and soil minerals: a multiscale approach. *Adv Agron* 94:135–179. doi:[10.1016/S0065-2113\(06\)94003-6](https://doi.org/10.1016/S0065-2113(06)94003-6)
- Baker JF, Andersen DS, Burns RT, Moody LB (2013) The Use of Phosphorus Sorption Isotherms to Project Vegetative Treatment Area Life. *Transactions of the ASABE*. doi:[10.13031/trans.56.9871](https://doi.org/10.13031/trans.56.9871). Accessed 2013
- Bhadha JH, Daroub SH, Lang TA (2012) Effect of kinetic control, soil: solution ratio, electrolyte cation, and others, on equilibrium phosphorus concentration. *Geoderma* 173:209–214. doi:[10.1016/j.geoderma.2011.12.027](https://doi.org/10.1016/j.geoderma.2011.12.027)
- Bolan NS, Syers JK, Tillman RW (1986) Ionic strength effects on surface charge and adsorption of phosphate and sulphate by soils. *J Soil Sci* 37:379–388
- Bolster CH, Sistani KR (2009) Sorption of phosphorus from swine, dairy and poultry manures. Publications from USDA-ARS/UNLV faculty. <http://digitalcommons.unl.edu/usdaarsfacpub/520>
- Bratieres K, Fletcher TD, Deletic A, Zinger Y (2008) Nutrient and sediment removal by storm water biofilters: a large-scale design

- optimisation study. *Water Res* 42:3930–3940. doi:[10.1016/j.watres.2008.06.009](https://doi.org/10.1016/j.watres.2008.06.009)
- Cartes P, Cea M, Jara A, Violante A, de la Luz Mora M (2015) Description of mutual interactions between silicon and phosphorus in Andisols by mathematical and mechanistic models. *Chemosphere* 131:164–170. doi:[10.1016/j.chemosphere.2015.02.059](https://doi.org/10.1016/j.chemosphere.2015.02.059)
- Chang NB, Hossain F, Wanielista M (2010) Filter media for nutrient removal in natural systems and built environments: I—Previous trends and perspectives. *Environ Eng Sci* 27:689–706. doi:[10.1089/ees.2009.0415](https://doi.org/10.1089/ees.2009.0415)
- Cho-ruk K, Morrison RJ (2004) Soil phosphorous adsorption and salinity influence. *Malaysian J Soil Sci* 8:1–11
- Cordell D, Drangert JO, White S (2009) The story of phosphorus: global food security and food for thought. *Glob Environ Change* 19:292–305. doi:[10.1016/j.gloenvcha.2008.10.009](https://doi.org/10.1016/j.gloenvcha.2008.10.009)
- Curtin D, Syers JK, Smillie GW (1987) The importance of exchangeable cations and resin-sink characteristics in the release of soil phosphorus. *J Soil Sci* 38:711–716. doi:[10.1111/j.1365-2389.1987.tb02168.x](https://doi.org/10.1111/j.1365-2389.1987.tb02168.x)
- Curtin D, Steppuhn H, Selles F (1993) Plant responses to sulfate and chloride salinity: growth and ionic relations. *Soil Sci Soc Am J* 57:1304–1310. doi:[10.2136/sssaj1993.03615995005700050024x](https://doi.org/10.2136/sssaj1993.03615995005700050024x)
- Dudal Y, Gérard F (2004) Accounting for natural organic matter in aqueous chemical equilibrium models: a review of the theories and applications. *Earth Sci Rev* 66:199–216. doi:[10.1016/j.earscirev.01.002](https://doi.org/10.1016/j.earscirev.01.002)
- Elser JJ, Bracken ME, Cleland EE, Gruner DS, Harpole WS, Hillebrand H, Nqai JT, Seabloom EW, Shurin JB, Smith JE (2007) Global analysis of nitrogen and phosphorus limitation of primary production in fresh water, marine and terrestrial ecosystems. *Ecol Lett* 10:1135–1142. doi:[10.1111/j.1461-0248.2007.01113.x](https://doi.org/10.1111/j.1461-0248.2007.01113.x)
- Garoma MD (1996) Biogeochemistry of phosphorus in the highland plateau soils of Ethiopia. North Carolina State University, Ph.D. Theses
- Gee GW, Bauder JW (1986) Particle size analysis. In: Klute A, editor. *Methods of soil analysis. Part 1*. Madison (WI): American Society of Agronomy and Soil Science Society of America; pp 383–411
