

PHOSPHORUS RETENTION IN PEAT AMENDED WITH IRON-CONTAINING CLINOPTILOLITE

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ABSTRACT

Although phosphorus (P) is a crucial plant nutrient, it is associated with environmental problems such as eutrophication. The effect of Fe(III)-containing natural clinoptilolite (FeCLI) on P retention in peat soil, an acidic soil typically high in organic matter, was studied by a batch method. The effect was investigated both in pure peat and lime-amended peat. The peat amount and the rate of lime influenced the retention efficiency of FeCLI. The acidity of both pure peat and peat that have been amended with lime was decreased in the presence of FeCLI. All obtained results suggested that FeCLI can be considered as a beneficial soil supplement to support both soil fertility and water preservation.

Key words: natural zeolite, iron–clinoptilolite, peat, organic soil, phosphorus.

INTRODUCTION

Because it affects soil fertility and environmental pollution, mitigation of P loss from soils has attracted much attention. One obvious reason for P loss is the intense threat to peat soils, an acidic soil typically high in organic matter, posed by increased forestry and agricultural activity. Although various soil supplements have been considered to enrich P retention in peat soil, there is still a need to develop new ones.

Due to their unique properties, natural zeolites have been used as soil amendments to improve the physicochemical properties of soils (especially for sandy soils), to enrich the retention of plant nutrients in the soil but also in the remediation of soils contaminated by a variety of toxic metals such as Ni, Cd, Pb, Zn, and Co^{1,2}.

Taking into account that FeCLI efficiently adsorbs phosphate from water solution³, this study aimed to examine the influence of FeCLI on P retention in pure peat soil and in lime-enriched peat soil as well as the influence of FeCLI on peat's acidity.

EXPERIMENTAL

Peat soil samples were collected from the top layer (0–20 cm) at various points in the field, which had been treated with different amounts of lime. Prior to the experiments, the samples were air-dried and homogenized at room temperature, sieved through a 2 mm sieve mesh, and stored in polyethylene bags. Samples were labeled as P0 – pure peat soil, P1 and P2, which are samples with different amounts of lime, which was used to raise the pH at a specific value. Ca(OH)₂ was used as the lime source.

The zeolitic tuff containing about 73 wt.% of clinoptilolite (CLI) was obtained from the Zlatokop deposit (Vranjska Banja, Serbia). Primarily, CLI was sieved to obtain particles of 0.063–0.125 mm, washed using deionized water several times and dried overnight at 105 °C until a constant mass. The cation exchange capacity (CEC) measured by the ion exchange with NH₄CH₃COO solution was determined to be 160 cmol/kg.

CLI was converted to FeCLI in accordance with the previously published procedure³. In short, CLI was treated with a Fe₂(SO₄)₃ solution in an acetate buffer (pH= 3.6). NaOH was added to raise the pH to 7, and the separated solid was heated to a constant mass at 90 °C.

Soil samples characterization: Standard procedures determined the soil samples' physicochemical properties. Soil pH was measured at a soil:water ratio 1:2.5 using a glass electrode pH meter. The organic matter (OM) content was determined as the loss on ignition at 550 °C. The concentration of exchangeable cations (Na, K, Mg, and Ca) was determined after treating the samples with 1 M NH₄CH₃COO solution at pH=7.0 using an atomic absorption spectrophotometer. Exchangeable H⁺ was determined by back titration back to pH= 7.00 by use of 0.05 M NaOH.

Zeolite characterization: Both CLI and FeCLI were characterized in detail using various instrumental techniques, and data were described in the previous report³.

Phosphorus adsorption experiments: Adsorption experiments were performed using the batch equilibrium method. Different amounts of peat soil ranged from 20 to 800 mg or a mixture of peat soil and FeCLI (10 mg) was weighed and placed into 50 cm³ centrifuge bottles. Then, 20 cm³ of a 2.00 mg dm⁻³ P solution containing 0.0025 mol dm⁻³ CaCl₂ solution (which serves to adjust ionic strength) was added to each bottle. Three drops of toluene were added to each tube to inhibit microbial activity. The suspensions were shaken in a temperature-controlled orbital shaker (125 rpm) at room 25 ± 1°C for 24 h to reach an equilibrium. Then, the suspensions were centrifuged (8,000 rpm for 10 minutes) and filtered through 0.45 µm filter. The P concentration was determined colorimetrically using the molybdenum–blue method. All adsorption tests were done in triplicate.

