

ANALYSIS OF PHOSPHATE ADSORPTION BASED ON ACID-BASE PROCESSES

FOSZFÁT ADSZORPCIÓ VIZSGÁLATA SAV-BÁZIS FOLYAMATOK ALAPJÁN

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Abstract

In our investigations - we developed a simple method to examine the surface ion exchange processes - where we could measure the amount of hydrogen and hydroxide ions leaving the surface of soil particles by bound phosphate ions. This type of analysis has been followed in the literature with a change in pH - which provides much less accurate results than the calculation of the surface ion balance. Soil samples were shaken with KH_2PO_4 solution in three replicates with P contents of 0 - 4 - 8 - 12 - 16 - 20 - 24 - 32 - 40 - 48 - 56 - 64 - 72 - 88 - and 100 mg/l. After two hours of shaking and centrifugation P content of samples was determined by photometry. The phosphorus concentration of the equilibrium solutions was used to determine the adsorption isotherm of soil phosphorus. The hydrogen ion content was determined from the separated equilibrium solutions and the original solutions used for adsorption using a high-sensitivity potentiometric titrator designed in our lab - with the addition of 0.01 M NaOH solution. The titration curves obtained for small amounts of dilute solutions - which are difficult to evaluate by other methods - were evaluated using a computer program developed in-house to determine the inflection points of the curve - i.e., the equivalence points. The missing amount of hydrogen ions from the solution was plotted as a function of the amount of phosphorus bound. Data shows that the change in the hydrogen ion content of KH_2PO_4 solution added to the soil - measured after equilibrium - is equal to three times the number of moles of phosphate ions bound. The slope of the fitted line was 0.35 and the correlation coefficient was 0.95. This means that each mole of phosphate bound is associated with the desorption process of three moles of OH^- ions or the equivalent of three moles of H^+ bound. Formally - this molar ratio expresses the binding of uncharged phosphoric acid molecules on the soil surface. Based on our measurements - several binding mechanisms for the binding of different hydrogen phosphate ions can be assumed under the given conditions. The findings indicate that some chemical reactions can be ruled out - although others could be established. During the adsorption of phosphate forms - only ion exchange reactions occur at the soil surface - which do not involve a change in surface charge - and the various hydrogen phosphate anions are exchanged for hydroxide ions.

Keywords: phosphate; adsorption isotherm; inflection point; surface-charge; ion exchange

Összefoglalás

Jelen tanulmányban egy egyszerű módszert dolgoztunk ki a felületi ioncsere-folyamatok vizsgálatára - ahol a talajrészecskék felületéről a megkötött foszfátionok által távozó hidrogén- és hidroxidionok mennyiségét tudtuk mérni. Ezt a fajta vizsgálatot a szakirodalomban pH-változással követték - ami sokkal kevésbé pontos eredményeket ad - mint a felületi ionmérleg számítása. A talajmintákat KH_2PO_4 oldattal rázattuk három ismétlésben 0 - 4 - 8 - 12 - 16 - 20 - 24 - 32 - 40 - 48 - 56 - 64 - 72 - 88 és 100 mg/l P-tartalommal. Két óra rázást követően a mintákat centrifugáltuk és a P-tartalmat fotometriás módszerrel határoztuk meg. Az egyensúlyi oldatok foszforkoncentrációját a talajfoszfor adszorpciós izotermájának meghatározására használtuk. Az elválasztott egyensúlyi oldatokból és az adszorpcióhoz használt eredeti oldatokból a hidrogénion-tartalmat a laboratóriumunkban tervezett nagy érzékenységgű potenciometriás titrátorral - 0,01 M NaOH oldat hozzáadásával határoztuk meg. A kis mennyiségű híg oldatokra kapott - más módszerekkel nehezen értékelhető titrálási görbéket egy saját fejlesztésű számítógépes programmal értékeltük ki a görbe inflexiós pontjainak - azaz az ekvivalenciapontoknak a meghatározására. Az oldatból hiányzó hidrogénionok mennyiségét a megkötött foszfor mennyiségének függvényében ábráztuk. Az adatok azt mutatják - hogy a talajhoz adott KH_2PO_4 -oldat hidrogénion-tartalmának az egyensúlyi állapot után mért változása a megkötött foszfátionok mólszámának háromszorosával egyenlő. Az illesztett egyenes meredeksége 0,35, a korrelációs együttható pedig 0,95 volt. Ez azt jelenti - hogy minden egyes mólnyi megkötött foszfáthoz három mólnyi OH⁻ ion deszorpciós folyamata vagy három mólnyi megkötött H⁺ -ionnak megfelelő mennyiség társul. Formálisan ez a molarány kifejezi a töltés nélküli foszforsavmolekulák kötődését a talajfelszínen. Méréseink alapján az adott körülmények között a különböző hidrogén-foszfátionok megkötésére többféle kötődési mechanizmus feltételezhető. Az eredmények azt mutatják - hogy egyes kémiai reakciók kizárhatók - bár mások megállapíthatók. A foszfátformák adszorpciója során a talajfelszínen csak ioncsere-reakciók játszódnak le - amelyek nem járnak felületi töltésváltozással - és a különböző hidrogén-foszfát anionok hidroxidionokra cserélődnek.

