

Phosphorus sorption by gyttja and its effect on the pH value and phosphorus in acidic soils

Kadir SALTALI* , Ahmet NEDİRLİ 

Department of Soil Science and Plant Nutrition, Faculty of Agriculture, Kahramanmaraş Sütçü İmam University, Kahramanmaraş, Turkey

Received: 19.10.2020 • Accepted/Published Online: 26.05.2021 • Final Version: 18.08.2021

Abstract: Tea and hazelnut cultivated soils are mainly distributed in Black Sea region of Turkey. Low pH value is a primary problem for those soils; therefore, farmers apply lime once every 3–4 years to raise the pH value of soil. Gyttja is highly rich in organic matter (40.59%) and lime (45.67%), and it is a low cost and considerably abundant in Afşin-Elbistan Coal Basin (estimated reserve is around 4.8 billion tons). The aim of this study was to determine the phosphorus (P) sorption characteristics of gyttja, and its efficiency on P availability and soil's pH value. Optimum P sorption conditions (pH, temperature, particle size, amount of sorbent and shaking time) and maximum sorption capacity (b) for gyttja were determined in laboratory condition. Phosphorus was sorbed to gyttja (G_1P_1) based on its b value, and the experiment was set as pot experiment according to a completely randomized factorial experimental design with five replications. Applications were control (G_0P_0), gyttja + P_0 (G_1P_0), sole P (G_0P_1), and gyttja + P (G_1P_1). The b value obtained from Langmuir isotherm for gyttja was found as 1.59 mgg^{-1} . The highest available P was obtained at treatment of (G_1P_1). Also, the treatment G_1P_1 was significantly different ($p < 0.01$) from the rest of the treatments. Gyttja application increased soil's pH value from 4.86 to 5.74 in a 6-month time period. Therefore, gyttja can be recommended for amending soil acidity and increasing available P contents in acid soils. Further studies should be conducted in field conditions to increase applicability of the results.

Key words: Acidic soil, gyttja, phosphorus, pH, sorption

1. Introduction

Hazelnut and tea cultivation in Turkey is carried out in Black Sea region. The pH value of 18% of soils in the Black Sea region is 5.5–6.5, of 12% is 4.5–5.5, and of 4% is below 4.5 (Eyüpoğlu, 1999). Farmers apply lime every 3–4 years to increase both pH value of acid soils and plant nutrients availability. Phosphorus (P) is one of the essential macro nutrients for optimum growth and development in plants. The P is involved in numerous physiological and biochemical reactions occurring in the plant and constitutes approximately 0.2% of the dry weight of the plant (Theodorou and Plaxton, 1993).

Phosphorous (P) fertilizers applied to soils with low soil's pH value react with Fe, Al, and Mn cations and colloidal Fe, Al, and Mn oxide and hydroxide compounds, forming P compounds such as Al (OH) $2H_2PO_4$ and Fe (OH) $2H_2PO_4$ that cannot have been taken in by plants (Frossard et al., 2002).

Lime is generally used for amending acid soils. If it is economical, organic materials can also be used in the amending of acid soils. Organic materials such as animal manure, green fertilization, compost, biochar adsorb H, Fe, Al, and Mn ions and compounds in acid soils and the concentration of these ions in the soil solution decrease.

This causes an increase in soil's pH value and, hence, the available P concentration in the soil also increases (Misra, 1995; Yusran 2010).

Acid soils should be amended to optimize soil's pH value for hazelnut and to reduce the reaction of applied P fertilizers with Fe, Al and Mn compounds. In general, the hazelnut producers in the Black Sea region apply lime in every 3–4 year to increase soil's pH value to a reasonable level (6.0–6.5). In many cases, the relatively high cost of lime makes it an important hazelnut production input for producers.

One of the alternative materials that can be used in the rehabilitation of acid soils is gyttja. It is an organomineral material and it comprises organic matter (35%–50%) and lime (30%–40%) (Saltalı and Korkmaz, 2015). First described by the Swedish scientist Hampust von Post in 1862, gyttja was defined as a deposit of chitin remains of insect skeletons, mollusc shells, organic particles of plant residues, and a mixture of inorganic particles ranging in color from grey to blackish and brown. Gyttja, as stated by many researchers, is also defined as sedimentary deposits, which are eutrophic due to the abundance of plants during rainy periods. The deposits are formed by the sedimentation of decayed materials in oxygen limited

* Correspondence: kadirs@ksu.edu.tr

conditions at the bottom of a lake. Organic matter of the deposits, which contains the shells of abundant aquatic creatures, is easily recognized (Myslinska, 2003; Lachacz et al., 2009)

There are approximately 1.8 billion tons of gyttja reserves that can be used for agricultural purposes in A and B power plants (units) in the Afşin - Elbistan Coal Basin (Yörükoğlu, 1991; Gökmen et al., 1993). Upon C, D and E units opening for lignite production, the gyttja reserve will be 4.8 billion tons (Kadioğlu et al., 2015). On the other hand, its high organic matter and lime contents make it possible to use gyttja as a soil conditioner in acid soils (Karaca et al., 2006; Saltalı and Korkmaz, 2015). Functional groups (- OH and - NH₂) of organic matter can form a positive charge as protone [(R -OH₂)⁺ and R - (NH₃)⁺] under low pH conditions, and these positive charges can adsorb negatively charged orthophosphate anion (H₂PO₄)⁻ in acid soils (Misra, 1995).

