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MAGNETITE Fe-Al-Zr TERNARY COMPOSITE FILLED DIALYSIS MEMBRANE TUBES (DMT-FeAlZr): A MODIFIED TECHNIQUE FOR PHOSPHATE DESORPTION STUDY FROM ACID SOIL

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ABSTRACT. Most soils cannot supply sufficient amounts of P to the plant due to various factors such as P fixation. To this effect, the development of a composite to monitor soil P supplies over time helps with fertilization recommendations. For this purpose, Fe-Al-Zr ternary composite adsorbent with 70%, 25%, and 5% of Fe, Al, and Zr, respectively, was synthesized by co-precipitation method. The as-synthesized adsorbent was characterized by X-ray diffraction (XRD), infrared spectroscopic (FTIR), atomic absorption spectroscopic (AAS) and scanning electron microscopy-energy dispersive spectroscopic (SEM-EDX) techniques. The study was conducted on four soil samples collected from West Wollega Zone, Oromia, Ethiopia, and incubated at 0, 50, 100, and 150 mg/kg phosphate. The amount of phosphate desorbed was higher at Nedjo (N) soil with 150 mg/kg treatment ranging from 4.51-32.62 mg/kg and lower in the control (1.42-15.591 mg/kg at all levels of extraction time for all soil types. The present study suggests that the dialysis membrane tube filled with the ternary composite DMT-Fe-Al-Zr method can serve as an analytical tool to assess the availability of residual P in soils. However, assessment of the reliability of this method at greenhouse and field levels is important to check the universality of this method.

KEY WORDS: Desorption, Dialysis membrane tubes, Fe-Al-Zr mixed oxide, Phosphorus, Two-component first order model

INTRODUCTION

Phosphorus (P) is a central element to life on Earth as living organisms rely on it. This is because it is crucially involved in most major metabolic processes such as energy transfer as adenosine triphosphate (ATP). As phospholipids, phosphorus is part of cell membranes and part of nucleotides, it is a major component in building up DNA and RNA. Furthermore, plants are dependent on phosphorus to secure energy production in photosynthesis [1, 2]. Compared with the other major nutrients, phosphorus is by far the least mobile and least available to plants in most soil conditions. It is therefore frequently a major or even the prime limiting factor for plant growth. Indeed, it is estimated that 5.7 billion hectares worldwide contain too little available phosphorus for sustaining optimal crop production [3, 4]. The poor mobility of soil inorganic phosphorus is due to the large reactivity of PO_4^{3-} ions relative to numerous soil constituents and to the consequent strong retention of most soil phosphorus onto them. Therefore, only a marginal proportion of soil phosphorus is present as PO_4^{3-} ions in the soil solution.

Phosphorus deficiency in soils is a widespread problem in the world [5]. It is believed to be the second most important soil fertility problem throughout the world next to nitrogen [6]. It is often the first limiting element in acid tropical soils [7]. The amount of available soil P has been more frequently evaluated than the rate of its release when studying the P nutrition of plants. The term “available-P” is often used to express the amount of soil P in solution which can be extracted or mined by plant roots and utilized by the plant for growth and development during its life cycle. It is also referred to as labile P. The concentration of available-P is always low because of continuous plant uptake. This is further complicated by the slow replenishment of the extracted P

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*Corresponding author. E-mail: leyahkassim@gmail.com from the soil solution by the labile pool which is dictated by the soil p equilibria [8]. It is, however, favored by an application of P-amendment sources like fertilizers or manure.

The concentration of the plant available P pool is dictated by the prevailing soil conditions at a particular time and the ability of the crop to extract the P from the soil solution. It is therefore a quantity or extensive parameter [8, 9]. Maintenance of plant available P in the soil is very imperative to avoid over-exploitation of soil P which will lead to P deficiency and consequently, low plant yield. This maintenance is a function of the concentration of P in the labile pool and how readily it is released into the soil solution from the solid phase. The availability of a nutrient to plants depends, among others, on the rate at which it is released to replenish the soil solution [10]. Soil tests for plant available P are used worldwide to determine the current P status of soils to estimate fertilizer P requirements for specific yield goals.

Soils receiving continuous applications of fertilizer P or manure over a long term can accumulate large amounts of residual P. This represents not only an uneconomic practice, as phosphate ores are expected to be depleted within approximately 100 to 150 years, but also the risk of P loss to surface waters exacerbating freshwater eutrophication [11]. The current P status is due to indigenous (native) P present in the soil and P from previous fertilizer P application (residual P) [12]. Since the actual plant available P is composed of solution P plus P that enters the solution as the result of desorption/dissolution from a solid phase, the traditional soil test approaches such as chemical extractants have been unsatisfactory in predicting the P uptake by the plant [13].

Much progress has been made in the past to develop long-term soil P extraction methods [14-17]. The dialysis membrane tubes filled with hydrated ferric oxide (DMT-HFO) technique has been employed to study long-term phosphorus desorption in acid soils. De Jager *et al.* [18], Ochwoh *et al.* [19], Dibabe *et al.* [20], and Hinsene *et al.* [21] used this technique on incubated soils to simulate soils fertilized for the long-term. Taddesse *et al.* [22] also used long-term fertilized soils to assess the potential of this technique to mimic plant mode of action both in greenhouse and field levels. Recently, Ahmed *et al.* [17] developed a modified technique using binary Fe-Al binary nanocomposite for acid soils from Ethiopia. In their work, they indicated the better performance of the binary system compared with the single reference hydrated iron oxide-filled dialysis membrane tube (DMT-HFO) reported by Freese *et al.* [23]. The present work attempted to assess the sorbent that serves as a P sink by employing a magnetite-based Fe-Al-Zr ternary composite. This composite was chosen from novelty ground and its remarkable specific surface area [24]. To the knowledge of the researchers, no work has been reported so far using the ternary composite employed here as a phosphate sink in attempting to characterize the desorption kinetics of acid soils.