Kulcsszavak: foszfát - adszorpciós izoterma - inflexiós pont - felületi töltés - ioncsere

JEL kód: Q01

Introduction

Along with increased food production, agricultural production also increased, resulting in an increased demand for phosphorus in soils (CORDELL ET AL. 2009). The phosphorus content of soils is primarily affected by artificial fertilization and the application of organic fertilizers (DRASKOVITS 2013). Indeed, a significant proportion of the phosphorus applied is not available to the crops grown. Soils can absorb large amounts of phosphorus in a form that is less absorbable by plants (LOCH & NOSTICIZIUS 2004). Phosphorus adsorption depends on environmental factors such as pH (BOLT & VAN RIEMSDIJK 1987), lime content (decrease phosphate content by precipitation), (KRASSOVÁN ET AL. 2013) quality and quantity of soil colloids (clay, aluminum- and iron oxides, and organic matter) (BOHN ET AL. 1980).

The organic matter content of soils provides directly an adsorption site, while indirectly inhibiting the crystallization of iron oxides. Furthermore, at acidic pH solvated organic matter (fulvic and humic acid) decreased phosphate adsorption by iron oxides, which means organic matters compete with phosphate for adsorption sites (ASOMANING 2020).

Approximately 1 day after application, the adsorption equilibrium is reached and phosphorus is bound on the surface of layer silicates by ligand exchange, which is a quick non-specific

anion adsorption and anion exchange. Subsequently in specific adsorption occurs exchangeable or lattice positions cations precipitated with phosphorus (BOHN ET AL. 1980; ELGARHY ET AL. 2022).

Phosphorus-specific adsorption processes include binding by iron and aluminium (adsorbents). These (amorphous) adsorbents maintain large specific surface area (SSA). Furthermore, these sesquioxides have a high density of single-coordinated surface hydroxyls (SCHWERTMANN ET AL 1986). On the surfaces of the amphoteric Al-OH and Fe-OH minerals exposed reactive single-coordinated hydroxyl (OH⁻) groups, where the oxygen coordinated to a metal ion and depended on the pH protonated and deprotonated. The phosphate anions can exchange or replace these single-coordinated hydroxyl groups (BORGGAARD 1986).

Ion exchange on a solid surface is also determined by measuring pH of the equilibrium solution. Information is then obtained on changes in the concentration of hydrogen and hydroxide ions present in the shaking solutions (TOLNER ET AL. 1996).

Material

The sorption experiment was conducted on a WRB soil type: Eutric Arenosol (Aeolic - Aric - Orchic - Raptic) from the Szárítópuszta (GPS Coordinates: 47°34'41.9"N 19°22'54.7"E) site in Hungary. The main physical and chemical parameters of soil samples are summarized in Table 1.

Table 1. Properties of the experimental soil.

Parameters	Measured data (with standard deviation)	Test method with reference
pH _{H2O}	5.2±0.13	MSZ-08-0206-2-1978
pH _{KCl}	4.9±0.2	MSZ-08-0206-2-1978
CEC (cmol/kg)	10.5±0.9	MSZ-08-0215-2-1978
C (%)	0.8	MSZ-08-0452-1980
Clay (%)	5.6	MSZ-08-0205-1978
Sand (%)	44.4%	MSZ-08-0205-1978
Silt (%)	50%	MSZ-08-0205-1978
CaCO ₃ (%)	0.0%	MSZ-08-0206-2-1978