Acidity measurements: The change in soil acidity was also studied by measuring the pH value of the soil mixture after the adsorption test. The average pH value was calculated and compared.

RESULTS AND DISCUSSION

Soil characterization: Selected physicochemical properties of the used peat samples are given in Table 1.

Table 1. Selected physicochemical properties of the studied soil samples.

Property	Sample		
	P0	P1	P2
pH	3.58	4.79	6.49
Base saturation, %	6.4	48.9	86.0
Loss on ignition, %	98.4		
Exchangable Na, cmol _c /kg	0.31	0.32	0.39
Exchangable K, cmol _c /kg	0.18	0.19	0.20
Exchangable Mg, cmol _c /kg	5.20	6.20	7.13
Exchangable Ca, cmol _c /kg	3.31	57.95	109.97
Exchangable H, cmol _c /kg	124.8	66.4	18.7
Total acidity, meq/g organic matter	3.65	2.45	1.53

As expected, an increase in pH and lime rate is evident. It increased from 3.58 to 4.79 (P1) and 6.49 (P2), most likely due to the precipitation of exchangeable Al and Fe and the deacidification of H⁺ by the carbonate ion in the lime. Consequently, the total acidity of peat was decreased with the addition of lime (from 3.65 to 2.45 and 1.53 meq g⁻¹ organic matter for P1 and P2, respectively). As a result of liming, the concentration of exchangeable Ca was

significantly increased, from 3.31 to 57.95 and to 109.97 $\text{cmol}_{\text{c}+} \text{kg}^{-1}$ for P1 and P2, respectively. Additionally, there was no notable difference in the exchangeable Na and K concentration before and after liming, whereas the concentration of exchangeable Mg was increased by lime addition, which agreed with the reported findings.

Zeolite characterization: The previous report provided a detailed characterization of the zeolitic tuff both before and after treatment with Fe(III) ³. Conversion of CLI to FeCLI resulted in a) an enrichment in Fe(III) (17 wt.% compared to 0.21 wt. % for CLI), b) an increase in specific surface area from 24 to 140 $\text{m}^2 \text{g}^{-1}$ due to the formation of amorphous Fe(hydro)oxide coverage onto the CLI surface which was confirmed by TEM analysis³.

Phosphorus adsorption in peat soil in the presence of lime and FeCLI

The obtained adsorption results are given in Figure 1. Increasing the amount of peat up to 800 mg increased the P concentration in the soil solution for both pure peat (P0) and peat with lime (P1 and P2). This can be attributed to increased soil organic matter (SOM). SOM affects P adsorption/desorption in the soil through various pathways, and is therefore one of the crucial parameters. SOM favors P release in soil solution by inhibiting P adsorption through competitive adsorption on metal oxides like Fe/Al oxides. In addition, SOM can raise the P concentration in solution by forming more soluble organophosphate complexes, replacing H_2PO_4^- by organic anion on adsorption sites, and increasing the amount of organic P mineralized to inorganic P.

The addition of lime (P1) raised the P concentration in the solution, and subsequent additions caused the P concentration in the soil solution to decrease (P2) (Figure 1). This can be explained by the fact that liming raises the pH of the soil, which encourages P to be released from the surfaces of Al- and Fe(hydro) oxides⁴. However, adding more lime leads to overliming, where P precipitates as insoluble Ca-phosphates.

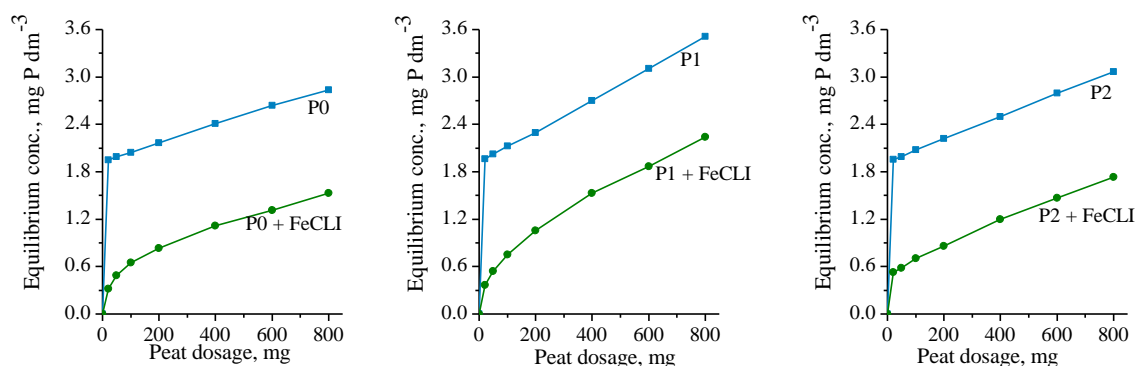


Figure 1. Equilibrium P concentrations for pure peat and amended peat.