EXPERIMENTAL

Chemicals and reagents

The chemicals and reagents required for this study included aluminum nitrate nanohydrate ($Al(NO_3)_3.9H_2O$, Blulux LR), ferrous chloride tetra hydrate ($FeCl_2.4H_2O$, Uni-chem chemical reagents), ferric chloride hexahydrate ($FeCl_3.6H_2O$, Blulux LR), zirconyl chloride octahydrate ($ZrOCl_2.8H_2O$, BDH chemicals Ltd, England), potassium dihydrogen phosphate (KH_2PO_4, 99% CDH Laboratory reagents), ammonium molybdate tetra hydrate ($(NH_4)_6Mo_7O_{24}.4H_2O$, 81-83% Riedel-DeHaen AG), potassium antimony tartarate ($KSb.C_4H_4O_6$, 98.5 % BDH chemicals Ltd, England), ascorbic acid ($C_6H_8O_6$, 99% Blulux laboratory reagents), sodium sulfate (Na_2SO_4, 99%, Merck), sulfuric acid (H_2SO_4, 98%, laboratory reagent, LOBA, India), hydrochloric acid (HCl, 36-37%, BDH chemicals Ltd, England), sodium hydroxide (NaOH, 97.5% BDH chemicals Ltd, England), potassium dichromate ($K_2Cr_2O_7$, 99% BDH chemicals Ltd, England), KCl, $CaCl_2$, ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2.6H_2O$, 97% BDH chemicals Ltd, England), sodium sulfate (Na_2SO_4, 99.5-100.5% BDH chemicals Ltd, England), copper sulfate ($CuSO_4.5H_2O$, 98.5% BDH chemicals Ltd, England), selenium powder (Se, 99.7%, Germany), boric acid (H_3BO_3, 99.8% BDH chemicals Ltd, England), dispersing agent (sodium hexa meta phosphate ($(NaPO_3)_6$, 97.5%, Germany), sodium hydrosulfite (dithionite) ($Na_2S_2O_4$, 99.5% BDH chemicals Ltd Poole, England), sodium citrate ($Na_3C_6H_5O_7.2H_2O$, 99.6% BDH chemicals Ltd, England), ammonium oxalate solution ($(NH_4)_2C_2O_4.H_2O$, 98% BDH chemicals Ltd Poole, England), oxalic acid solution ($H_2C_2O_4.2H_2O$, 99%, Switzerland), ammonium fluoride (NH_4F). All the chemicals used in this work were used as received with no further purification.

Characterization methods

X-Ray diffractometer (XRD, D8-Advanced, Germany, power 40 kW with 35 mA at 25 °C) was used to determine the X-ray diffraction (XRD) pattern of the adsorbent from which to determine the phase composition and estimate the crystallite size of the powders. Fourier transform infrared spectrophotometer (FT-IR, Bruker Optics EQUINOX 55 at 25 °C) was used for functional identification of the as-synthesized adsorbent and flame atomic absorption spectroscopy (FAAS) was used for elemental determination of as-synthesized adsorbent. UV-Vis spectrophotometer was used to determine the concentrations of phosphate. The morphology and particle size distribution of the solids were determined by scanning electron microscopy (SEM) using a Hitachi TM1000 with EDX detector.

Description of study area and experimental site

Soil samples were collected from the west Wollega Zone, Oromia Region, Ethiopia at about 477 - 575 km west of Addis Ababa. The selected districts for sample collection are Mana-sibu, Kiltu-kara, Nedjo, and Boji-dirmeji. The altitude, the mean annual rainfall, and the minimum and maximum temperature of these areas range from 1300-1800 masl, 1000-2400 mm yr^{-1}, and 12.5-29 °C, respectively. According to Mesfin [25], the major soil type of western and southwestern Oromia is oxisols. The major crops grown in the zone include cereals (maize, teff, millet, sorghum, and barley), pulses (faba bean and field peas), and oil crops (niger seed, rape seed, and sesame).

Soil sampling and preparation

Surface soil sample (0-30 cm) was randomly collected from each of the sampling sites in each district. The randomly collected soil samples were thoroughly mixed to form one composite sample for each site and a total of four composite soil samples were collected and packed in plastic bags and brought to Haramaya University, Ethiopia. A portion of the collected samples were air-dried and ground to pass through a 2 mm sieve and used to study selected soil physicochemical parameters: bulk density, texture, pH, exchangeable acidity, organic carbon (OC), total nitrogen (TN), CEC, available P, total P, MnO_2, Fe_2O_3 following standard laboratory procedures.

The four study areas' soil samples (3 kg/pot) were also incubated with known concentrations of P in the form of KH_2PO_4 at the rate of 0, 50, 100, and 150 mg P/kg for about 112 days. During incubation, the samples were kept wet to field capacity for four days at 24 °C and air-dried for three days and this was repeated for fifteen wet-dry cycles with mixing of the soil samples for uniform distribution of P. At the end of the incubation period, soils were air-dried again and the extraction process of soil P using DMT-Fe-Al-Zr was conducted.

