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Tracking Materials with Low Phosphorus Adsorption for Use in Constructed Wetland Aiming at Wastewater Treatment for Irrigation Purposes

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Abstract

Wastewater is well known to contain significant amounts of essential crop nutrients including Phosphorus (P). Therefore, in the light of water reuse, nutrients available in wastewater need to be retained to serve as alternative source of plant nutrients for the crops to be irrigated by the effluent. P-adsorption experiments of four selected locally available substrate materials (dolomite marble, andesite, basalt and scoria) were conducted in laboratory. The aim of the study was to characterize the material and determine their P-Adsorption capacity, deduce their suitability for use as substrate material for constructed wetland aiming to treat wastewater for reuse in irrigation. It also aimed at establishing the baseline information for the available materials in Arusha. The chemical composition of each of the materials was determined using the XRF analysis method, and the P-adsorption capacity of each material was determined by studying the removal rates at different known P-concentrations (5, 10, 20 and 50). Highest P-adsorption capacity was observed in dolomite marble (99-100%) and lowest in andesite (40-46%). It is therefore concluded that with the aim of retaining phosphorus in the final effluent andesite, should be selected as a suitable substrate material for constructed wetland systems.

Keywords: Phosphorus adsorption; constructed wetland; wastewater treatment; irrigation; plant nutrients

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1. Introduction

Phosphate (P) is one of the essential elements for plant growth which its deficiency can lead to limited plant growth and ultimately crop yield. [3, 10]. Due to its importance, P has been traditionally supplemented by fertilizer application to soils deficient of it. The cost and accessibility of these fertilizers has been widely reported to be limited especially to smallholder farmers resulting to low crop yields. [20]. Therefore alternative reliable and affordable nutrient sources need to be sought.

Wastewater is well known to contain significant amounts of essential nutrients including phosphate [1, 26, 6].Therefore wastewater can be a good source of crop nutrient if it is treated in such a way that phosphate is retained in the final effluent such that the effluent is used as nutrient-source for crop production. In addition to the nutrients, treated effluent provides water needed for crop growth hence when used for irrigation it avails dual advantage [9, 7]. While this is true, it has been a tradition to employ wastewater treatment systems that are aimed at complete removal of the nutrients including phosphorus failing to tackle the benefit from wastewater. This has been done with the purposed of protecting the environment as phosphorus is one of the pollutant limiting algal growth in fresh waters [4]. But in the light of sustainable wastewater management, nutrient recovery becomes an important element to consider. Therefore, treatments aiming at meeting reuse criteria and later at meeting the discharge requirements need to be emphasised. Retaining nutrients such as phosphorus and nitrogen in the effluent for irrigation becomes the focus in this case.

One of the technologies used for wastewater treatment is constructed wetland whereby partially treated wastewater passes through a porous media [21]. Constructed wetland is known for its ability to handle variable wastewater loadings and the fact that it can be easily constructed, operated and maintained [15, 2, 27]. CW is also known to remove P content from the wastewater. Though the removal mechanisms and the dynamics of phosphorus are complex, many constructed wetlands (CW) are meant to remove it to the lowest levels possible. The main removal mechanism of phosphate is through adsorption [24, 23] which depends mainly on the physical and chemical properties of the substrate (P-retention) material. It follows that use of materials with high adsorption capacity and use of plants that uptake enough phosphorus can foster higher phosphorus removal capacity [8]. On the other hand the use of materials with less adsorption capacity can avail P in the final effluent. However it must be noted that, the adsorption capacity can as well be influenced to some extent by other factors such as chemical precipitation, bacterial immobilization, plant uptake and sediment accretion [23] though their influence to P removal can be minimal. Therefore with the purpose of retaining enough amounts of phosphorus in the effluent for use in agriculture, it is essential to use substrate materials with less P-adsorption capacity in constructed wetlands assuming that the other factors have less influence on P adsorption.

