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Influence of the Fe(III)-modified clinoptilolite on phosphorus leaching from different soil types

ABSTRACT

Influence of the iron(III)-modified clinoptilolite (FeCLI) on phosphorus leaching from two different Norwegian soil types (sand and clay loam soil) was studied using a column system at room temperature. FeCLI was used in different amounts of 0.5, 1.5 and 2.5 wt. %. The obtained results indicate that the presence of FeCLI causing a reduction of phosphorus leaching from both soil types. The reduction efficiency increases with the FeCLI amount. Addition of 2.5 wt.% FeCLI to the soils decreased the phosphorus leaching by 48 % from clay loam soil and by 42 % from sand soil compared to the control systems. FeCLI also increased pH of the soils from 5.1 to 7.0 for sand and from 5.7 to 7.7 for clay loam soil. All obtained results indicate that FeCLI is a promising soil supplement for the studied soil types due to phosphorus preservation and a decrease of soil acidity.

Keywords: phosphorus, soil, phosphorus leaching, eutrophication, natural zeolite, iron-clinoptilolite.

1. INTRODUCTION

Natural zeolites are crystalline, hydrated aluminosilicates widely used in ion-exchange, adsorption and catalytic reactions due to their unique physical and chemical properties. Being inexpensive, nontoxic and environmental-friendly minerals, natural zeolites have been used in agriculture as soil amendments and fertilizers. Generally, addition of zeolites to soil can increase retention of plant nutrients in the root zone and prevent their leaching through the soil [1-3]. Moreover, many studies have reported the use of natural zeolites in remediation of contaminated soils showing a crucial role of zeolites in the capture of Pb, Zn and Cd and prevention of plant systems to uptake these toxic metal cations [4-6]. Also, zeolites have a positive role in improving the agricultural production (yield and quality of crops) of sunflower [7], maize [8, 9], spring wheat [10], rice [11] and lettuce [12].

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In agricultural practice, there has been an increasing interest for soil amendments which not only improve agricultural production but also prevent degradation of groundwater quality through nutrients leaching. Thus, phosphorus is an essential plant nutrient but it is also responsible for eutrophication of water bodies. Some agricultural areas are particularly vulnerable because of the excessive leaching of phosphorus. These areas usually receive an excessive amounts of phosphorus due to soil type and are prone to erosion and leaching.

Taking this into account the present study has two general aims: 1) to investigate the influence of addition of the iron(III)-modified natural zeolite - clinoptilolite on the phosphorus leaching from two different soil types, and 2) to study the influence of the zeolite on soil pH. Since the as-received natural zeolites have no affinity towards anions because of the negatively charged aluminosilicate lattice, the zeolite was previously modified with iron(III) in order to obtain an iron oxide coating which has been known to readily adsorb phosphates [13-15].

2. EXPERIMENTAL

2.1. Preparation of the FeCLI

The zeolitic tuff (CLI) used in this study was provided from Iran (Semnam mine). The tuff contained about 90 wt.% of clinoptilolite and quartz

and feldspars as major impurities. Prior to the experiments the as-received sample was sieved and washed with deionized water. Particle size in the range of 0.063-0.125 mm was chosen for the experiments.

FeCLI was prepared as follows. The CLI sample (10.00 g) was suspended in 400 cm³ of 0.05 mol dm⁻³ Fe₂(SO₄)₃ in an acetate buffer (pH = 3.6). Then the pH of the suspension was adjusted to 7 using NaOH solution and the suspension was magnetically stirred for 24 h at 70 °C. After filtering, the obtained product was washed with deionized water until a negative reaction for sulfate ions and then dried at 90 °C to a constant mass.

2.2. Characterization of the zeolite samples

2.2.1. Chemical analysis

Elemental composition of the samples was obtained by an energy dispersive X-ray spectroscopy (EDS) using a scanning electron microscope (SEM, Jeol, JSM-6610LV). In order to obtain elemental composition of the clinoptilolite phase an intersection view of the crystallite grains was prepared. The procedure consisted of embedding grains in an epoxy film, polishing the crystallites, cutting them with a fine-grid diamond cutter and coating them with gold.