To obtain the lignite coal to be used the Afşin - Elbistan Thermal Power Plant, it is necessary to remove the approximately 10 m thick soil and the parent material, followed by the 10–15 meters thick gyttja material above the lignite layer. The excavated gyttja is often used to refill the mining pits. Currently, the approximate selling price of gyttja is 2.5 \$ ton⁻¹. Therefore, it can be considered as a low cost material.

Phosphorus sorption characteristics of gyttja and the effect on available P content of gyttja and P mixing in acidic soil conditions have not been studied to date. The aim of this study was to determine P sorption characteristics of the Afşin - Elbistan's gyttja and to evaluate soil's pH value and available P contents in acid soils for its usability as low cost materials.

2. Material and methods

2.1. Materials

Acidic soils taken from the Black Sea region (Perşembe, Ordu City) and a gyttja taken from Afşin - Elbistan Coal Basin were used in this study. Some physical and chemical

properties of the acidic soil are given in Table 1, and those of the gyttja are given in Table 2.

The pH value, organic matter and lime contents of the gyttja area is 7.18, 40.6% and 45.7%, respectively. The gyttja is composed of two layers: a grey layer comprising approximately %75 lime and less than 10% of organic matter and a brown black layer comprising over 60% of organic matter (Figure 1a). The materials from the both of the layers are mixed when excavated with large excavators. A mixture of gyttja after excavated was used in the experiment (Figure 1b).

2.2. Methods

2.2.1. Determination of phosphorus (P) sorption properties of gyttja

The gyttja brought from Afşin - Elbistan Thermal Power Plant was pounded in porcelain mortars and passed through 0.42 mm, 1 mm, and 2 mm sieves. A series of preliminary studies were carried out to determine the optimum sorption conditions of the gyttja. Therefore, effects of particle size (0.42 mm, 1 mm, and 2 mm), sorbent amount (5, 10, 20, 30, 40 and 50 gL⁻¹), solution's pH value (3, 4, 5, 6, 7, 8 and 9), the shaking time (equilibrium time; 0.5, 1, 2, 4, 8, 12 and 24 h), and temperature (20, 30, 40 and 50 °C) were investigated.

A P solution of 100 mgL⁻¹ was prepared, solving KH₂PO₄ in 0.01 M CaCl₂, to determine a proper combination of particle size, pH value, shaking duration, and temperature to achieve optimum P sorption by the gyttja. Phosphorous sorption of the gyttja were characterized by batch experiments. After determining the optimum conditions for P sorption for the gyttja, series of sorption isotherms were determined with different solution P concentrations, in 0–600 P mgL⁻¹ concentration range, using the same batch experiments.

In the experiments carried out the optimum conditions for isotherms, the P solution and sorbents placed in polyethylene bottles were shaken in a shaker at 200 rpm for 12 h, and the solution was filtered with Whatman filter (No.42) paper. The sorbed P was calculated from

Table 1. Some chemical and physical properties of the experimental soil.

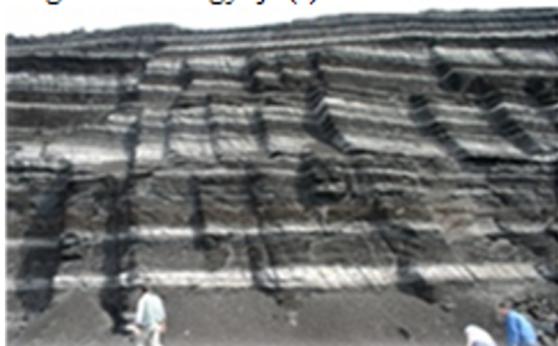
pH (1/2.5)	O.M ...	Lime ...	Sand %	Loam ...	Clay ...	CEC Cmolkg ⁻¹	P ...	K ...	Na mgkg ⁻¹	Ca ...	Mg ...
4.86	2.05	0.79	29	49	22	25	7	30	17	642	256

O.M: organic matter

Table 2. Analysis results of the gyttja material.

pH (1/2.5)	EC dSm ⁻¹	Organic P mgkg ⁻¹	Inorganic P mgkg ⁻¹	O.M	Lime %	Total N ...
7.18	2.61	7	10	40.59	45.67	0.25

Original view of gyttja (a)



After excavation view of gyttja (b)



Figure 1. Original (a) and after excavation (b) views of the gyttja used in the experiment (Saltalı and Korkmaz, 2015).

the difference between the initial and equilibrium concentrations using the following equations (Equations 1 and 2).

$$q_e = \frac{(C_o - C_e)V}{g} \quad (1)$$

$$\text{Sorption (\%)} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

where, q_e is the amount of P sorbed (mgg^{-1}) by gyttja, C_o and C_e are the initial and equilibrium P concentration in solution (mgkg^{-1}), respectively, V is solution volume (L) and m is weight (g) of the gyttja used in the experiment.

Coefficients for P sorption energy and maximum P sorption capacity (b) of the gyttja were determined using a linear Langmuir isotherm. Commonly used linear form of Langmuir (Langmuir, 1918) is given in equation 3.

$$\frac{C_e}{q_e} = \frac{1}{kb} + \frac{C_e}{b} \quad (3)$$

where, C_e is the equilibrium concentration P (mgL^{-1}), q_e is the amount of P sorbed by the gyttja (mgg^{-1}), b is the maximum sorption capacity (mgg^{-1}), and k is the sorption energy coefficient (sorption affinity) (Lmg^{-1}). Also, the sorption type (physical or chemical sorption) of P sorbed by the gyttja was determined using the linear shape (Eq. 4) of the Dubinin-Redushkevich (DR) isotherm (Dubinin et al., 1947; Ho et al., 2002; Donat et al., 2005; Saltalı et al., 2007).