Several studies have been conducted to investigate the phosphorus adsorption capacity of different substrate materials. By using Laterite [16] reported P-removal efficiency of 89%. [18] did a study on limestone and found it to have a removal efficiency of 61%. Other studies done is on bauxite and alunite reported a removal efficiency of 67.3% and 80% respectively [25]. In all these studies the main focus contrary to the goal of study was to achieve higher phosphorus removal efficiencies while the interest in this study is to have lower removal efficiencies. In addition to this less is documented about the materials locally available the volcanic zones of Tanzania such as Arusha.

This study therefore, aimed at characterization, determination of the phosphorus adsorption capacity and documentation of the potential substrate materials (with low P-adsorption capacity) for use in constructed wetland so that at the end phosphorus is made available for crop growth when the effluent is used for agriculture. The need to reuse phosphorus follows the soil infertility problems in the area as reported by [19] and the high demand of irrigation water causing the people in the area use untreated wastewater for irrigation [14]. The scope of the study was limited to determination of the properties of the materials available in the area and understanding their adsorption capacity.

2. Materials and Methods

2.1 Selection of the materials

The selected substrate materials for the experiment were collected from Arusha Region and the neighbouring areas that are within the cenozoic volcanic zone. Arusha was selected for study because of the presence of unregulated urban agriculture using partially treated and untreated wastewater for irrigation and the reported soil infertility both of which calls for scientific research. The materials were selected based on their availability and suitability for use as substrate materials for constructed wetland systems. The interest was to have substrate material with low phosphorus adsorption capacity so that when used for treatment, significant amounts of phosphorus will be retained in the effluent ready to be used as nutrient for crop growth. The selected materials were andesite, scoria, basalt and dolomite marble. The first three were collected from within the municipality while the last one was collected from Mererani area which is very close to the Tanzanite mining quarries about 40km from Arusha city. Literature indicated that most of these materials have not been investigated for phosphorus removal except for basalt whose sorption ability have been investigated in Portugal and indicated a removal capacity of 270mg P/kg filling material [17].

2.2 Characterization of the materials

In order to understand the nature and composition of the materials under the study, the physicochemical analysis as well as the determination of the chemical composition was done. The analyses helped to deduce the behaviour indicated by the materials in P-adsorption.

The physicochemical parameters of the materials such pH, conductivity, Total Dissolved Solids (TDS), porosity, specific gravity and moisture content were measured at the Ngurdoto deflouridation centre laboratory of the ministry of Water. The choice of the parameters was based on their capacity to inform about experimental conditions and the nature of the materials. pH determines the degree of acidity or alkalinity which is important condition for experimentation, conductivity and TDS avails some information about the presence of the dissolved inorganic solids, porosity tells about how much pore spaces does the material have and the moisture content about the amount of water contained within the material. The porosity was measured using the fluid saturation method where the equivalent volume filled with water in the pore spaces was determined. Moisture content was obtained as a difference between the air dried and the oven dried weight after subjecting the samples to 103^0C for 12 hours. pH was measured using a pH meter (Orion5), TDS and conductivity were measured and conductivity meter (HACH SensION5) .

Samples for chemical composition were analysed at the Southern and Eastern African Mineral Centre (SEAMIC) laboratory in Dar es Salaam. As part of the sample preparation, at first step the sample materials were crushed with a jaw and roller crushers to fragments of < 2 cm, then the crushed sample was homogenised and split consecutively using a raffle splitter until the sample was reduced to about 300 g. The reduced sample was then pulverized in an agate mill, sealed in polyvinyl chloride (PVC) bags and submitted to the X-ray fluorescence (XRF) laboratory.