2.2.2. X-ray diffraction

Crystallinity of the samples was checked at room temperature by a powder X-ray diffraction analysis (PXRD) using APD2000 Ital Structure diffractometer with CuK α radiation ($\lambda = 0.15418$ nm). Prior to analysis the samples were thoroughly homogenized in an agate mortar. The data were collected in the 2θ range of 5–50° with a step 0.02° s⁻¹ and with a scan step time of 0.5 s.

2.2.3 Thermal analysis

Thermal analysis was used for the determination of water content. The analysis was conducted using a SDT Q600 simultaneous TGA–DTA instrument (TA Instruments). The samples were heated from the room temperature to 800 °C, at a heating rate of 10 °C min⁻¹ under air (flow rate of 100 ml min⁻¹).

2.2.4. Textural characteristics

The specific surface area and porosity of zeolite samples were determined by the N₂-BET adsorption method (Micromeritics ASAP 2020) at -196 °C. Prior to the measurements the samples were degassed under vacuum at 150 °C for 10 hours. The specific surface area was obtained according to the BET (Brunauer, Emmett, Teller) method. The total pore volume was determined from the desorption isotherm at $p/p_0 = 0.998$. The pore size distribution was determined using the BJH method (Barrett, Joyner and Halenda).

2.3. Soil samples characterization

The soil samples were collected from Norway (59°39'47" N and 10°45'42" E). The samples were air dried, sieved (2 mm) and stored in polyethylene bags. According to the World Reference Base [16] the sample containing (wt.%) clay - 25, silt - 40 and sand - 35 is classified as clay loam type whereas the other one containing (wt.%) sand - 94, clay - 3 and sand - 3 belongs to sand soil type.

Selected physico-chemical properties of the soil samples were determined by standard procedures. Soil pH was measured in distilled water (with a soil to solution ratio of 1 : 2.5). The content of organic matter (OM) was determined as the loss on ignition at 550 °C. Concentration of the plant available phosphorus was determined by the Egners Al-method [17]. The measurements were done by extracting the soil sample with an ammonium lactate solution and phosphorus content in the solution was determined colorimetrically using the molybdenum-blue method [18].

2.4. Leaching experiments

The leaching experiments were conducted at room temperature using a column system (Figure 1).

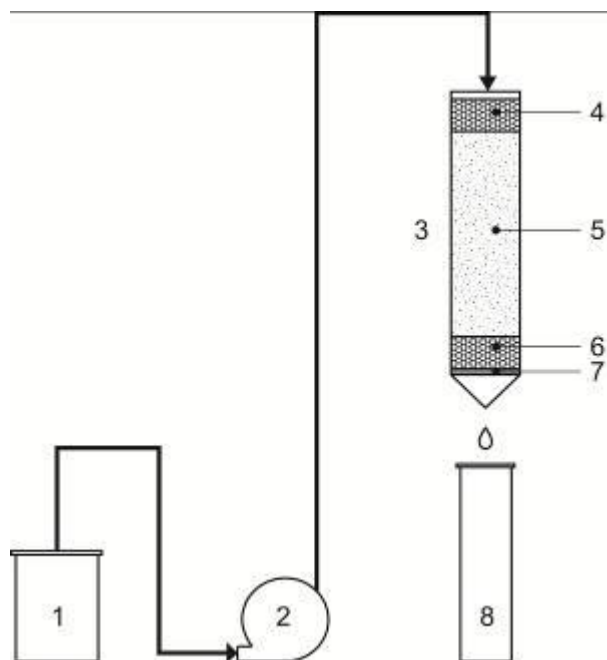


Figure 1 - The experimental setup for leaching experiments: (1) water tank; (2) peristaltic pump; (3) plexiglass column; (4) PVC balls; (5) soil or soil/FeCLI mixture; (6) PVC balls; (7) PVC filter; (8) sample collector

The plexiglass columns of 24 mm in diameter and 30 cm long were organized in the following systems with three replications of each: A (only

soil, Control), B (Soil + 0.5 wt.% FeCLI), C (Soil + 1.5 wt.% FeCLI) and D (Soil + 2.5 wt.% FeCLI).