Methods

The soil samples were shaken for 2 hours with an adequate concentration solution of KH₂PO₄ before being left to stand overnight at 25 °C for equilibration. Phosphorus concentrations ranged from 0 to 4 - 8 - 12 - 16 - 20 - 24 - 32 - 40 - 48 - 56 - 64 - 72 - 88 - and 100 mg/l. Centrifugation (5 minutes to 3000 rpm) and filtration (Whatman No.42 filter paper (0.25 µm)) were used to separate the equilibrium phases. The phosphorus concentrations were determined based on Egner et al (1960) (the test was carried out with sulphuric acid ammonium molybdenate and ascorbic acid tin chloride). Following that - equilibrium phases and original phosphorous-containing solutions were titrated (0.05 ml accuracy) with 0.01 mol/l NaOH solution and measured with a pH meter equipped with a glass electrode. Each solution form was repeated three times - and the results were statistically analyzed. Determined of the H⁺ ion concentration based on inflection points of the titration curves.

The Langmuir adsorption isotherm was used to analyse data on equilibrium phases and original phosphorus content solutions. Phosphorus adsorption is best characterised by the Freundlich isotherm. In general, phosphorus adsorption studies not only involve adsorption, but also the formation of polyphosphates, which cause the adsorption curve to be non-asymptotic. In the present experiment, it can be seen from the data obtained that the formation of polyphosphates was presumably not produced during the adsorption experiment, so that the Langmuir isotherm was a better fit to the data. The isotherm and other calculations were performed using ORIGIN software (Ver. 6. - 2022).

Results

The data reported in Figure 1 and Table 2 indicate that there was a linear relationship between the concentration of KH_2PO_4 and the H^+ ion content of the shaking solutions - this relationship was described by plotting the measured H^+ concentration (mmol/l) against the calculated H^+ concentration with an R-value of 0.99954.

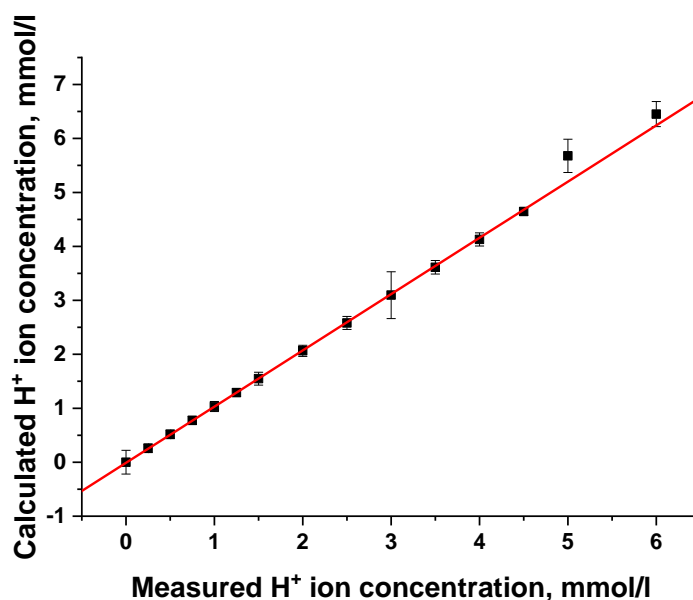


Figure 1. Relationship between calculated and measured H^+ concentration of KH_2PO_4 solutions

Table 2. Parameters of the linear relationship between calculated and measured H^+ ion concentration.

Linear equation	$A + B x$
A	-0.01222 ± 0.02173
B	1.0425 ± 0.0088
R	0.99954
SD	0.52472
P	<0.0001

This indicates that the ratio of P to hydrogen ion mole was 1:2 as calculated stoichiometrically. Therefore - Figure 1 shows that - in the equilibrium system there was no other H^+ ion source.

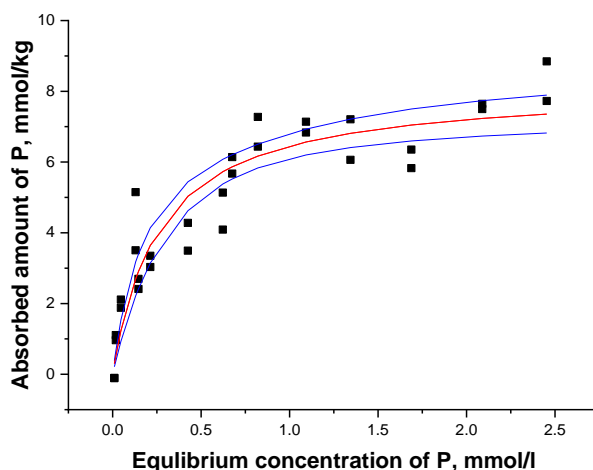


Figure 2. Soil P adsorption isotherm with 95% confidence interval (blue line).