Synthesis of Fe-Al-Zr mixed oxide composite

The adsorbent, ternary oxide composite was prepared by the chemical co-precipitation method as reported by Liyuan *et al.* [26] with modifications. For the 0.5 Fe^{2+}/Fe^{3+}mole ratio, the product obtained was a homogeneous magnetic particle with uniform size and composition. So, in all samples, the mole ratio of Fe^{2+}/Fe^{3+} is selected to be 0.5 [27, 28]. Accordingly, 1.564 g of $FeCl_2.4H_2O$ and 3.130 g of $FeCl_3.6H_2O$ were weighed and the calculated amounts were dissolved in 100 mL of 0.3 M HCl solution. Then, to the above mixture was added a 120 mL of 3 M NaOH (pH 11) solution dropwise and the entire mixture was under vigorous stirring at 80 °C for 2 h, in an N_2 atmosphere. During this process, the pH of the mixture was kept at 11.0 using dilute concentration (0.1, 0.01, and 0.001 M) of NaOH or HNO_3 solutions as required. The suspension was allowed to settle undisturbed for 4 h and washed with deionized water (DI) several times to obtain a suspension of Fe_3O_4 ferro-fluid.

The magnetite-based Fe-Al-Zr ternary composite was prepared by adding 100 mL of $Al(NO_3)_3.9H_2O$ and $ZrOCl_2.8H_2O$ (obtained by dissolving stoichiometric amounts of both salts in 100 mL of DI) into the prepared Fe_3O_4 suspension and ultrasonicated for 10 min before use. The pH of the mixtures is adjusted to 8.0 using 0.1, 0.01, and 0.001 M NaOH or HNO_3. Then the mixture was magnetically stirred under an N_2 atmosphere for 1.5 h at 70 °C. Finally, each resulting magnetic compound was separated by a permanent magnet, washed with DI water several times to remove impurities such as Cl^-, NO_3^-, and excess OH^- ions, and then dried at 60 °C for 24 h.

Desorption study

A desorption study was carried out using a DMT (Visking, size $3^{20/32}$ inches, approximate pore size 2.5-5.0 nm; membrane thickness 3 μm, MWCO 12000 kDa) that was cut into 0.15 m strips and boiled in DI water twice as described by Freese *et al.* [23]. The 0.15 m DMT strip was then filled with 20 mL of 0.1 g. Fe-Al-Zr composite sorbent. The DMTs comprising the phosphate sink were closed with a nylon thread on both ends and placed in a soil solution. Before the placement of the sink-filled DMTs, the pH of the sorbent suspension was adjusted to the pH (KCl) of the soils using 0.5 M HCl or NaOH. The sorbent suspension was stirred vigorously during the filling. Then, the P sink-DMT system was placed in 200 mL polyethylene containers filled with 1 g of soil and 80 mL of 2 mM $CaCl_2$ and 0.3 mM KCl solution. All the experiments were carried out in triplicate. The polyethylene containers were continuously shaken for 28 days on an end-over-end shaker at 120 oscillations per minute (opm). At each of the seven-day intervals (1, 7, 14, 21, and 28), the DMT-Fe-Al-Zr was replaced with new ones. A glass rod was used to remove any attached soil from the DMTs. At each time interval, three tubes were removed, cut open, and the contents transferred to glass bottles. Phosphate in each solution was determined calorimetrically [29].

Data analysis

To compare the effects of the treatments statistical analysis of variance (ANOVA) and general linear model (GLM) was computed to determine the existence of any statistical difference among the treatments. Separations of significant differences between and among treatment means were made using SAS software (SAS, 9.3 version). A simple correlation and regression analysis was conducted to test the relationship between desorbed P (P-Fe-Al-Zr) and other selected soil parameters such as available P, total nitrogen, exchangeable acidity, organic carbon, organic matter, bulk density, and soil texture (silt, clay, and sandy).

RESULTS AND DISCUSSION

Powder X-ray diffraction

The X-ray diffraction pattern of as-synthesized Fe-Al-Zr mixed oxide powder is shown in Figure 1. The diffraction pattern revealed very weak intensities on a broad background suggesting the amorphous nature of the adsorbent. However, the presence of some low-intensity peaks at 2θ values of 36.46, 43.6, 53.87, and 63.54 were noted. This result could be attributed to the formation of magnetite (Fe_3O_4) (JCPDS: 96-900-5840). This result is in close agreement with a similar report made by Kassahun *et al.* [28]. The presence of weak intensity peaks indicated the formation of some crystals at a very small scale up on the formation of composite structure [30]. No specific peaks were observed that can be attributable to alumina (Al_2O_3) and zirconia (ZrO_2) implying that both might exist in amorphous forms at the temperature of synthesis. These results indicated that the principal component of the magnetic Al-Fe-Zr ternary oxides composite is found to be magnetite (Fe_3O_4).

The crystallite size (Ds) of the powder was also estimated using Dubye Scherrer equation [31]:

$$D_s = \frac{0.9\,\lambda}{\beta\,\cos\theta} \tag{1}$$

where, Ds is the mean crystallite size (nm), λ wavelength of the incident radiation ($\lambda = 0.15405$ nm), β pure diffraction broadening (radians), and θ the Bragg angle (degrees, half-scattering angle). The average crystallite size is estimated to be 9 nm. The Specific surface area of the adsorbent (296.50 m^2/g) was determined previously in our lab as reported in the work of Kassahun *et al.* [28].

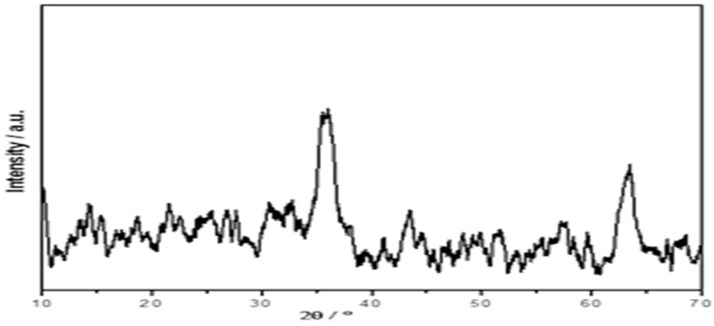

Figure 1. XRD pattern of $Fe_3O_4/Al_2O_3//ZrO_2$ mixed oxide.