Amounts of the added FeCLI corresponded to about 10, 30 and 50 t FeCLI ha⁻¹, respectively. Prior to filling the columns, mixtures of soil and FeCLI were homogenized in a rotating shaker overnight. Then, each column was filled up to a 20 cm height with the soil or soil/FeCLI mixture. To prevent loss of soil from the columns the bottom of the columns was covered with a PVC filter and PVC balls (about 2 cm in height). Also, the top of each column was covered with the balls in order to provide an effective distribution of water.

During the leaching experiments the filled columns were saturated and then irrigated with distilled water. To simulate the effect of heavy precipitation on the phosphorus leaching, the water flow was for a short time period about 1.3 ml h⁻¹ (500 mm of precipitation during 7 days). The leaching experiments were performed in the absence of light.

2.5. Leachate analyses

The leachates were collected at the column bottom every day for seven days (or twelve days for sand soil). The P concentration in the collected leachates was determined colorimetrically, using the molybdenum-blue method [18].

2.5.1 pH analysis of leachates

At the end of leaching experiments, pH of leachates (collected during the last day of the leaching experiment) was measured (Orion SA720).

3. RESULTS AND DISCUSSION

3.1. Characterization of the zeolite samples

Elemental analysis of the clinoptilolite phase in CLI and FeCLI is given in Table 1. For both samples the Si/Al molar ratio of about 5 proves the presence of the clinoptilolite mineral phase. The ratio is significantly lower for feldspars being in the range of 2.5-2.7 [19]. It is also evident that the modification of CLI led to a significant increase of the Fe content (from 0.75 to 17.2 at. %).

Table 1 - Elemental composition of the clinoptilolite phase obtained by EDS analysis

Sample	at. %							
	O	Na	Mg	Al	Si	K	Ca	Fe
CLI	55.0	0.90	0.73	6.34	32.3	1.33	2.30	0.75
FeCLI	45.3	2.32	0.29	5.26	27.7	1.19	0.73	17.2

The PXRD patterns of samples given in Fig. 2 show that the zeolitic tuff is rich in the clinoptilolite phase and that quartz and feldspars are the major satellite minerals. It is also evident that the crystallinity of the clinoptilolite remains unaffected after the modification and that no crystalline iron oxide phase is present.

Figure 3 shows the TG/DTG curves indicating a rather continuous water release. It is evident that water content increases by the modification from 10.5 wt.% (CLI) to 13.5 wt.% (FeCLI) which could be attributed to the formation of hydrous iron oxide species.

The modification significantly affects the specific surface area and porous characteristics of the clinoptilolite phase (Table 2). The specific surface area increases from 29 to 140 m² g⁻¹ and the total pore volumes from 0.1045 to 0.2460 cm³ g⁻¹. The change suggests formation of a secondary pore structure at the clinoptilolite surface during

modification. Namely, flaky amorphous hydrous iron oxide precipitate has been detected by a TEM analysis (data not given).