At the XRF laboratory, the analysis of the samples was done using the Semi quantitative XRF analysis method. In this method, the ground sample was pressed into a pellet using boric acid as binder. The HERZOG pellet maker machine was used to press boric acid and sample in the ratio of 7.00g boric acid: 5.00g sample; at 20kN with 15 second hold time. In the calculation the elements were calculated as metal oxides. The loss on ignition (LOI) was determined by furnace method and was inserted in the raw data for evaluation by the software. Checking of results was done by running certified reference materials (CRM). The program was recalibrated using Glass standard samples supplied by the manufacturer.

2.3 Phosphorus adsorption experiment

The collected materials were firstly manually crushed to make them available into smaller (0.1-0.7inch) sizes and then sieve analysis was conducted to retain particles with diameters in between 4.76mm and 9.53mm. The retained materials were thereafter cleaned with distilled water and air dried. The air dried and oven dried (103^0C for 12 hours) sample weights were determined using the weigh balance.

For the prepared materials, 250g of each was shaken for 48 hours in 300mls of 0.01M Potassium chloride (KCl) solution containing different concentrations of phosphate (5, 10, 20 and 50) at 150rpm and 25^0C temperature. The shaker was stopped at 0.5, 2, 4, 12, 18, 38 and 48 hours where 1ml of the sample was filtered and analysed for phosphate using the ascorbic method by a spectrophotometer (DR 2700). The phosphorus content that was not recovered in the solution was considered as the amount adsorbed by the media.

2.4 Data analysis

The results observed from the phosphorus adsorption experiment were compared with the properties of each material to deduce the possible cause of the behaviour exhibited. The P-values obtained for different materials were correlated and the plotted by *Origin version* 8 software. The P removal efficiencies of the different materials were analysed using the analysis of variances (ANOVA) to see whether there is statistically significant differences.

3. Results and discussion

The Semi quantitative XRF analysis of the four selected materials for phosphorus adsoption aiming at wastewater treatment for irrigation purposes showed the major physicochemical composition as presented in Table.1.

Table 1: Physicochemical properties of dolomite marble, scoria, basalt and andesite as substrate materials for CW

S/N	Parameter/Substrate type	Dolomite Marble	Scoria	Basalt	Andesite
1	pH	9.41	6.61	6.77	9.22
2	Conductivity (μS/cm)	26.9	15.7	28	51
3	TDS (mg/L)	12.7	7.7	13.8	25.1
4	Moisture content (g)	31.82	11.97	11.03	7.1
5	Specific gravity (g/cm^3)	2.87	1.98	2.43	2.37
6	Porosity	0.4310	0.4675	0.4775	0.4935

From the results, it has been indicated that dolomite marble had the highest pH value, moisture content and specific gravity while andesite had the high pH value, highest conductivity, TDS and most porous (Table 1). The pH values are however the recommended range for microbial activity (6-8) and the porosity of all the materials was within the recommended value for substrate materials for constructed wetlands which is 0.4 [23].
Results from table 2 indicate that dolomite marble is mainly composed of calcium and magnesium and small amount of the iron and aluminium. Its loss on ignition (LOI) is also higher as compared to the rest of the materials. Higher LOI value indicates that the material consist of significant amount of organic volatile substances [13]. Scoria, basalt and andesite are mainly composed of silicon and aluminium and small amounts of iron, calcium, sodium and potassium and they have relatively lower LOI values.

From the analysis of variance (Table 3) the calculated F value is very high as compared to the F limit value. This proposes that there is a statistically significant variation in the P removal efficiencies ($F (3, 12) = 3.49$, $p = .005$). This is also supported by the observations (Figure 1). The phosphorus removal efficiency of dolomite marble for example was the highest (99%-100%) with the highest values and fast removal rate at lower concentrations (Figure 1). This can be caused by the high levels of calcium and magnesium (Table 2) as reported in previous studies their presence can enhance phosphorus adsorption [12, 25]. The recorded removal efficiency is in agreement with the prior studies where marble has recorded removal efficiency of 94-99% [5, 25]. This implies that if dolomite marble is used as a substrate material in constructed wetland aimed to treat wastewater for reuse in irrigation, it will not avail phosphorus to the crops to be irrigated. Therefore is not recommended for use as a substrate material. However when wastewater treatment is meant to meet the discharge requirements and phosphorus removal is the target, dolomite marble can be good substrate as it will protect the environment by removing phosphorus of which would otherwise cause eutrophication to the receiving water bodies.