2.2.2. Pot trials

In the experiment, acid soil (pH: 4.86) taken from the district of Perşembe of Ordu province and the gyttja from the coal basin of Afşin-Elbistan Thermal Power Plant were used. The b value (1.59 mgg^{-1}) of the gyttja was calculated from graph slope by using the Langmuir isotherm. Annual P_2O_5 requirement of hazelnut is approximately 75 kg ha^{-1} (Ergin, 2019). From this point of view, the gyttja amount that needed to adsorb P fertilizers applied to the hazelnut

annually ($75 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$) was calculated. There are usually 500 hazelnut plants on per hectare (Ergin, 2019). It has been determined that 40 kg of gyttja would be applied to each hazelnut bush. Accordingly, the amount of gyttja to be mixed in each pot was calculated as 24 g (the pot contains 3 kg of soil). Then, according to the annual P requirement of the hazelnut ($75 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$), the amount of P needed 3 kg of soil placed in a pot was calculated as 39 mg. To uniformly apply the amount of P needed for a pot, KH_2PO_4 was dissolved in purified water and homogeneously mixed with gyttja and the mixture was dried in room conditions. The gyttja-P mixture was mixed with the experimental soils and then used in experiments. The experiment was set up with five (5) replications according to the factorial trial in random plots. The treatments were control (G_0P_0), sole gyttja (G_1P_0), sole P (G_0P_1) and gyttja-P mixture (G_1P_1). At the beginning of the experiment, each pot has been set to field capacity and the water content of experimental soils were adjusted to field capacity when needed. The samples were taken on the 5th, 10th, 15th, 30th, 60th, 90th, 120th, 150th and 180th days, and the available P content and pH in the soils were determined.

2.2.3. Soil and gyttja analyses

Soil texture was determined with a Bouyoucos hydrometer (Bouyoucos (1951), pH and EC (dSm^{-1}) with glass electrodes in saturation paste. Lime (CaCO_3) was measured with a Scheibler calcimeter (Allison and Moodie 1965). Determination of cation exchange capacity (CEC) in soil samples was carried out as reported by Bower et al. (1952). Organic matter content was measured according to the modified Walkley-Black method (Nelson and Sommers, 1996). P content of the gyttja was determined by Olsen method (Olsen et al., 1954). Available P contents in the soil-gyttja mixtures were determined according to the method specified by Bray and Kurtz No: 1 (1945), as soil's pH value of the mixtures was less than 6. Extractable potassium, calcium, magnesium, and sodium were measured by the method of the ammonium acetate (Helmke and Sparks, 1996).

2.2.4. Statistical analysis

Analysis of variance (ANOVA) was performed on the data obtained in the study. Data were evaluated with COSTAT and MSTATC package programs. The statistical analysis of the pH-change in the soils was performed by Mann-Whitney Test in SPSS package program. A null hypothesis was rejected at the significance level of 0.05 unless specified otherwise.

3. Results and discussion

3.1. Effect of particle size on phosphorus sorption of gytija

To find the optimum conditions for P sorption capacity of the gytija samples, the effect of particle-size of the gytija was first examined. As the particle-size of gytija becomes smaller, the P sorption of gytija increases as seen in Figure 2, which can be attributed to that a decrease in particle-size of the gytija results in an increase in its surface area. A greater surface area stimulates P sorption of gytija. The greatest P sorption was obtained in 0.42 mm (29.42%) particle size. Therefore, particle-size of 0.42 mm was kept identical in the rest of the experiments.

3.2. Effect of pH value on phosphorus sorption of gytija

Solution's pH value affects the anion and cation retention of the sorbents. We determined solution pH and P sorption

relations in the gytija (Figure 3). P sorption increased with increasing pH value, and maximum P adsorption occurred at pH = 9. At pH values > 9.0, P may precipitate as Ca-P compounds in the soil. High lime content of the gytija (45.67%) may enhance the precipitation of P. Also, P becomes unavailable for plants in acid soils (pH = 4.5–6.0) as it reacts with cations such as Fe, Al, Mn or their hydroxides. In calcareous-alkaline soils, P reacts with Ca and CaCO_3 and it undergoes fixation, decreasing P availability to plants (Samadi and Gilkes, 1999).

In sorption studies, crystallization or precipitation of the sorbent with the sorbed ion is not desirable. In the P sorption experiments, KH_2PO_4 was used as the P source to reduce the probability of P precipitation during mixing with the P solution with the gytija. The solution (0.44 g L^{-1}) pH of KH_2PO_4 was 6.12. Therefore, the solution's pH value was set to 6.12 in the rest of the experiments.