Table 3. Parameters of the fitted Langmuir isotherm - where A = maximum adsorption of per unit mass; k = distribution coefficient.

Fitted equation (Langmuir)	$y = \frac{A k x}{1 + k x}$
R ²	0.86287
Chi ²	0.88304
A	8.14535 ± 0.40886
k	3.8031 ± 0.72136
RMSE	0.210456

The amount of H⁺ ions missing from the solution was then plotted as a function of the amount of phosphorus bound (Figure 2).

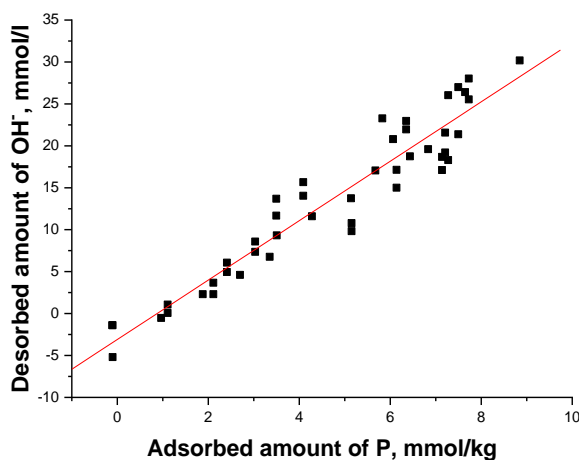


Figure 3. Correlation between adsorbed P and desorbed OH⁻ averaged over three measurements.

Table 4. Parameters of the relationship between adsorbed P and desorbed OH ion

Linear equation	A + B x
A	-3.09681± 0.87646
B	3.54294± 0.16568
R	0.95606
SD	2.75696
P	<0.0001

Data presented (in Figure 3 and Table 4) show that the change in the hydrogen ion content of KH_2PO_4 solution (added to the soil after equilibrium) is equal to three times the moles of phosphate ions bound. This result was similar to the calculation by Tolner and Füleky in 1995. The slope of the fitted line was 0.35 and the correlation coefficient was 0.95. This means that each mole of phosphate bound is associated with desorption of three moles of OH^- ions - or the equivalent of three moles of H^+ bound. This molar ratio expresses the binding of uncharged phosphoric acid molecules on the soil surface in formal terms.

As might be expected - this does not express the actual mechanism of the reaction - but only that there is no gross change of charge on the surface during adsorption. Since the concentration of undissociated phosphoric acid in the solution is very low - as is its adsorption capacity, it can be assumed that ion exchange processes occur at the surface where the phosphate-hydrogen ion balance is measured.

Explanation of the phenomenon

To explain the measured phenomenon - the following processes can be hypothesized - and the ions or molecules present in the shaking solution are indicated below:



Depending on the pH - the four phosphate forms - as well as the hydrogen and hydroxide ions contents of the solution - are in dynamic equilibrium with each other - and the equilibrium is shifted towards the formation of PO_4^{3-} ions by the addition of alkali during the titration used. The amount of NaOH consumed during the titration is equal to the total hydrogen ion content of the solution - which can derive from both hydrogen phosphates and previously from the soil surface. Thus - by this method - the total hydrogen ions in solution can be measured either in the free form or in the phosphate-bound form as it was originally. Because of the shift in the pyrophosphate-dihydro phosphate equilibrium measured during titration - it can be seen that the phosphorus/hydrogen ion ratio is irrelevant which form of hydrogen phosphate is used to write down the reaction equations.

As shown in the diagram (Figure 4) - there are several adsorption processes take place on the soil surface. One of these processes is the specific binding of the soil by chemisorption. This is the process by which phosphate ion, hydroxide ion etc. are bound to the surface of the soil particles. (Figure 4. right side). On the other hand - molecules for example hydrogen phosphate ion and dihydrogen phosphate ion with a charge can bind reversibly to soil particles with the opposite charge in a non-specific way (Figure 4. left side).