FT-IR analysis

The FT-IR spectrum of the Fe-Al-Zr mixed oxide sample is depicted in Figure 2, indicating the main absorption peaks located at 3434, 1620, 1384, 1022, 820, and 585 and 441 cm^{-1}. The strong and broad band between 3800–3100 cm^{-1} region may be assigned to the O-H stretching vibration of coordinated water molecules. The band at 1620 cm^{-1} can be primarily attributed to the bending vibration of H-O-H physisorbed water molecules [32]. The peak observed at 1022 cm^{-1} may correspond to Al-O stretching [33]. In addition, to this, bending vibrations of Zr-OH bonds may appear at 1620 cm^{-1} and Al-O vibration at 1384 cm^{-1} [34]. The second predominant broadband at 585 cm^{-1} may be assigned to Fe-O stretching vibration. Another important adsorption band can be observed at 441 cm^{-1}, which corresponds to the vibration of the Zr-O bond in the Fe-Al-Zr powders.

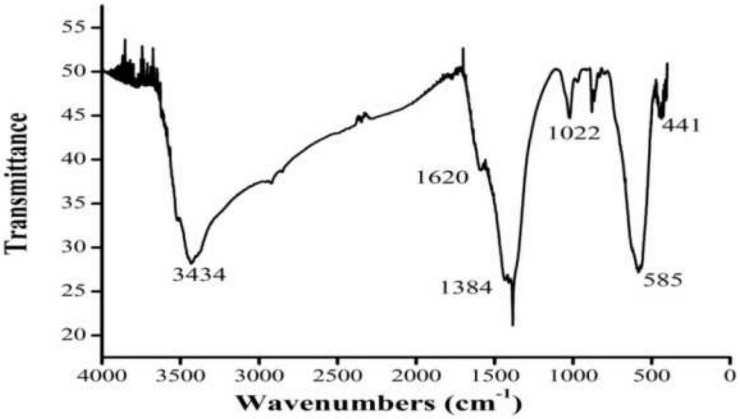

Figure 2. FTIR spectrum of the selected nano-sized Fe-Al-Zr mixed oxide adsorbent.

Elemental analysis

The elemental analysis of as-synthesized Fe-Al-Zr powder by FAAS using a standard solution of each analyte prepared at a series of concentrations depicted in Table 1. The results indicated that the percentage compositions of Fe and Zr in the as-synthesized mixed oxide were found to be 72.1 and 3.75, respectively.

Table 1. Actual yield and theoretical composition the as-synthesized adsorbent.

Element	Theoretical composition (%)	Actual composition (%)
Fe	70	72.1
Al	25	Nd
Zr	5	3.75

The expected values of the oxides are 70% for iron, 25% for aluminum, and 5% for zirconium and the observed values are not far from the theoretical compositions of the metals: Fe and Zr, respectively. We did not determine Al due to lamp shortage. The difference in the percentage compositions of iron and zirconium (between actual and theoretical values) could be due to insufficient dissolution, vaporization, and lack of atomization.

SEM and EDX analysis

Figure 3 depicts the scanning electron microscopy (SEM) coupled with energy-dispersive X-ray (SEM-EDX) graphs of the as-synthesized sample. As shown in the figure, the particles exhibit no distinct morphology. They are rather aggregates of irregular shaped particles.

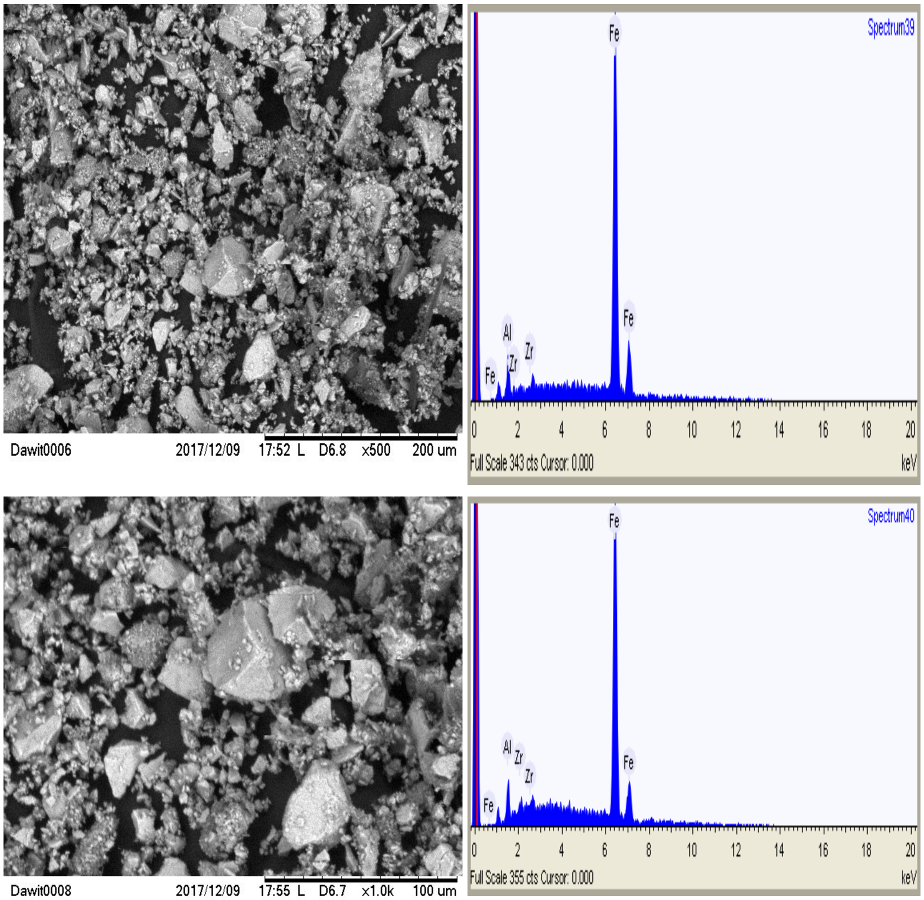

Figure 3. Scanning electron microscopic images of (a) 100 µm and (b) 100 µm resolution for $Fe_3O_4/Al_2O_3/ZrO_2$ composite with corresponding EDX spectra.