3.3. Temperature effect on phosphorus sorption of gytija

Temperature is one of the key factors, affecting extent of ion sorption by gytija. Temperature effect on P sorption of gytija was evaluated at different temperatures (20, 30, 40 and 50 °C) (Figure 4). The results evidenced that increasing temperature increased the P sorption and desorption of soils. Similarly, it was reported that sorption

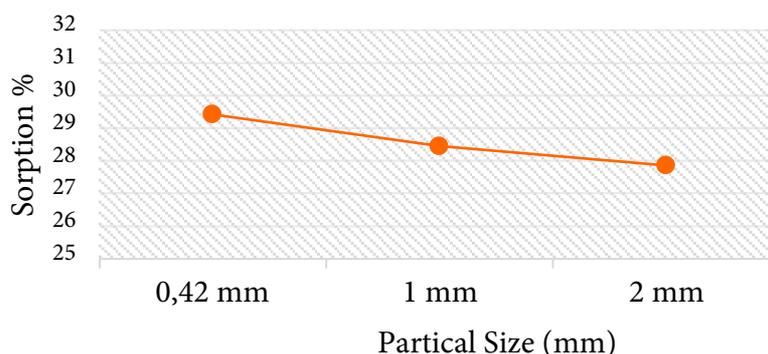


Figure 2. The effect of particle size on P sorption (C_0 ; 100 mg L^{-1} , shaking time; 4 hours, amount of sorbent; $1 \text{ g} / 30 \text{ mL}$, temperature; $21 \pm 2 \text{ }^\circ\text{C}$, pH = 6.12)

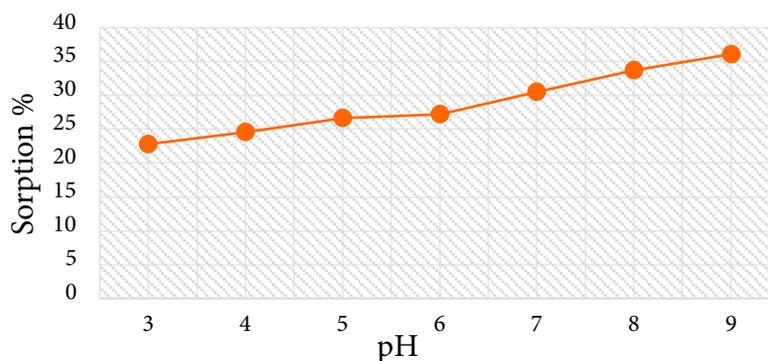


Figure 3. The effect of pH on P sorption (C_0 ; 100 mg L^{-1} , shaking time; 4 h, amount of sorbent; $1 \text{ g} / 30 \text{ mL}$, temperature; $21 \pm 2 \text{ }^\circ\text{C}$, particle size; 0.42 mm)

and desorption of P increased as temperature increased (Singh and Jones., 1976). However, in terms of application and practicality, it was deemed appropriate to carry out the sorption study at laboratory temperature (21 ± 2 °C), since increasing the temperature of the solution in such studies will bring additional costs.

3.4. Effect of shaking time on the phosphorus sorption of gytija

Longevity of shaking or contact time affects the amount sorbed by a sorbent. The effect of shaking time on the P sorption of the gytija is given in Figure 5, which depicts that increasing shaking time up to 4 h had no significant effect on percent P sorption. However, percent P sorption increased rapidly from 4 h to 12 h. P sorption was 29.1% for shaking time of 12 h and 29.5% for 24 h. Since the shaking (equilibrium) time is 0.4% sorption difference between 12 and 24 h, the 12-h shaking time was chosen as optimum shaking time to save time and cost.

3.5. Effect of solution concentration on phosphorus sorption of gytija

The solution P concentrations and sorption values depicted that sorption is high at low solution concentrations and

decreases as the solution concentration increases (Figure 6). Moreover, after P solution concentration 300 mgL^{-1} , sorption starts to increase again. This increase may be attributed to precipitation reactions rather than sorption at high concentrations. It was reported that there may be crystallization and precipitation processes rather than adsorption in soils with high lime content and high solution concentrations (Derici et al., 1995).

3.5. Sorption isotherms

Langmuir isotherm is the most commonly used model in evaluation of adsorption of an adsorptive by sorbent in equilibrium conditions (Veith and Sposito, 1977; Ho et al., 2002). With the Langmuir isotherm, the maximum sorption capacity (b) value of the sorbent can also be determined. Therefore, determining the b value of the gytija for P is important in practice. In this study, linear Langmuir adsorption model was used to evaluate the experimental data.

Results are shown in Figure 7, which depicts that R^2 value for the fit is 0.95, suggesting that the linear Langmuir model described the experimental data successfully. The b value calculated using the slope of the graph was 1.59 mgg^{-1} .

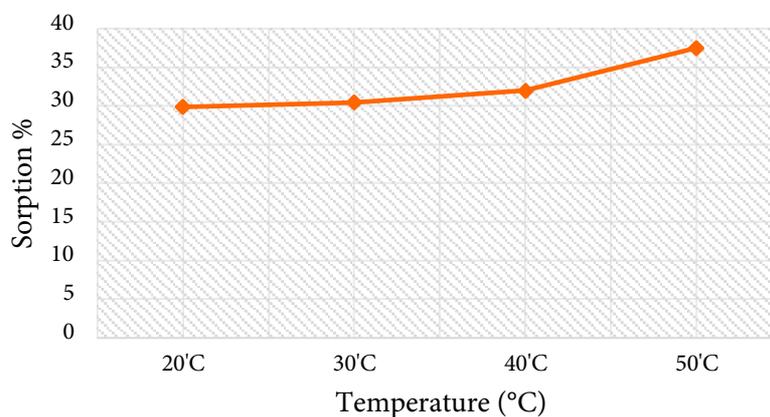


Figure 4. The effect of temperature on P sorption (C_0 ; 100 mg L^{-1} , shaking time; 4 h, sorbent amount; 1 g / 30 mL, particle size; 0.42 mm, pH = 6.12).