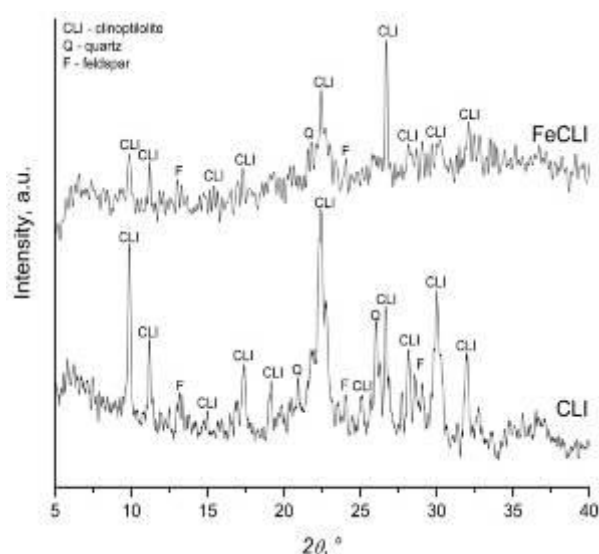


Figure 2 - PXRD patterns of the zeolite samples

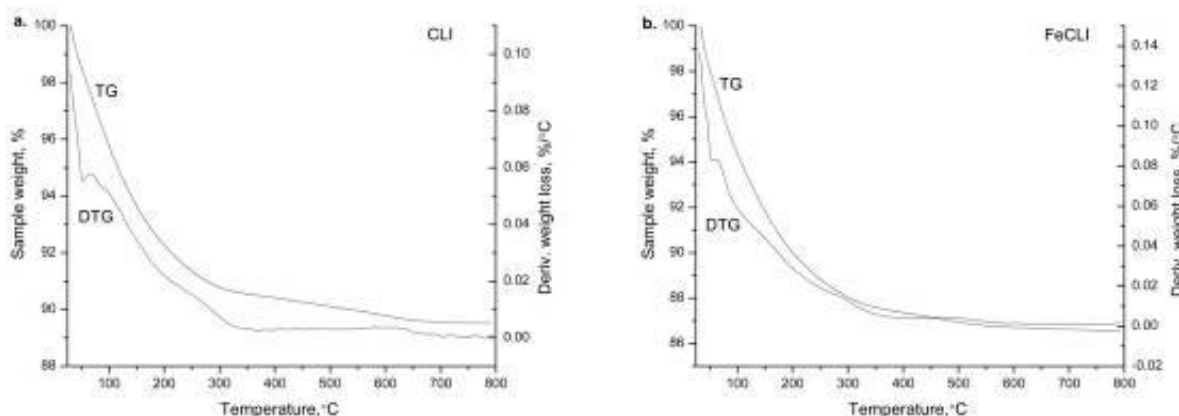


Figure 3 - TG/DTG curves of CLI (a) and FeCLI (b)

Table 2 - Textural properties of the zeolite samples

Sample	S _{BET} , m ² g ⁻¹	V _{tot} , cm ³ g ⁻¹	V _{meso} , cm ³ g ⁻¹	V _{micro} , cm ³ g ⁻¹
CLI	29	0.1045	0.1026	0.0095
FeCLI	140	0.2460	0.2340	0.0431

3.2. Soil characterization

Both soil samples are acidic with pH = 5.1 (sand soil) and 5.7 (clay loam). Their other physico-chemical properties depend on the soil type. Sand soil is poor with the OM content (1.3 wt.%) compared to the clay loam soil (5.7 wt.%). Also, the sand soil has a significantly lower content of the plant available P (16 mg kg⁻¹) than clay loam soil (179 mg kg⁻¹).

3.3. Leaching experiments

The results of the leaching experiments are presented as breakthrough curves (the presented graphs show relationships between phosphorus concentration in collected samples over time).

Comparing the phosphorus amount leached from the soil samples (Figures 4 and 5), it is evident that the phosphorus leaching is significantly higher from clay loam than from sand soil for all the analyzed systems. This could be ascribed both to a high phosphorus content as well as to a low adsorption capacity of clay loam soil. It is probable that the phosphorus adsorption sites on the clay loam soil particles are already occupied and not available for adsorption. Moreover, the total amount of phosphorus collected in leachates from the clay loam soil (system A) was about 0.2 mg P dm⁻³ (Figure 4). Addition of FeCLI to this soil reduces the phosphorus leaching and the effect increases with the rise in the FeCLI amount. The rise in the FeCLI amount from 0.5 to 1.5 wt.% (systems B and C, respectively) increases

efficiency by about six times (the phosphorus leaching reduces for 3.5 and 22.5 %, respectively) whereas the highest applied amount (2.5 wt.% FeCLI, system D, Fig. 4) reduces the phosphorus leaching for 48 %.