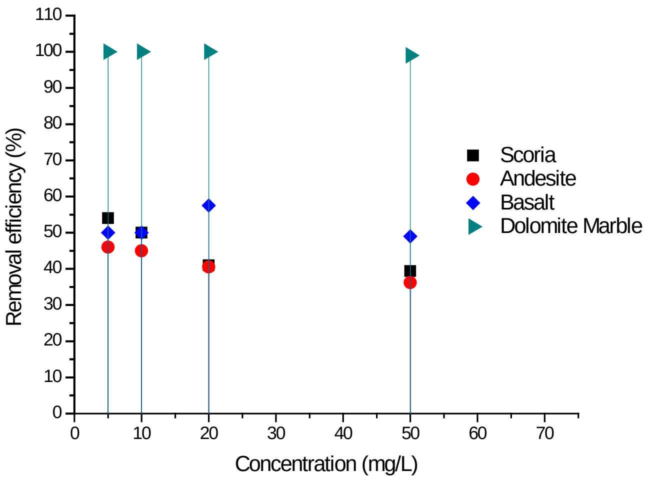

Figure 1: The removal efficiencies of the substrate materials at different concentrations

Table 2: Chemical composition of substrate materials for CW

Parameter	Dolomite Marble	Scoria	Basalt	Andesite
$Si0_2$ (%)	1.00	53.22	52.57	48.76
Al_20_3 (%)	0.63	19.33	18.99	19.40
SrO (%)	<0.01	0.17	0.18	0.24
Fe_20_3 (%)	0.21	6.47	6.65	7.14
MgO (%)	19.11	0.67	0.77	0.45
SO_3 (%)	0.07	0.08	0.07	0.07
CaO (%)	37.23	3.67	3.99	3.77
P_20_5 (%)	<0.01	0.44	0.40	0.27
Na_20 (%)	<0.01	7.88	7.97	9.22
Ti02 (%)	<0.01	1.35	1.37	1.26
CI (%)	<0.01	0.20	0.27	0.41
K_20 (%)	0.06	4.76	4.85	5.66
$Zr0_2$ (%)	<0.01	0.06	0.06	0.06
MnO (%)	<0.01	0.14	0.15	0.19
MoO_3 (%)	<0.01	<0.01	<0.01	0.37
BaO (%)	<0.01	0.22	0.20	0.25
LOI[a] (%)	41.69	1.29	1.34	2.27

[a]LOI=Loss on ignition which represent the amount of volatile substances within the materials

Table 3: ANOVA values for the P removal efficiencies for the potential substrate materials

	Removal efficiencies			
Concentration (mg/L)	**Scoria**	**Dolomite**	**Basalt**	**Andesite**
5	54	100	50	46
10	50	100	50	45
20	41	100	57.5	40.5
50	39.4	99	49	36.2
Mean (+SD)	46.1 ±6.09	99.75±0.43	51.625± 3.41	41.925±3.90
Source of variation	**SS**	**d.f**	**MS**	**F-Ratio**
Between sample	8680	(4-1)=3	2893.33	135.65
Within sample	256	(16-4)=12	21.33	
				F limit (from Table) F(3,12)=3.49