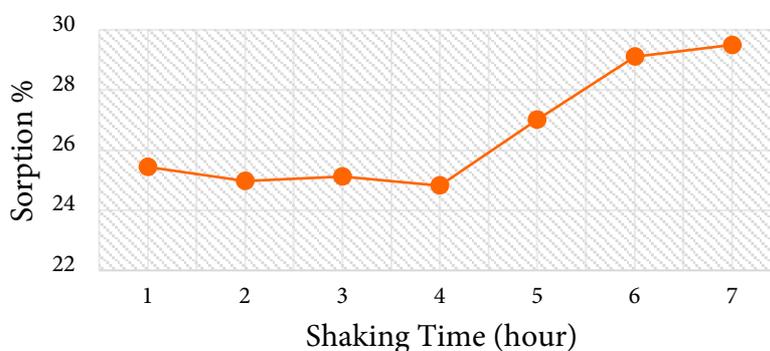


Figure 5. The effect of shaking time on P sorption (C_0 ; 100 mg L^{-1} , sorbent amount; 1 g / 30 mL, temperature; 21 ± 2 °C, particle size; 0.42 mm, pH = 6.12).

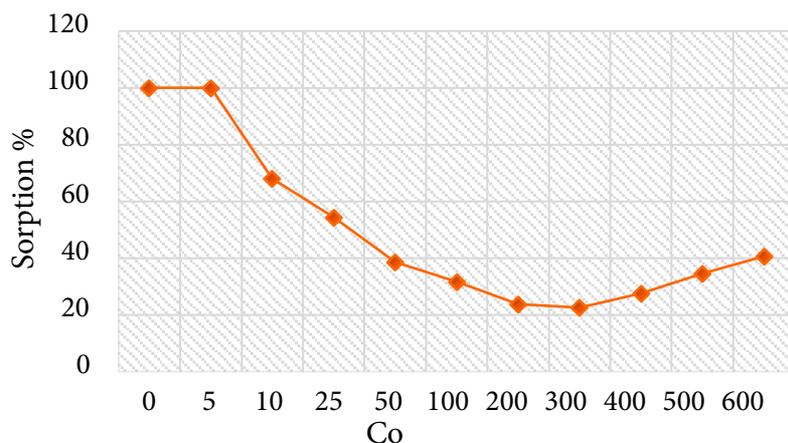


Figure 6. The effect of solution concentration on P sorption (Sorbent amount; 1 g / 30 mL, temperature; 21 ± 2 °C, particle size; 0.42 mm, shaking time; 12 h, pH = 6.12)

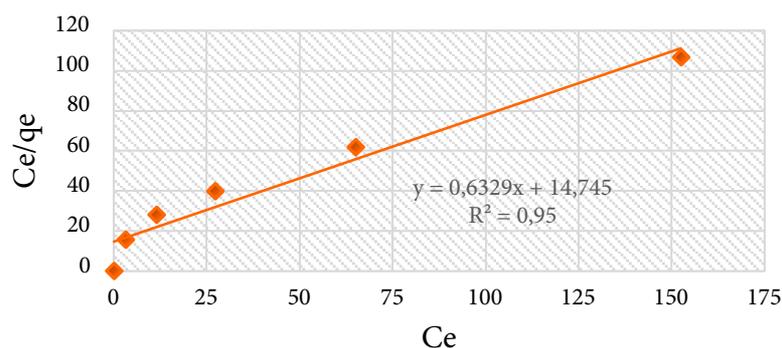


Figure 7. Phosphorus sorption of gyttja according to the Langmuir isotherm (Sorbent amount; 1 g / 30 ml, temperature; 21 ± 2 °C, particle size; 0.42 mm, shaking time; 12 hours, pH; 6.12)

The same b value was used to determine the amount of P to be sorbed by the gyttja. Similarly, the Langmuir k coefficient (sorption affinity or sorption energy coefficient), calculated using the intercept of the graph, was 0.043 Lmg^{-1} . Wolde and Haile (2015) used Langmuir isotherm to model fertilizer P sorption of soils, they concluded that the linear Langmuir model successfully described the experimental data ($R^2 = 0.93$). In a study (Yu et al., 2013) conducted to evaluate effect of different organic materials on P adsorption, it was reported that experimental data were generally compatible with the Langmuir isotherm.

We evaluated chemical and physical binding state of P sorption by using a linear form of the Dubinin-Redushkevich (D-R) isotherm as seen equation 4 (Dubinin et al., 1947; Gonzales-Paradas et al., 1994).

$$\ln(q_c) = \ln(q_m) - \beta \epsilon^2 \quad (4)$$

Where q_c is the amount of P sorbed by gyttja (mol^{-1}), q_m is theoretically the sorption capacity (molg^{-1}), β is the sorption energy constant ($\text{mol}^2\text{J}^{-2}$) (Dubinin et al., 1947; Ho et al., 2002). As seen in Figure 8, the slope of the line

obtained by plotting $\ln q_c$ against ϵ^2 was found to be the constant β ($-7 \times 10^{-9} \text{ mol}^2\text{J}^{-2}$), and q_m was calculated from the intercept of the line and found $1.80 \times 10^{-4} \text{ molg}^{-1}$.