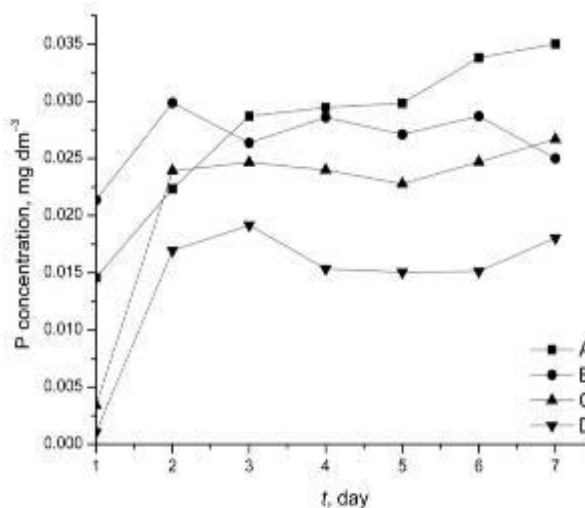


Figure 4 - The phosphorus concentration in leachates collected from clay loam soil (A - Soil; B - Soil + 0.5 wt.% FeCLI; C - Soil + 1.5 wt.% FeCLI; D - Soil + 2.5 wt.% FeCLI)

The reduction the phosphorus leaching from the sample of sand soil contained FeCLI is also evident. The leaching experiment for this systems was conducted longer (twelve days instead of seven) since the leached amount of phosphorus was very low and almost constant during seven

days (Figure 5). In order to examine the effect of the FeCLI addition to the sand soil, powdered KH_2PO_4 (in an amount equal to 300 kg P ha^{-1}) was added to the columns containing sand soil after seven days. The addition of KH_2PO_4 caused an increase in the phosphorus leaching. The total amount of the leached phosphorus was $0.0048 \text{ mg dm}^{-3}$ and the presence of FeCLI in the sand soil reduces the phosphorus leaching. Similarly to the clay loam soil case, the effect depends on the FeCLI amount. An increase of the FeCLI amount from 0.5 to 1.5 wt.% (systems B and C, respectively) increases efficiency by about six times (the phosphorus leaching reduces for 4 % and 25 %, respectively), whereas the highest applied amount (2.5 wt.% FeCLI, system D, Fig. 5) reduces the phosphorus leaching for 42 %.

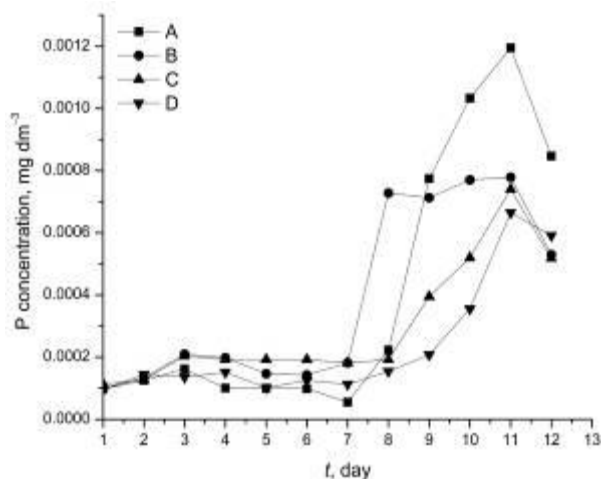


Figure 5 - Phosphorous concentration of in the collected samples from sand soil (A - Soil; B - Soil + 0.5 wt.% FeCLI; C - Soil + 1.5 wt.% FeCLI; D - Soil + 2.5 wt.% FeCLI)

The effect of FeCLI on the phosphorus preservation in the examined soil samples could be ascribed to its unique physico-chemical properties. Firstly, FeCLI has a high specific surface (five times higher than the parent zeolite) which significantly improves the adsorption capacity of the zeolite. Secondly, in contrast to the CLI itself, FeCLI possesses the phosphorus adsorption sites which prevent phosphorus leaching. Finally, addition of FeCLI to the soils probably affects the physical and hydraulic properties of soils [2].