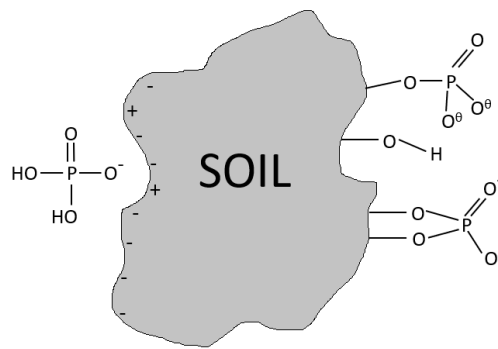
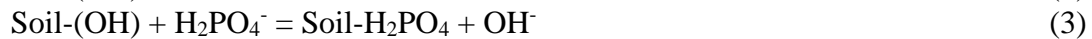
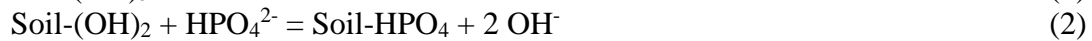


Figure 4. Schematic diagram of the adsorption process on the surface of soil particles

Source: A. B. Dálnoki by I. Czinkota

During adsorption - the following processes are expected to occur - in which solution constituents become bound to the surfaces of soil particles.

The primary adsorption processes according to the reactions shown in the equations, which described similarly by Syers et al 1983.



In all three cases - the following reactions are possible:

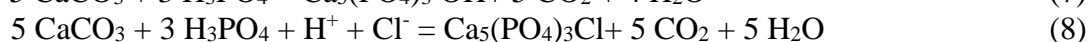


In the first reaction - three water molecules are formed - in the second reaction - two - in the third reaction - one - and in the fifth reaction - no water molecules are formed - resulting in a loss of three hydrogen ions in the liquid phase for each bound P-mole in all cases - together with the hydrogen ions bound on the solid phase. The number of moles of hydrogen ions in solution in the preceding cases is only three times the number of moles of phosphorus bound. The most likely reactions under the given conditions are 2 and 3 - but this can't be proven by this experiment - because the four phosphate forms can freely transform into each other in solution without changing the total number of hydrogen ions. Case 5 has a very low probability of occurring in an extremely acidic medium when the surface is saturated with H⁺ ions.

According to the experiment - if the soil contains lime - the following reactions are also possible:

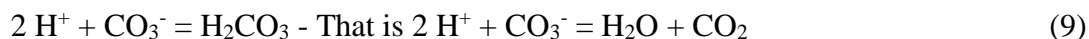


This reaction can occur with all phosphate forms - and the formation of hydroxyl apatite cannot be excluded; however - the formation of halogen apatite does not provide the measured hydrogen ion/phosphorus ratio.

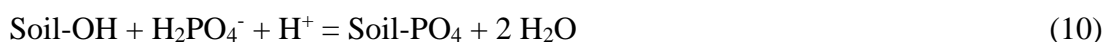


Descriptions of these reaction (6-8) are similar to the study by Siebielec et al. 2014.

According to Equation 8 - more hydrogen ions than the stoichiometric 1/3 ratio are used in the process. The accompanying equilibrium reaction is shown here:



Up to this point - the measurements indicate that this reaction is unlikely to occur - as the titration curve does not show a step characteristic of carbonates - but this can only be proven by measuring more concentrated solutions.



Furthermore - the measurements show that there is no barrier to the formation of polymer phosphate forms on the soil's surface.

Based on the experiment, by ion exchange reactions, OH^- and CO_3^{2-} (the final reaction product of which is CO_2 gas) ions are desorbed so that the next reaction does not take place in the soil.



There can be no binding reactions where the surface charge of the soil changes for instance:



In both of these cases - the adsorbed phosphorus carries only two hydrogen ions to the solid phase surface.

Conclusion

Based on the results of our tests, the method described in this study able to measure the concentration of H^+ and OH^- ions leaving the surface by ion exchange processes with high accuracy, which can be used to estimate the phosphorus binding capacity of soils.

The method can also be used for other soils, as in principle adsorption is not affected by soil type, but our experiments were carried out on only one soil, as a consequence further research is needed.

The results suggest that some types of chemical reactions can be excluded - while others can be confirmed. It can be concluded that in all cases - only ion exchange reactions take place at the soil surface during the adsorption of phosphate forms that do not involve a change in surface charge - and the different hydrogen phosphate anions are exchanged for hydroxide ions.

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