Polanyi potential (ϵ) was calculated using equation 5.

$$\epsilon = RT \ln \left(1 + 1 / C_e \right) \quad (5)$$

where R is the gas constant ($\text{J mol}^{-1}\text{K}^{-1}$), T is the temperature (K), and C_e is the equilibrium constant of P. Sorption energy (E) can be calculated using the D-R parameters using equation 6 (Gonzales-Parodos et al., 1994; Ho et al., 2002; Donat et al., 2005).

$$E = \frac{1}{\sqrt{-2\beta}} \quad (6)$$

An E value gives information about chemical and physical sorption. The E value ranges between 1 and 8 kJmol^{-1} for physical sorption and 8 and 16 kJmol^{-1} for chemical sorption (Gonzales-Parodos et al., 1994; Ho et al., 2002; Saltali et al., 2007). In this study the E value of for gyttja was 8.45 kJmol^{-1} . The data obtained are very close to the limit values of physical and chemical sorption.

Therefore, it can be concluded that both of physical and chemical sorption mechanisms are important in P sorption by gytija.

3.6. Incubation experiment

The pH value readings performed in study acid soils (treatment of G_0P_0) at the start and the end of the incubation experiment. It was observed that the pH value was 4.86 and did not change during the incubation. In soils where gytija and P (G_1P_1) are mixed, the initial soil's pH value increased from 4.86 to 5.47, 5.58, 5.64, 5.73 and 5.74 on the 30th, 60th, 90th, 120th and 180th days, respectively. The difference between the initial pH value of the soils (4.86) and the pH value of the G_1P_1 (5.74) was statistically significant ($p < 0.05$). Therefore, the results suggested that the application of gytija increased the pH value of study acidic soils. Similar to our results, Ergin (2019) found that a soil's pH value of 5.1 increased to 6.1 after one year and to 5.9 following two years of 20 tonha⁻¹ in hazelnut orchards.

We obtained a gytija P mixture using the P as much as Langmuir to value (1.56 mgkg), applied the mixture to study soils. Accordingly, gytija and P application to the soil

and the change and statistical evaluation of the available P in the soil depending on the time are shown in Table 3. As seen in Table 3 that the available P content decreases depending on time and it is obtained at the lowest 150 to 180 days. In the study, the average highest P content was found with 9.37 mgkg⁻¹ on the 5th day in soils. The available P contents in soils between treatment were statistically significant at the $p < 0.01$ level. The available P content in the soils is similar to each other on the 10th, 15th and 30th days and there is no statistical difference between them. The next 90th and 120th days were in the same group, while the 150th and 180th days were in a different group. As a result, the available P content of the soils decreased depending on the time and this decrease was found to be statistically significant ($p < 0.01$). In a study examining the time dependent (30, 60, 90, 120, 150 and 180 days) change of P applied to soils with different properties, it was reported that the available P content in the soils was the highest on the 30th day, the lowest on the 180th day, and the available P contents decreased depending on the time (Sharpley et al., 1989). Also, in other similar studies on

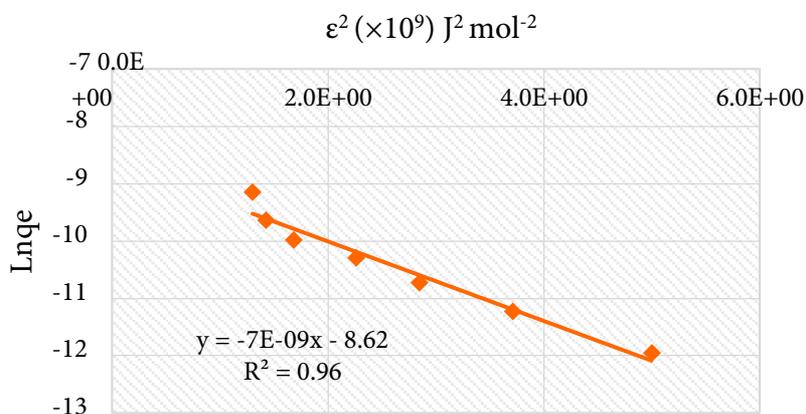


Figure 8. Evaluation of P sorption by gytija with D-R isotherm (Sorbent amount; 1 g / 30 mL, temperature; 21 ± 2 °C, particle size; 0.42 mm, shaking time; 12 h, pH = 6.12)

Table 3. Differences in soil available P contents on days following different P and gytija applications.

Time (Day)										
Treatments	5	10	15	30	60	90	120	150	180	Mean
G_0P_0	7.31ij	6.39jklmn	6.96ijkl	7.24ijk	6.8ijklm	5.66nop	5.45nop	5.45nop	5.55nop	6.31d
G_1P_0	8.48fg	7.16ijk	7.5hi	7.63ghi	7.23ijk	5.46nop	5.56nop	5.4p	5.42op	6.65c
G_0P_1	9.55de	9.32ef	8.78ef	8.81ef	8.39fgh	6.85ijklm	6.87ijklm	5.93mnop	6.01mnop	7.83b
G_1P_1	12.15a	10.57bc	11.43ab	10.44cd	8.76ef	7.33ij	7.17ijk	6.35klmno	6.03lmnop	8.91a
Mean	9.37a	8.36b	8.67b	8.53b	7.80c	6.33d	6.26d	5.78e	5.75e	

G: Gytija. P: Phosphorus. GP: $P < 0.01$. LSD = 0.18; Day: $P < 0.01$. LSD = 0.27; GP x Day: $P < 0.01$. LSD = 0.11. Means with different letters in the same column and same row are different at the significance level of 0.01 based on a Tukey test.

this subject, it was reported that the available P content in soils decreased over time (Lindsay, 1979; Mengel and Kirby, 2001).