The EDX elemental analysis of these micrographs showed the presence of all three metal constituents in the ranges of 94.7 – 96.6% (Fe), 2.5 – 3.5% (Al), and 0.9 – 1.8% (Zr). The observed variation of the Fe-Al-Zr metals percent weight ratio distribution could be due to the dispersion technique employed in the co-precipitation method [35].

Physico-chemical properties of the soil

The physicochemical properties of the soils is determined (data not shown) to evaluate which soil parameters correlate better with the P desorption indices. The results revealed that on average, the soil samples studied appeared to be sandy clay loam in texture. The soil samples studied are acidic with values ranging from 4.24-.5.07 and 3.32-3.53 pH(H_2O) and pH(KCl), respectively. According to Tekalign [36], they fall in the category of very strongly to strongly acidic soils. Since the pH of all soil samples are in the acidic range and pH < 5.5, the added P could be liable to fixation by Al- and Fe-oxyhydroxides that lowered desorption of phosphate from soil. The exchangeable acidity which was found to be > 2 meq/100 g is also indicative of high P-fixation in these soils. The organic carbon ranges from 0.45-0.92% and very low (< 0.5%) in Mana-sibu and low in the rest of the soils which could be due to edaphic factors, types of crops, and the harvesting system [36]. The available phosphorous in the soil samples was low (< 10 ppm) in three of the treatments based on the criteria developed by Landon [37] for the Bray II method. Such low P status indicated that the soils under investigation are highly phosphorous fixing due to inherent low soil pH. The lowest total P was observed at Bojii-dirmiji with a value of 384.1 mg/kg [38] and the highest value of 714 mg/kg for the Kiltu-kara district soil sample. For all soil samples in this study, the total P content was found to be in the medium range (200 to 1000 mg/kg) [39]. The total N for Bojii-dirmiji (0.18%) and Kiltu-kara (0.17%) soils were rated as medium and for that of Nadjo (0.03%) was rated as low according to Landon [39]. The percentage of Fe extracted by the dithionite citrate bicarbonate (DCB) method was higher than the percentage of Fe, extracted by the acid ammonium oxalate method, revealing the predominantly crystalline constituents of the soils under investigation [40].

Table 2 shows phosphate (P) extracted over 1-28 days at different P treatments (0-150 mg/kg P) by using the DMT-Fe-Al-Zr mixed oxide composite on four different soil samples. The amount of P desorbed by DMT-Fe-Al-Zr was significantly influenced ($\alpha = 0.05$) both by the treatments and extraction time for all soil samples in this study. When no P was added, little P was extracted as DMT-Fe-Al-Zr-P but significantly more P was extracted with increasing P application rate and desorption time. This result is in agreement with the previous findings by Gemechu *et al.* [41] and Taddesse *et al.* [42].

Table 2. Desorption of phosphorus from four different soils for 28 days with different P treatment (n = 3).

Soil type (code)	P treatment (mg kg^{-1})	P desorbed per day					Average P (mgkg^{-1})
		1	7	14	21	28	
BP0	0	z1.42^{c}	y3.80^{c}	x5.91^{d}	w8.51^{d}	v12.38^{d}	6.40
BP1	50	z3.11^{b}	y6.95^{b}	x11.41^{c}	w16.166^{c}	v21.65^{c}	11.86
BP2	100	z3.59^{a}	y7.73^{a}	x12.72^{b}	w17.705^{b}	v23.72^{b}	13.09
BP3	150	z3.83^{a}	y8.05^{a}	x14.78^{a}	w21.50^{a}	v28.14^{a}	15.26
MP0	0	z2.12^{d}	y4.57^{d}	x7.12^{d}	w10.31^{d}	v13.33^{d}	7.49
MP1	50	z3.35^{c}	y7.17^{c}	x13.05^{c}	w18.32^{c}	v23.86^{c}	13.15
MP2	100	z3.67^{b}	y8.04^{b}	x14.21^{b}	w19.99^{b}	v26.90^{b}	14.56
MP3	150	z4.27^{a}	y8.94^{a}	x15.57^{a}	w22.38^{a}	v29.70^{a}	16.17
KP1	0	z2.01^{d}	y5.07^{d}	x7.28^{d}	w11.36^{d}	v14.91^{d}	8.13
KP2	50	z3.23^{b}	y7.98^{c}	x13.29^{c}	w19.53^{c}	v26.85^{c}	14.18
KP3	100	z3.89^{c}	y8.79^{b}	x15.19^{b}	w21.89^{b}	v29.56^{b}	15.86
KP4	150	z4.51^{a}	y9.56^{a}	x16.75^{a}	w23.82^{a}	v32.06^{a}	17.34
NP0	0	z2.26^{c}	y5.32^{c}	x7.93^{d}	w11.80^{d}	v15.89^{d}	8.64
NP1	50	z4.03^{b}	y8.55^{b}	x14.13^{c}	w20.31^{c}	v27.33^{c}	14.87
NP2	100	z4.19^{b}	y8.90^{b}	x14.97^{b}	w21.72^{b}	v29.04^{b}	15.76
NP3	150	z4.63^{a}	y9.71^{a}	x17.24^{a}	w24.39^{a}	v32.62^{a}	17.72

Mean values in rows with different letters z, y, x, w, and v are significantly different ($\alpha = 0.05$). Mean values in columns with different letters a, b, c, and d are significantly different ($\alpha = 0.05$).