- Goldberg S, Scalera E, Adamo P (2008) Molybdenum adsorption by volcanic Italian soil. *Commun Soil Sci Plant Anal* 39:693–706. doi:[10.1080/00103620701879281](https://doi.org/10.1080/00103620701879281)
- Hamdi W, Pelster D, Seffen M (2014) Phosphorus sorption kinetics in different types of alkaline soils. *Arch Agron Soil Sci* 60:577–586. doi:[10.1080/03650340.2013.830287](https://doi.org/10.1080/03650340.2013.830287)
- Hanudin E, Sukmawati ST, Radjagukguka B, Yuwono NW (2014) The Effect of humic acid and silicic acid on P adsorption by amorphous minerals. *Procedia Environ Sci* 20:402–409. doi:[10.1016/j.proenv.2014.03.051](https://doi.org/10.1016/j.proenv.2014.03.051)
- Harmsen J (2007) Measuring bioavailability: from a scientific approach to standard methods. *J Environ Qual* 36:1420–1428. doi:[10.2134/jeq2006.0492](https://doi.org/10.2134/jeq2006.0492)
- Hemmannuella CS, Fábio HT, Ignácio HS, Adailson PS, Valério DM (2011) Kinetics of phosphorus sorption in soils in the state of Paraíba. *R Bras Ci Solo* 35:1301–1310
- Hinsinger P (2001) Bioavailability of soil inorganic P in the rhizosphere as affected by root induced chemical changes: a review. *Plant Soil* 237:173–195. doi:[10.1023/A:1013351617532](https://doi.org/10.1023/A:1013351617532)
- Jing J, Rui Y, Zhang F, Rengel Z, Shen J (2010) Localized application of phosphorus and ammonium improves growth of maize seedlings by stimulating root proliferation and rhizosphere acidification. *Field Crops Res* 119:355–364. doi:[10.1016/j.fcr.2010.08.005](https://doi.org/10.1016/j.fcr.2010.08.005)
- Khan MS, Zaidi A, Ahemad M, Oves M, Wani PA (2010) Plant growth promotion by phosphate solubilizing fungi—current perspective. *Arch Agron Soil Sci* 56:73–98. doi:[10.1080/03650340902806469](https://doi.org/10.1080/03650340902806469)
- Large D, Muller K, Reiche I (2011) Analytical approach for the study of archaeological ivory elephant tusks from the site of Jinsha (1200–650 BC, Sichuan, China). *Archeo Sci* 35:167–177
- Li Y, Cai J, Song G, Ji J (2015) DRIFT spectroscopic study of diagenetic organic–clay interactions in argillaceous source rocks. *Spectrochim Acta Part A Mol Biomol Spectrosc* 148:138–145. doi:[10.1016/j.saa.2015.03.131](https://doi.org/10.1016/j.saa.2015.03.131)
- Madejova J, Komadel P (2001) Baseline studies of the clay minerals society source clays: infrared methods. *Clays Clay Miner* 49:410–432
- Mahmood A, Rahmatullah MS, Yousaf M (2000) Soil properties related to phosphorus sorption as described by modified Freundlich equation in some soils. *Int J Agric Biol* 2:290–302
- Martins MA, Santos C, Almeida MM, Costa ME (2008) Hydroxyapatite micro- and nanoparticles: nucleation and growth mechanisms in the presence of citrate species. *J Colloid Interface Sci* 318:210–216. doi:[10.1016/j.jcis.2007.10.008](https://doi.org/10.1016/j.jcis.2007.10.008)
- McKenzie RH, Bremer E, Kryzanowski L, Middleton AB, Solberg ED, Heaney D, Coy G, Harapiak J (2003) Yield benefit of phosphorus fertilizer for wheat, barley and canola in Alberta. *Can J Soil Sci* 83:431–441. doi:[10.4141/S02-078](https://doi.org/10.4141/S02-078)
- Mehlich A (1984) Mehlich3 soil test extractant: a modification of Mehlich 2 extractant. *Commun Soil Sci Plant Anal* 15:1409–1416
- Mihiri CW, Tee BG, Olalekan OA (2016) Response of Manitoba soils to banding phosphorus with sulfate or carbonate salts. *Can J Soil Sci* 96:447–460. doi:[10.1139/cjss-2015-0083](https://doi.org/10.1139/cjss-2015-0083)
- Morel C, Tunney H, Plénet D, Pellerin S (2000) Transfer of phosphate ions between soil and solution: perspectives in soil testing. *J Environ Qual* 29:50–59. doi:[10.2134/jeq2000.00472425002900010007x](https://doi.org/10.2134/jeq2000.00472425002900010007x)