We obtained highest available P content (8.91 mgkg^{-1}) from the treatment of G_1P_1 , which was significantly ($p < 0.01$) different from other applications. The G_1P_1 was followed by G_0P_1 and G_1P_0 , respectively. The lowest available P content (6.31 mgkg^{-1}) was obtained at control treatment (G_0P_0) as seen Table 3.

The interaction effect between the gytija and P application and the effects of time-dependent variation on the available P content was found to be significant at the $P < 0.01$ level. The highest interaction value was obtained on the 5th day in soils where G_1P_1 was applied. It was determined that the interaction effect decreased with time and also the available P in the soil gradually decreased. As time progresses and the 180th day, the effect of the gytija on available P in the soil decreases. When applied by mixing gytija and P, the organic matter (40.59%) contained in the gytija can react with the Fe, Al and Mn compounds, which adsorb the P under acidic soil. In addition, the high content of lime (45.57%) and soil's pH value increase from 4.86 to 5.74 may cause an increase in the available P content in acidic soils. Iyamuremye et al. (1996) reported that following application of farmyard manure and plant wastes to acid soils, proton (H) was consumed in microbial decomposition of organic compounds and decarboxylation of organic acid anions ($R - \text{COO}^- + \text{H}^+ \rightarrow R - \text{COOH} + \text{CO}_2$), resulting in an increased soil pH value. Moreover, organic compounds reacted with Fe, Al and Mn compounds to precipitate, thus increasing the available P contents in acidic soils. On the other hand, the addition of organic materials to soils causes a decrease in P sorption by soil components.

References

- Allison LE, Moodie CD (1965). Carbonate. In: Black CA et al. (editors). *Methods of Soil Analysis Part 2*. Madison, USA: American Society of Agronomy Publication, pp.1379-1400.
- Bouyoucus GJ (1951). A recalibration of the hydrometer for making mechanical analysis of soils. *Agronomy Journal* 43: 434-438. doi: 10.2134/agronj1951.0002196200430009005x.
- Bower CA, Reitemeier RF, Fireman M (1952). Exchangeable cation analysis of saline and alkaline soils. *Soil Science* 73: 251-261.
- Bray RH, Kurtz LT (1945). Determination of total, organic and available forms of phosphorus in soils. *Soil Science* 59: 39-45.
- Derici MR, Brohi AR., Saltalı K, Kılıç M, Kılıç K (1995). A Study on phosphorus adsorption of the great soil groups of the Tokat region. In: *Proceeding of the 9 th CIEC International Symposium on Soil Fertility and Fertilizer Management*. Kuşadası, Turkey. pp.143-149.
- Donat R, Akdoğan A, Erdem E, Cetisli H (2005). Thermodynamics of Pb and Ni adsorption onto natural bentonite from aqueous solution. *Journal of Colloid and Interface Science* 286: 43-52 doi: 10.1016/j.jcis.2005.01.045
- Dubinin MM, Zaverina ED, Radushkevich LV (1947). Sorption and structure of active carbons. I. Adsorption of organic vapors. *Zhurnal Fizicheskoi Khimii* 21: 1351-1362.
- Ergin MR (2016). Gıda uygulamasının fındıkta verim ve kalite üzerine etkisi. MSc., Ordu Üniversitesi, Ordu, Türkiye (in Turkish with abstract in English).
- Eyüpoğlu F (1999). Türkiye Topraklarının Verimlilik Durumu. Ankara, Turkey: T.C.Başbakanlık KHGM, Toprak ve Gübre Araştırma Enstitüsü Yayınları (in Turkish).

This decrease can be attributed to the fact that the formed organic acids occupy the P adsorption areas in soils and prevent P adsorption by forming a complex of Fe and Al oxides and organic matter. Thus, the available P content in acid soils increases. (Yusran 2010).

4. Conclusion

We studied P sorption of gytija and its usability to increase pH value of acidic soils and available P content. Adsorption experiments resulted in a b value of 1.59 mgg^{-1} for Langmuir isotherm and an E value of 8.45 kJmol^{-1} Dubinin - Redushkevich isotherm. According to the E-value, it may be deemed that physical and chemical bonding are equally important in P sorption of gytija.

Application of gytija and P mixture to acidic soils increased soil available P content significantly ($p < 0.01$). The greatest increase in soil available P occurred at G_1P_1 treatment. Moreover, the pH value of the studied soils also increased at applications that include gytija.

As a result, the application of P mixed with gytija to acid soils increased the available P content and the pH value of the soils. Therefore, it is possible to use gytija as a soil conditioner in acidic soils. The low cost and abundance of gytija make it a promising conditioner of acid soils. However, further studies should be conducted in field conditions for safely adaptation of its field scale use as soil conditioner.

Acknowledgment

This study has been prepared from the data of the TUBITAK project (TUBITAK -115O858). The authors thank TUBITAK for the given financial support. A part of data used here was presented at the Eurosoil Congress in 2016, İstanbul, Turkey.