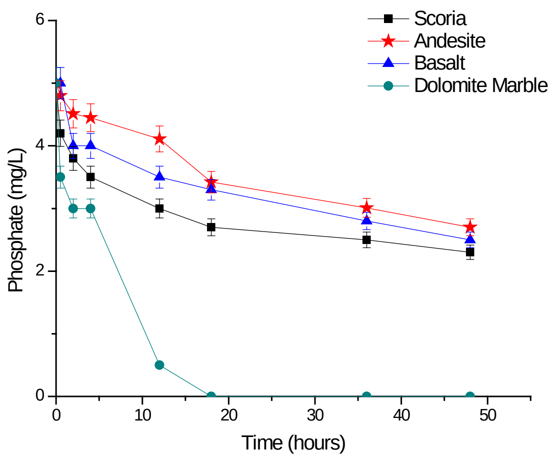

Figure 2: The phosphate removal trend of 5mg/L concentration at 25^0 C and shaking speed of 150rpm

The phosphate adsorption capacity of basalt, andesite and scoria are slightly comparable. Andesite indicated the lowest adsorption capacity with the lowest removal efficiencies of 40-46% (Figure 1). Basalt had the highest adsorption capacity and high removal efficiencies (49-58%) of the three except at the 5mg/L adsorption experiment where the removal efficient was lower than that of scoria that recorded the removal efficiencies of 39-54% (Figure 1). The results show that the three materials can be used as substrate materials for treating wastewater for irrigation though andesite emerges to be the best of the three. There was no clear record of the prior performance of the three materials in P adsorption from literature. Also, the authors feel that use of blended materials to change their properties and alteration of the experimental conditions would lead to different P adsorption behaviour hence this is an area recommended for further research.

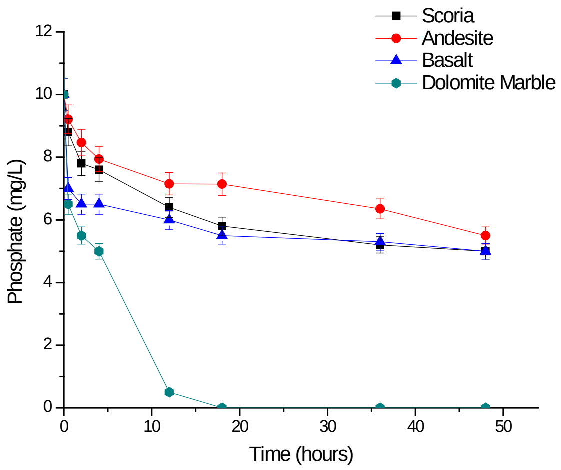

Figure 3: The phosphate removal trend of 10mg/L concentration at 25^0 C and shaking speed of 150rpm

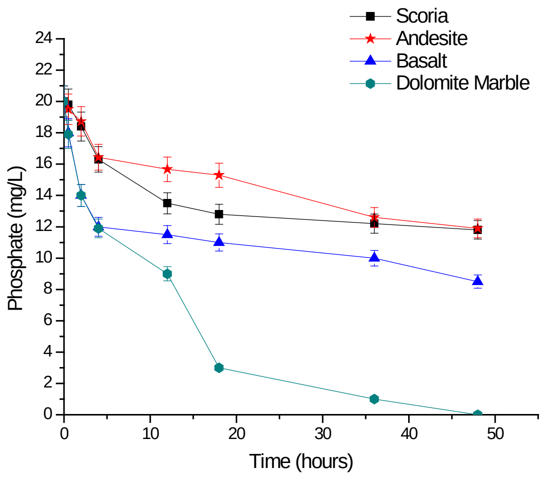

Figure 4: The phosphate removal trend of 20mg/L concentration at 25^0 C and shaking speed of 150rpm

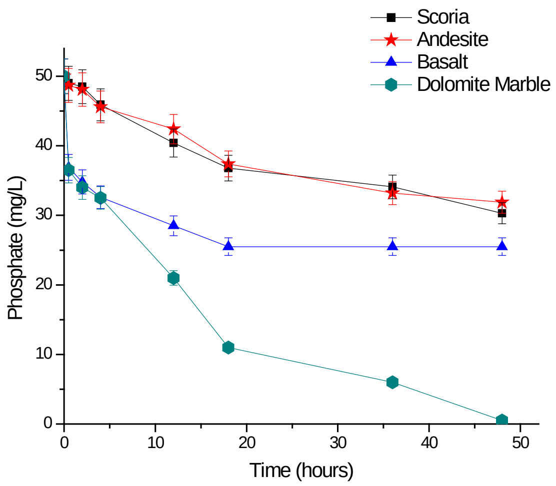

Figure 5: The phosphate removal trend of 50mg/L concentration at 25^0 C and shaking speed of 150rpm