The cumulative P desorbed was higher at Kiltu-kara soil for 150 mg/kg treatment over the extraction time, ranging with the value of 4.51-32.06 mg/kg. Nedjo soil also showed a similar trend of comparable results of 4.63 -32.62 mg/kg with no significant difference among the two soil samples. Hinsene *et al.* [43] reported a similar trend for soil samples collected from these areas. The lower P extracted was for the control of Bojii-dirmiji (1.42-12.38 mg kg^{-1}) at all levels of extraction time for all soil types. The rate at which the Nedjo soil P was desorbed from the soil is relatively higher than all other soil samples in this study. This could be due to high availability and total P as well. The amount of extracted P over different periods of extraction indicated that less phosphorus was extracted from Bojii-dirmiji soil compared to the other soils in this study.

Table 3. Desorption of phosphorus from four different soil for 28 days with similar P treatment in triplicate (n = 3).

Soil type	P treatment (mg kg^{-1})	P desorbed per day					
		1	7	14	21	28	Average P (mgkg^{-1})
BP0	0	z1.42 ^{a}	y3.80^{c}	x5.91^{c}	w8.51^{c}	v12.38^{d}	6.40
MP0	0	z2.12 ^{ba}	y4.57^{b}	x7.12^{b}	w10.31^{b}	v13.33^{c}	7.49
KP0	0	z2.01 ^{b}	y4.57^{a}	x7.28^{ba}	w11.36^{a}	v14.91^{b}	8.02
NP0	0	z2.26 ^{a}	y5.32^{a}	x7.93^{a}	w11.80^{a}	v15.89^{a}	8.64
BP1	50	z3.11^{c}	y6.95^{c}	x11.41^{c}	w16.16^{d}	v21.65^{c}	11.85
MP1	50	z3.35 ^{b}	y7.17^{c}	x13.05^{b}	w18.32^{c}	v23.86^{b}	13.15
KP1	50	z3.23 ^{cb}	y7.98^{b}	x13.29^{b}	w19.53^{b}	v26.85^{a}	14.17
NP1	50	z4.03^{a}	y8.55^{a}	x14.13^{a}	w20.31^{a}	v27.33^{a}	14.87
BP2	100	z3.59 ^{b}	y7.73^{b}	x12.72^{c}	w17.70^{c}	v23.72^{c}	13.09
MP2	100	z3.67 ^{b}	y8.04^{b}	x14.21^{b}	w19.99^{b}	v26.90^{b}	14.56
KP2	100	z3.89^{ba}	y8.79^{a}	x15.19^{a}	w21.72^{a}	v29.04^{a}	15.72
NP2	100	z4.19^{a}	y8.90^{a}	x14.9^{ab}	w21.89^{a}	v29.14^{a}	15.80
BP3	150	z3.83^{c}	y8.05^{c}	x14.78^{c}	w21.50^{c}	v28.14^{a}	15.26
MP3	150	z4.27 ^{b}	y8.94^{b}	x15.57^{b}	w22.38^{b}	v29.70^{b}	16.17
KP3	150	z4.51 ^{ba}	y9.56^{a}	x16.75^{a}	w23.82^{a}	v32.069^{a}	17.34
NP3	150	z4.63 ^{a}	y9.71^{a}	x17.24^{a}	w24.39^{a}	v32.62^{a}	17.71

Mean values in rows with different letters z, y, x, w, and v are significantly different ($\alpha = 0.05$). Mean values in columns with different letters a, b, c, and d are significantly different ($\alpha = 0.05$)

In addition, a linear relationship was observed between the total P and initial P released from soil, during consecutive extraction by using DMT-Fe-Al-Zr (Figure 4). This is because, as the rate of added P to the soil increases, the amount of initial and total P released from the soil also increases [44]. The increase of P released during the extraction processes with the increase of the added P rates into the soils implies its direct relationship with the rate of added P in the soils. Generally, the cumulative desorption of P for all soil samples extracted by DMT-Fe-Al-Zr within 28 days was very low as compared to the total P, but it is larger as compared to the availability of P (Tables 2 and 3).

Table 3 depicts a comparison of extracted P from soils of four areas under similar P treatments. The results indicated that the extracted P was significantly different from the control on the 28th day of desorption. However, the difference was not significant for some pairs of the soils treated with 50, 100, and 150 mg/kg phosphate and extracted for 28 days. This could be attributed to comparable physicochemical properties towards added P.

The impacts of the applied p on phosphate desorption

Tables 3 and 4, indicated less P was extracted by DMT-Fe-Al-Zr from the control and high P from a soil treated with a high P rate showing an increasing trend for the period studied in this experiment (28 days) for all treatments. This result is in agreement with previous work reported [22, 41, 42]. Referring to ANOVA and LSD values, there were highly significant variations ($P=0.05$) in the successive DMT-Fe-Al-Zr extracted P, from all the different phosphorus treatments. The desorption data fitted to regression equations and the R^2 values ($\geq$0.987) indicated very good correlations between treatments and P extractions.