The findings indicated that FeCLI influences P adsorption, resulting in a drop in P concentration in the soil solution (Figure 1). Both pure peat and peat that had been amended with lime showed the effect. Furthermore, the effect is visible for every studied peat amount. This can be attributed to a high affinity of FeCLI toward P. FeCLI's role in P retention may also be explained by SOM's ability to complex iron present on FeCLI, creating $\text{FeCLI-PO}_4\text{-SOM}$ complexes that increase the number of P adsorption sites.

The P concentration in the soil solution increased as the amount of peat increased, indicating competition between SOM and P functional groups for more adsorption sites on FeCLI. The curved line at low peat doses, especially for P0 and P1 in Figure 1, indicates this. FeCLI lowers the P concentration in the solution by approximately 84% (P0), 70% (P1), and 73% (P2) for 20 mg of peat. The P concentration in the solution decreased by 46% (P0), 36%

(P1), and 43% (P2) by using 800 mg of peat, indicating the significance of the FeCLI amount added in peat.

Acidity measurements

Figure 2 displays the findings from measuring the pH of the soil solutions following the adsorption tests. As expected, a higher peat content causes the pH to drop: in P0, from 4.06 to 3.12; in P1, from 4.94 to 4.31; and in P2, from 6.17 to 5.84. Up to 200 mg of peat, the pH decreased more noticeably before slowing down. Many acid functional groups, including carboxylic and phenolic ones, are present in SOM, allowing H^+ ions to dissociate and lower pH. The presence of FeCLI raised the pH of the solution, indicating that its addition can lessen soil acidity. This may be explained by the decrease of SOMs due to their adsorption onto FeCLI. However, as SOM levels rise, the effect becomes less pronounced.

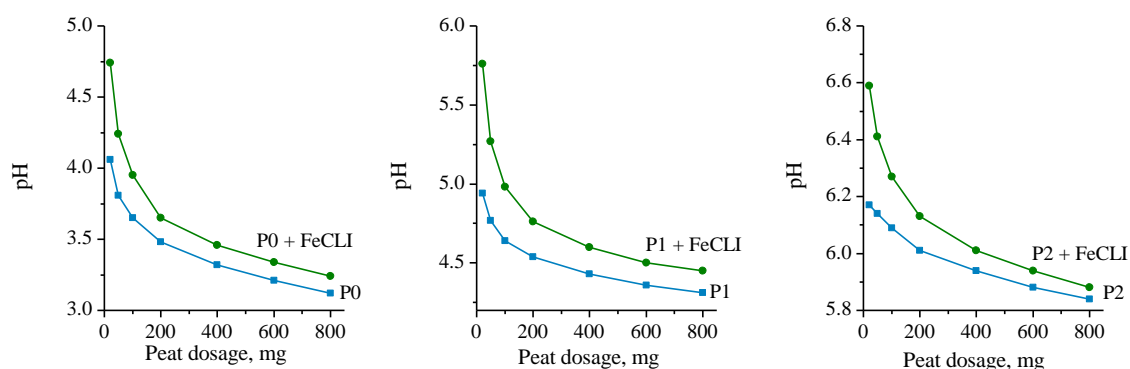


Figure 2. The effect of FeCLI presence on soil pH.

CONCLUSION

The presented results suggest that FeCLI can be a beneficial soil supplement supporting agricultural practices and water conservation. FeCLI enhances the P retention in both pure peat soil and peat that has been lime-amended. With more peat present, the supplement's impact has been less apparent, with a reduction in P concentration in the range of 46% to 84%. The reduction in P concentration in the lime-amended peat ranged from 36% to 73%. Both pure peat and lime-enriched peat have a lower acidity when FeCLI is present.

ACKNOWLEDGEMENT

The study was supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Project No. 451-03-66/2024-03/200011) and was done in collaboration with the Faculty of Ecology and Environmental Protection (University "Union - Nikola Tesla" Belgrade, Serbia) and Faculty of Environmental Science and Natural Resource Management, Norwegian University of Life Sciences.

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