Comparing the adsorption of the materials at different phosphate concentration, results indicate that the adsorption rate was the fastest for dolomite marble at lower concentration (Figure 2-5). Also the adsorption rate exhibited by andesite, basalt and scoria was with a relative constant removal rate at all concentrations (Figure 2-5). Though the reason for this behaviour is not known but can have been caused by the nature of the materials such as the presence of calcium and magnesium in dolomite marble that enhances the P adsorption.

Recalling from literature that the typical concentration of phosphorus in wastewater ranges from 6-20mg/L [11, 22], and with assumption that most municipal wastewater would contain the average levels, then it means that wastewater will follow the trend described by the 10mg/L phosphorus adsorption curve (Figure 3). In this case, the computed effluent phosphorus concentration would be 5mg/L, 5.5mg/L, 5mg/L and 0mg/L for scoria, andesite, basalt and dolomite marble respectively at the P removal rates shown in Figure 1. With this concentrations, the phosphate amount that can be retained in the final effluent at an application rate of $5000m^3$/ha.year would be 25kg/ha.year, 27.5kg/ha.year, 25kg/ha.year for scoria, andesite and basalt respectively. Therefore the phosphate fertilizer contribution to the soil when treated wastewater is used for irrigation is highest when andesite is used as a substrate material for P-adsorption in constructed wetland systems. The P fertilizer requirement for growing crops will however depend on a number of other factors such as the available P content, the crop P requirement and the soil P retention capacity.

The substrate material property has been highlighted in this article as the main factor affecting phosphorus removal in constructed wetland. This however does underrate the contribution of the other factors that influence P adsorption. Therefore these factors need to be considered as well before making a well grounded conclusion. For example, it has been pointed earlier that bacterial immobilization is one of the factors. This can have a significant contribution especially in constructed wetlands where bacterial growth is encouraged. Studies indicates phosphorus removal is also possible by filamentous mat-forming cyanobacteria, tropical cyanobacterium and purple photosynthetic non-sulfur bacterium to mention some [8].

4. Conclusion

Constructed wetlands as one of the treatment technologies need to be well designed so that it can render the effluent of desired quality. The type of substrate material used for constructed wetland can influence the removal of nutrients including phosphorus thus, when phosphorus need to be retained in the final effluent, proper selection of the substrate materials should be done. The selection can be guided by looking on the physical and chemical properties of the materials. Like in this study it has been confirmed that the presence of magnesium and calcium salts in a material can influence P-adsorption as it has been the case for dolomite marble which had significant amounts of magnesium and calcium salts.

Among the materials that have been investigated in this study, it has been shown that, andesite, basalt and scoria have lower adsorption capacity as compared to dolomite marble. Among the three, andesite had the lowest and best adsorption capacity in terms of rendering P in the effluent as nutrient. Therefore it has been recommended as the most suitable materials for use in constructed wetland systems when considering treatment for reuse in irrigation. The use of andesite can avail relatively significant amounts of phosphate that can be used as fertilizer needed to raise the crop. On the other hand dolomite marble had the highest phosphate adsorption capacity making it unsuitable when wastewater treatment is meant for agricultural reuse purposes. However further studies can be required for dolomite marble to see if it can be the suitable material for P removal when the target for treatment is to meet the discharge requirements. These recommendations have been done merely based on its P adsorption capacity but it should be noted that the overall suitability of the material to be used as a substrate material for CW may involve consideration of other factors as well.

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