Kinetics of phosphorus desorption

To investigate the P desorption kinetics of these soils, a two-component first-order model was selected since, such a kinetic model was considered one of the best to describe the phosphate desorption process from acid soils and to make the comparison easier with previous similar reports [18-20, 22, 23, 37-39, 41-42]. Accordingly, for a long-term desorption study (28 days), one might expect two pools: fast (pool A) and slow (pool B) to play their role. However, in this study, only fast P release of soil phase to solution was observed. This could probably be associated with the high specific surface area of the ternary component (Fe-Al-Zr) sorbent system compared with previous binary and single systems [17, 25] employed for a similar purpose.

Table 4. P desorption rate and rate constants of soil samples.

Soil type (code)	P treatment (mg kg^{-1})	Rate constant (R) k_A (day^{-1})	P desorption rate (mg/kg) day^{-1}				
			1	7	14	21	28
BP0	0	0.613	1.42302	0.543714	0.422729	0.405276	0.442276
BP1	50	0.563	3.11709	0.993761	0.815127	0.769981	0.773254
BP2	100	0.547	3.59542	1.105323	0.908626	0.843167	0.84719
BP3	150	0.586	3.83458	2.115625	1.056054	1.024209	1.005194
MP0	0	0.535	2.12058	0.654173	0.508604	0.491016	0.476199
MP1	50	0.578	3.35625	1.025226	0.932226	0.872468	0.852235
MP2	100	0.581	3.67514	1.149133	1.015396	0.952334	0.960812
MP3	150	0.566	4.27304	1.277777	1.112721	1.066058	1.060919
KP0	0	0.578	2.01295	0.725254	0.520572	0.541051	0.532773
KP1	50	0.613	3.23667	1.140531	0.949804	0.930312	0.95911
KP2	100	0.59	3.89437	1.256101	1.085383	1.042405	1.055878
KP3	150	0.571	4.51221	1.365979	1.196898	1.134386	1.145324
NP0	0	0.561	2.26009	0.76056	0.566513	0.562182	0.567668
NP1	50	0.554	4.03388	1.221997	1.009395	0.967327	0.976289
NP2	100	0.562	4.19332	1.271791	1.069654	1.034633	1.03735
NP3	150	0.57	4.63179	1.388466	1.231715	1.161667	1.165075

On top of this, the duration of the phosphate release experiment might not be long enough to involve the slow P-releasing kinetics (28 days in the current experiment versus 56 days in most of the previous reports). Table 4 predicts the fast P desorption kinetic of soil was found to follow first-order model (first order kinetic) which is given by $SP_A(t) = SP_{A0}e^{-kAt}$ where SP_A is solid phase soil P in fast P releasing pool (A) and k_A is the conditional rate constant of P desorption of the soil from fast pool [23]. Table 4 depicts soil P desorption of soils in this study and the corresponding P desorption rate constant k_A of from this pool.

The rate constant k_A over P-levels ranges for Bojii-dirmiji (0.547-0.613), for Mana-sibu (0.535-0.581), for Kiltu-kara (0.571-0.613) and Nedjo (0.554-0.57) day^{-1}. Taddesse *et al.* [42] reported k_A in the range of 0.0059-0.104 day $^{-1}$ for the soil plots collected from University of Pretoria and 0.2294-0.1313 day^{-1} for Ermelo soils under the studies of kinetics of residual phosphate desorption from long-term fertilized soils of South Africa. As depicted in Table 4 the desorbed P of the treatments were linearly significant. According to our finding the highest desorption rate was found on day 1 of the Nadjo soil sample with a value of 4.63 mg/kg/day and the lowest was observed on day 28th of Bojii-dirmiji with a value of 0.44 mg/kg/day (Table 4).

Correlation of soil parameter with cumulative P desorbed

Correlation between phosphate P desorbed and selected soil properties are displayed on Tables 5 and 6. In general, the negative sign indicates the physico-chemical properties of soil that are negatively correlated to the amount of phosphate released and positive numbers are those parameters that are positively correlated to the amount of phosphate desorbed. The correlation value varies with different amount of added P and also with the soil sample considered. The low P-release was observed when compared with total phosphorus. Such a low P status indicated that the soils under investigation are highly phosphorous fixing due to inherent low soil pH. Such high phosphorous fixing tends to maintain low phosphorous concentration in soil solution and is a characteristic feature of Fe/Al/Mn dominated soil [17] .The result in this case showed that there is positive and significant correlation between cumulative desorbed P and BP1 with Fe_{Ox} and Mn_D for Boji dirmeji soil which has the value of (r = 0.952) and (r = 0.992) respectively (Table 5). In this study positive and high significant correlation between BP1 and pH-H_2O (r = 0.998) was also observed. In addition, there is significant correlation between cumulative desorbed P for soil sample BP0 with pH-KCl, Av. P, TP and TN with the following correlation value (r = -0.948), (r = -0.953), (r = 0.874) and (r = 0.948), respectively.

In the case of Mana sibu soil sample positive and significant correlation between MP2 and exchangeable acidity (r = 0.990**) is observed. There is also negative and significant correlation between MP1 and OM of that soil with(r = -0.971). In addition, negative significant correlation between KP0 and pH_{H_2O} (r = -0.981) and Ex Al (r = -0.89) was observed (Table 6) for Kiltu Kara soil while a positive significant correlation is shown between KP3 and TP (r = 0.97), TN (r = 0.961) and Fe_D (r = 0.948) for the same soil sample. Generally, the physicochemical properties of the soils were highly correlated with cumulative desorbed P either negatively, positively or not significantly. Correlation values near +1 or −1 means a good linear or reciprocal relation between two variables.

Table 5. Correlations of desorbed phosphorus level and soil properties for Boji Dirmeji (B) and Mana Sibu (M) soil samples.