- Morgan MA (1997) The behavior of soil and fertilizer phosphorus. In: *Phosphorus Loss from Soil to Water*. H. Tunney, O.T. Carton, P.C. Brookes, A.E. Johnston (eds.). Cab International, Wallingford, Oxon, UK, 137–150
- Mostafa SM (1999) Effect of fertilizers P, effluent P, and soil properties on P adsorption-desorption potentials and soil P fractions. Mississippi State University, Ph.D. theses
- Mtimet O (1999) Soils of Tunisia, Mediterranean options. Series B 34:246
- Nacry P, Canivenc G, Muller B, Azmi A, Van Onckelen H, Rossignol M, Doumas P (2005) A role for auxin redistribution in the responses of the root system architecture to phosphate starvation in Arabidopsis. *Plant Physiol* 138:2061–2074. doi:[10.1104/pp.105.060061](https://doi.org/10.1104/pp.105.060061)
- Olsen SR, Watanabe FS, Cole CV (1960) Phosphorus in calcareous soils as affected by neutral salts. *Transitional 7th International Congress of Soil Science* 2:397–403
- Rengel Z, Marschner P (2005) Nutrient availability and management in the rhizosphere: exploiting genotypic differences. *New Phytol* 168:305–312. doi:[10.1111/j.1469-8137.2005.01558.x](https://doi.org/10.1111/j.1469-8137.2005.01558.x)
- Rogers ME, Grieve CM, Shannon MC (2003) Plant growth and ion relations in lucerne (*Medicago sativa* L.) in response to the combined effects of NaCl and P. *Plant Soil* 253:187–194
- Rogers K, Saintilan N, Heijns H (2005) Mangrove encroachment of salt marsh in Western Port Bay, Victoria, the role of sedimentation, subsidence, and sea level rise. *Estuaries* 28:551–559
- Saikia BJ, Parthasarathy G (2010) Fourier transform infrared spectroscopic characterization of kaolinite from Assam and Meghalaya, Northeastern India. *J Mod Phys* 1:206–210. doi:[10.4236/jmp.2010.14031](https://doi.org/10.4236/jmp.2010.14031)
- Shaheen SM, Tsadilas CD, Eskridge KM (2009) Effect of common ions on phosphorus sorption and lability in Greek Alfisols with different pH. *Soil Sci* 174:21–26
- Shen J, Yuan L, Zhang J, Li Haigang, Bai Z, Chen X, Zhang W, Zhang F (2011) Phosphorus dynamics: from soil to plant. *Plant Physiol* 156:997–1005

- Suarez DL (1999) In Soil Physical Chemistry; Sparks, D. L., ed.; CRC Press: Boca Raton, 1999, ch. 3
- Vance CP, Uhde-Stone C, Allan DL (2003) Phosphorus acquisition and use: critical adaptations by plants for securing a nonrenewable resource. *New Phytol* 157:423–447. doi:[10.1046/j.1469-8137.2003.00695.x](https://doi.org/10.1046/j.1469-8137.2003.00695.x)
- Von Wandruszka R (2006a) Phosphorus retention in calcareous soils and the effect of organic matter on its mobility. *Geochemical Transactions* 7:6. doi:[10.1186/1467-4866-7-6](https://doi.org/10.1186/1467-4866-7-6)
- Walkley A, Black IA (1934a) An examination of Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid in soil analysis. *Soil Sci* 37:29–38
- Von Wandruszka R (2006b) Phosphorus retention in calcareous soils and the effect of organic matter on its mobility. *Geochemical Transactions* 7:6. doi:[10.1186/1467-4866-7-6](https://doi.org/10.1186/1467-4866-7-6)
- Walkley A, Black IA (1934b) An examination of Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid in soil analysis. *Soil Sci* 37:29–38
- Wang YP, Law RM, Pak B (2010) A global model of carbon, nitrogen and phosphorus cycles for the terrestrial biosphere. *Biogeosciences* 7:2261–2282. doi:[10.5194/bg-7-2261-2010](https://doi.org/10.5194/bg-7-2261-2010)
- Wang H, Zhu J, Fu Q, Hong C, Hu H, Violante A (2016) Phosphate adsorption on uncoated and humic acid-coated iron oxides. *J Soils Sediments*. doi:[10.1007/s11368-016-1383-8](https://doi.org/10.1007/s11368-016-1383-8)
- Watanabe FS, Olsen SR (1965) Test of an ascorbic acid method for determining phosphorus in water and NaHCO_3 extracts from soils. *Soil Sci Soc Am Proc* 29:677–678