3.3.1. pH analysis

The addition of FeCLI to both soil types decreases their acidity (Figure 6). A degree of efficiency is similar for both analyzed soils. The addition of 2.5 wt.% FeCLI increases pH value from 5.7 to 7.7 for clay loam and from 5.1 to 7.0 for sand soil.

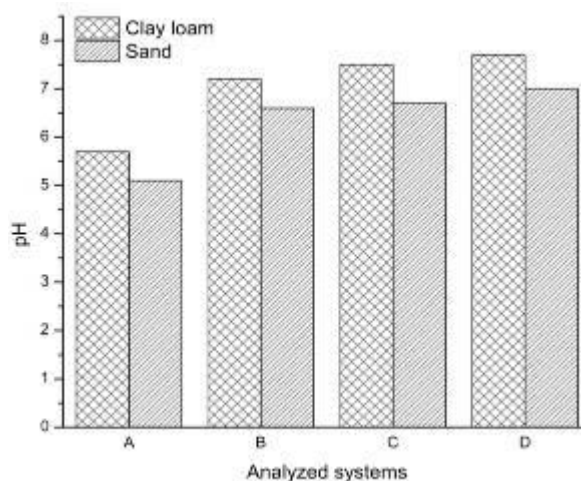


Figure 6 - Influence of the FeCLI addition on the soil pH (A - Soil; B - Soil + 0.5 wt.% FeCLI; C - Soil + 1.5 wt.% FeCLI; D - Soil + 2.5 wt.% FeCLI)

The obtained results are especially important for sandy soils which are generally infertile and require special treatments to reduce acidity [20].

4. CONCLUSION

The presented results show that the iron(III)-modified clinoptilolite is a promising soil supplement. It is effective in the reduction of phosphorus leaching from both the clay loam and the sand soil types. Its use at the rate of 2.5 wt.% reduces the phosphorus leaching for 42-48 % depending on the soil types. It also decreases the soil acidity which is one of the most important prerequisites for a high crop production. Finally, the obtained results indicate that natural zeolites after a slight modification could find wide use in the agricultural practice.

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IZVOD

UTICAJ Fe(III)-MODIFIKOVANOG KLINOPTILOLITA NA IZLUŽIVANJE FOSFORA IZ RAZLIČITIH VRSTA ZEMLJIŠTA

U radu je ispitan uticaj gvožđe(III)-modifikovanog klinoptilolita (FeCLI) na izluživanje fosfora iz dve različite vrste norveškog zemljišta (pesak i glinovita ilovača). Eksperimenti su izvedeni u kolonama na sobnoj temperaturi. FeCLI je dodavan u različitim koncentracijama 0,5; 1,5 i 2,5 mas. %. Dobijeni rezultati ukazuju da FeCLI doprinosi smanjenju izluživanja fosfora kako iz peskovitog, tako i iz glinovito ilovačastog zemljišta. Efikasnost FeCLI raste sa povećanjem koncentracije FeCLI u zemljištu. U koncentraciji 2,5 mas.% FeCLI smanjuje izluživanje fosfora za 48 % (iz glinovite ilovače) i 42 % (iz peskovitog zemljišta). Takođe, FeCLI povećava pH zemljišta: od 5,1 do 7,0 (pesak) i 5,7 do 7,7 (glinovita ilovača). Dobijeni rezultati ukazuju da je FeCLI perspektivan suplement koji doprinosi zadržavanju fosfora u zemljištu i smanjenju kiselosti obe vrste ispitivanih zemljišta.

Ključne reči: fosfor, zemljište, izluživanje fosfora, eutrofikacija, prirodni zeolit, gvožđe-klinoptilolit.

Naučni rad

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