Corr.	pH H_2O	pH KCl	Ex.A	Ex.Al	C	OM
BP0	-0.94	-0.94	-0.61	-0.84	-0.98	0.01
BP1	0.99	0.99	0.27	0.98	0.83	0.38
BP2	0.42**	0.42**	0.99	0.19	0.81	0.71**
BP3	0.77**	0.77**	0.85	0.59	0.98	0.34**
Corr	TN	AvP	TP	FeD	MnD	MnOx
BP0	0.94	-0.95	0.87	0.69	-0.71	-0.61
BP1	-0.99	0.99	0.99	-0.37	0.92	0.27
BP2	0.42**	0.43	0.25	1.00	0.01**	0.99**
BP3	0.77**	0.78	0.64	-0.90	0.41**	0.85**
Corr	PH H_2O	PH KCl	Ex.A	Ex.Al	C	OM
MP0	0.34	-0.34	1.00	-0.51	-0.64	0.98
MP1	-0.27	0.27	0.99	0.45	0.69	-0.97
MP2	0.18	-0.18	0.99**	-0.37	-0.75	0.94
MP3	-0.28	0.28	0.99	0.45	0.69	-0.97
Corr	TN	AvP	TP	FeD	MnD	MnOx
MP0	1.00	0.73	0.14	-0.01	-0.01	-0.98
MP1	0.99	-0.69	0.07	-0.05	-0.08	0.99
MP2	-0.99	0.62**	0.01	0.14	-0.17	1.00
MP3	-0.99	-0.69	0.07	-0.04	0.08	0.99

**Correlation is significant at the 0.01 level (2-tailed); Corr. = correlation, Av. P = availability of P, Ex. A = exchangeable acidity, C = carbon, OM = organic matter, TN = total nitrogen, TP = total phosphorus; FeD = iron extracted by dithionite, MnD = manganese extracted by dithionite, MnOx = manganese extracted by oxalate; B = soil samples from Boji Dirmeji, M = soil sample from Mana Sibu; P0 = cumulative phosphate desorbed from control, P1 = cumulative phosphate desorbed from soil incubated with concentration of 50 mg P kg^{-1} , P2 = cumulative phosphate desorbed from soil incubated with concentration of 100 mg P kg^{-1}; P3 = cumulative phosphate desorbed from soil incubated with concentration of 150 mg P kg^{-1} .

Table 6. Correlations of desorbed phosphorus level and soil properties for Kiltu Kara (K) and Nedjo (N) soil samples.

Corr.	pH H_2O	pH KCl	Ex.A	Ex.Al	C	OM
KP0	-0.98	0.32	-0.23	-0.89	0.96	0.04
KP1	-0.39	0.99	1.00	0.24	0.47	0.98
KP2	-0.80	0.91	-0.87	-0.27	0.85	0.77
KP3	-0.50	-0.49	0.57	-0.92	0.42	-0.71
Corr.	TN	Av.P	TP	FeD	MnD	MnOx
KP0	0.84	0.70	0.45	0.86	0.77	0.14
KP1	-0.35	0.83	0.77	-0.31	0.78	-0.93
KP2	0.16	0.99	0.35	0.20	0.98	-0.63
KP3	0.96	-0.06	0.97	0.94	0.03	0.83
Corr.	pH H_2O	pH KCl	Ex.A	Ex.Al	C	OM
NP0	0.95	0.93	-0.97	0.71	0.74	-0.74
NP1	0.73	0.99	-0.98	0.34	0.95**	-0.95
NP2	0.97	0.63	-0.72	0.96	0.30	-0.30
NP3	0.93	0.50	-0.60	0.99	0.15**	-0.15
Corr.	TN	Av.P	TP	FeD	MnD	MnOx
NP0	-0.02	-0.74	0.83	0.85	0.41	0.85
NP1	0.39	-0.95	0.98	0.99	-0.01	0.99
NP2	-0.52	-0.30	0.44	0.47	0.81	0.47
NP3	-0.64	-0.15	0.29	0.33	0.89	0.33

**Correlation is significant at the 0.01 level (2-tailed); Corr. = correlation, Av. P = availability of P, Ex. A = exchangeable acidity, C = carbon, OM = organic matter, TN = total nitrogen, TP = total phosphorus; FeD = iron extracted by dithionite, MnD = manganese extracted by dithionite, MnOx = manganese extracted by oxalate; K = soil samples from Kiltu Kara, N = soil sample from Nedjo; P0 = cumulative phophate desorbed from control, P1 = cumulative phosphate desorbed from soil incubated with concentration of 50 mg P kg^{-1}, P2 = cumulative phosphate desorbed from soil incubated with concentration of 100 mg P kg^{-1}; P3 = cumulative phosphate desorbed from soil incubated with concentration of 150 mg P kg^{-1}.

CONCLUSION

In this study, desorption of phosphate from soils by using DMT filled with Fe-Al-Zr ternary composite was conducted. The desorbed-P increased with increasing added P and desorption time for all soil samples and high P release was observed on the 28th day. The study revealed cumulative P released over time followed the same pattern for all P-treated soils. The P desorption kinetics for all soil was found to follow first-order kinetics and the rate constants of P desorption by DMT-Fe-Al-Zr was found in the range from 0.535-0.613 day^{-1} for the soils studied. The ternary composite (Fe-Al-Zr) was found to exhibit high sorption capacity which makes the desorption process faster. Only fast releasing of P was attained during the experimental periods and no desorption of the stable phase was reached during the entire period of extraction time, indicating that desorption can continue for a longer period than 28 days. This information is paramount to properly characterize the P-supplying capacity of soils, to design P-fertilizer management to optimize efficiency, reduce environmental pollution, and to develop guidelines for the disposal of P-rich wastes. This technique could serve as an analytical tool to assess the availability of residual P in soils. However, assessment of the reliability of this method at greenhouse and field levels is important to check the application of this method for various soils.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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