- Frossard E, Skrabal P, Sinaj S, Bangerter F, Traore O (2002). Forms and exchangeability of inorganic phosphate in composted solid organic wastes. *Nutrient Cycling in Agroecosystems* 62: 103-113. doi: 10.1023/A:1015596526088
- Gökmen V, Memikoğlu O, Dağlı M, Öz D, Tuncalı E (1993.) Türkiye Linyit Envanteri. Ankara, Turkey: MTA (in Turkish).
- Gonzales-Paradas E, Villafranca-Sanchez M, Canton-Cruz F, Fernandez-Perez M (1994). Adsorption of cadmium and zinc from aqueous solution on natural and activated bentonite. *Journal of Chemical Technology and Biotechnology* 59: 289-295. doi: 10.1002/jctb.280590312
- Ho YS, Huang CT, Huang HW (2002). Equilibrium sorption isotherm for metal ions on tree fern. *Process Biochemistry* 37: 1421-1430. doi:10.1016/S0032-9592(02)00036-5
- Iyamuremye F, Dick RP, Baham J (1996). Organic amendments and phosphorus dynamics: I. Phosphorus chemistry and sorption. *Soil Science* 161: 426-435.
- Kadioğlu YK, Namlı A, Kadioğlu S, Kılınç CÖ, Akça MO (2015). EÜAŞ Aşın-Elbistan havzası linyit işletmesinin havza araştırılmasının jeolojik ve jeofizik yöntemlerle organik ve inorganik bileşenlerin belirlenmesi (Tanım, Tespit, Etüt). In: IV. Uluslararası Katılımlı Toprak ve Su Kaynakları Kongresi; Kahramanmaraş, Turkey. 01-04.09. 2015 (in Turkish).
- Karaca A, Turgay OC, Tamer N (2006). Effects of a humic deposit (gyttja) on soil chemical and microbiological properties and heavy metal availability. *Biology Fertility of Soils* 42: 585-592. doi: 10.1007/s00374-005-0056-3
- Lachacz A, Nitkiewicz M, Pisarek W (2009). Soil conditions and vegetation on gyttia lands in the Masurian Lakeland. *Contemporary Problems of Management and Environmental Protection Vol. 2. Wetlands-Their Function and Protection: 61-94.*
- Langmuir I (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society* 40: 1361-1403. doi: 10.1021/ja02242a004
- Li HX, Zhang XM, Liu YJ (2000). Soil components affecting phosphota sorption parameters of acid paddy soils in guangdong province. *Pedosphere* 10 (4): 317-321.
- Lindsay W L (1979). *Chemical Equilibria in Soils*. New York, USA: John Wiley.
- Mengel K, Kirkby AE (2001). *Principles of Plant Nutrition*. 5th edition. Dordrecht, Netherlands: Kluwer Academic.
- Misra UK (1995). Charge Characterization of Acid Soils. In: Mohsin, MA (editor). *Acid Soil Management*. New Delhi, India: Kalyani Publisher, pp. 69-81
- Myslinska E (2003). Classification of organic soils for engineering geology. *Geological Quarterly* 47 (1): 39-42
- Nelson DW, Sommers LE (1996). Total carbon, organic carbon and organic matter. In: Sparks DL (editor). *Methods of Soil Analysis Part 3, Chemical Methods*. Madison, USA: Soil Science Society of America Book Series Number 5, pp. 961-1011.
- Olsen SR, Cole CV, Watanabe FS, Dean LA (1954). Estimation of available phosphorus in soils by extraction with sodium bicarbonate. *USDA Circular* 939: 19.
- Saltalı K, Korkmaz K (2015). Gıda organomineral toprak düzenleyicisi olarak değerlendirilebilir mi?. IV. Uluslararası Katılımlı Toprak ve Su kaynakları Kongresi 01-04.09.2015, Kahramanmaraş, Turkey (in Turkish).
- Saltalı K, Sarı A, Aydın M (2007). Removal of ammonium ion from aqueous solution by natural Turkish (Yildizeli) zolite for environmental quality. *Journal of Hazardous Materials B* 141(1): 258-263. doi: 10.1016/j.jhazmat.2006.06.124
- Samadi A, Gikes RJ (1999). Phosphorus transformations and their relationships with calcareous soil properties of Southern Western Australia. *Soil Science Society of America Journal* 63: 809-815. doi: 10.2136/sssaj1999.634809x
- Sharpley AN, Singh U, Uehara G, Kimble J (1989). Modeling soil and plant phosphorus dynamics in calcareous and highly weathered soils. *Soil Science Society of America Journal* 53: 153-158. doi: 10.2136/sssaj1989.03615995005300010029x
- Singh BB, Jones JP (1976). Phosphorous sorption and desorption characteristics of soil as affected by organic residues. *Soil Science Society of America Journal* 40: 389-394. doi: 10.2136/sssaj1976.03615995004000030025x
- Theodorou ME, Plaxton WC (1993). Metabolic adaptations of plant respiration to nutritional phosphate deprivation. *Plant Physiology* (101): 339-344. doi:10.1104/pp.101.2.339
- Veith JA, Sposito G (1977). On the use of the Langmuir equation in the interpretation of adsorption phenomena. *Soil Science Society of America Journal* 41: 697-702. doi: 10.2136/sssaj1977.03615995004100040015x
- Wolde, Haile W (2015). Phosphorus sorption isotherms and external phosphorus requirements of some soils of southern Ethiopia. *African Crop Science Journal Vol. 23, (2): 89-99.*
- Yörükoğlu M (1991). Aşın-Elbistan projesi ve TKİ Kurumu, AELİ müessesesinde madencilik çalışmaları. *Madencilik* 30 (3): 13-30 (in Turkish).
- Yu W, Ding X, Xue S, Li S, Liao, X, et al. (2013). Effects of organic-matter application on phosphorus adsorption of three soil parent materials. *Journal Soil Science and Plant Nutrition* Vol.13 (4): 1003-1017. doi: 10.4067/S0718-95162013005000079
- Yusran FH (2010). The relationship between phosphate adsorption and soil organic carbon from organic matter addition. *Journal of Tropical Soils* 15 (1): 1-10