



Suitability of Moshi Pumice for Phosphorus Sorption in Constructed Wetlands

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KEYWORDS: Phosphorus sorption; Sorption Equilibrium; Sorption Models; Behaviours and Properties.

ABSTRACT: The study of Moshi Pumice's phosphorus sorption behaviours and properties was carried out in laboratory scale where by 1-2 mm, 2-4 mm and 4-8 mm grains were tested using batch experiments. The results show that Moshi Pumice has high phosphorus sorption capacity. The sorption capacity for the Moshi Pumice was 2.5 g P/kg. For 1-2mm and 4-8mm grains; about 50% of phosphorus sorption in Moshi Pumice occurs in the first 18 and 20 hours, respectively. Compared to 4-8mm and 2-4mm grains, temperature didn't significantly influence phosphorus sorption on 1-2mm grain. Moshi Pumice has high potential for phosphorus removal from wastewaters and it can be recommended to be used as a substrate in constructed wetlands to remove phosphorus. © JASEM

<http://dx.doi.org/10.4314/jasem.v18i1.19>

Introduction: Phosphorus (P) is an essential macronutrient in all organisms. However, loadings of phosphorus in effluent discharges are detrimental to the quality of receiving surface water bodies. Phosphorus concentrations in excess of allowable levels have been associated with algal blooms, which lead to the eutrophication of lakes and rivers. Eutrophication occurs when surface waters become over-enriched with nutrients such as nitrogen and phosphorus. This stimulates plant and algal growth, which subsequently dies and decomposes; thereby reducing, dissolved oxygen concentrations in water columns, which is detrimental to aquatic life. For this reason, the treatment of wastewater is necessary to correct its characteristics in such a way that the use or final disposal of treated effluent can take place without causing an adverse impact on the ecosystem of the receiving water bodies (Headley *et al*, 2001).

Subsequently, many technologies in association with management systems have been devised both to prevent and mitigate the loss of phosphorus, which can cause eutrophication of surface waters. One approach, which is a land-based ecologically engineered method, is the use of wetlands. Wetland ecosystems both constructed and natural are becoming important mitigating measures in water resource management around the world, as they have the ability to cycle and retain nutrients such as phosphorus (Braskerud, 2002).

Phosphorus removal in wetlands mainly occurs by sorption and plant uptake. Phosphorus sorption in wetland substrates occurs by adsorption and precipitation. Phosphorus retention in the substrate via adsorption and precipitation is controlled by properties of the substrate (Fe, Mg, Al-, Ca-minerals, specific surface area and porosity) and the physico-chemical environment (pH, redox potential, dissolved ions) (Grüneberg and Kern, 2001).

Wetland substrates (e.g. clay, soil, gravel) for wastewater treatment are normally not considered efficient for continual removal of phosphorus. Phosphorus removal above 20-30% in long-term monitoring (> 5 years) is seldom reported. So, in order to achieve high phosphorus removal, specialized substrates which are effective in sorption of phosphorus like granite, limestone, metal oxide-rich natural sands, mining industry by-products and slags (Salnacke, 1999) are to be used in a subsurface flow constructed wetland or in a vertical flow column. The capacity for phosphorus sorption is finite in all media and longevity with respect to phosphorus sorption depends on the loading rates. The design regarding phosphorus removal in substrates with high phosphorus sorption is quite different from other water quality parameters, the intention being to exhaust a short-term capacity, regenerate the filter and repeat the cycle (Braskerud, 2002).

Moshi Pumice is a substrate that is rich in minerals that facilitate sorption of phosphorus. Test results have shown that Moshi Pumice substrate has a high potential for phosphorus removal compared to granite, gravel and clay soil (Njau *et al*, 2002). However, little is known about its behaviours and properties in sorption of phosphorus and its potential for the use as constructed wetland substrate.

MATERIALS AND METHODS

Moshi Pumice is the material (substrate) used in this study. It is a potential filter media in constructed wetlands. It is a porous and volcanic, found near the slopes of Mount Kilimanjaro, collected from a village known as *Uchira* about 15 km from Moshi town.

The chemical composition of Moshi Pumice was analyzed by X-ray fluorescence (XRF) technique. Crushed soil particles of less than 420 μm were dried in an oven at 110°C to determine moisture content. A known weight of the dried sample was used to

determine loss on ignition at 1,100°C. The calcined sample was mixed with sodium borohydrate at a ratio of 1:9 w/w, respectively. The mixture was melted to obtain the specimen disc for the XRF analysis. The porosity and the specified surface area of the substrate was measured by the Brunauer Emmett and Teller (BET) standard method for particle sizes ranging from 125 $\mu\text{m} < d < 420 \mu\text{m}$. The particle density of the substrate was measured by displacing water by a known mass using stopped bottle. Particle sizes less than 420 μm were used.

Study of Phosphorus Sorption Behaviours: Phosphorus sorption experiments in batch experiments were carried out at ambient temperature with a slow rotating shaker (25 rpm) to avoid material alteration as shown in plate 1. Only one experiment was carried out for each sorption behaviour experiment and four samples of each experiment were analyzed.



Plate1: Phosphorus sorption experiments in a slow rotating shaker

The analysis of phosphorus sorption behaviours of the substrates involved, determination of Phosphorus sorption isotherms, determination of Phosphorus sorption capacity of the substrates, determination of Phosphorus sorption as the function of time and determination of effect of temperature on the phosphorus sorption.

To determine phosphorus sorption isotherms, twelve 8 g samples of each substrate grain size (1-2mm, 2-4mm, and 4-8mm) were suspended in 200ml of solution containing different phosphorus concentrations (0, 2, 4, 8, 16, 20, 40, 80, 160, 320, 600 and 1200 mg P/L). The solutions were filled in 300 ml glass bottles. The bottles with incubated solutions were placed on a 25-rpm shaker for twenty-four hours. The experiment was kept at 8 pH using NaOH and room temperature (28°C - 29°C). The

solutions were filtered with a 0.45 μm filter membrane and the filtrates analyzed for phosphorus (APHA, AWWA and WEF, 1998). The phosphorus sorption isotherms (expressed in mg P/Kg substrate) were calculated from the change in the phosphorus concentration of the contact solutions, per mass of the substrate, times the volume of the solution in the flask.

To study phosphorus sorption as a function of time experiment, four 300ml glass bottles were employed. The bottles were filled with 200 ml solutions containing phosphorus concentration of 20 mg P/L, and 8g of substrates. In this experiment, grain sizes used, were 1-2mm, and 4-8mm. Then the bottles with incubated solutions were placed on a slow rotating shaker (25 rpm) where contact time was varied from 1 to 300 hours. The experiment was kept at 8 pH

using NaOH and room temperature (28°C - 29°C). The solutions were filtered with a 0.45 µm filter membrane and the filtrates analyzed for phosphorus (APHA, AWWA and WEF, 1998).

To investigate the effect of temperature on phosphorus sorption, twenty-four 300ml glass bottles were employed. One 8g sample of each substrate grain size (1-2mm, 2-4 mm, and 4-8mm) were suspended in 200 ml of solution with phosphorus concentration of 30 mg P/L. The experiment was conducted at 35°C water bath (Julabo type, ECO Temp TW8, German), and at 21°C, 40°C, and 45°C incubator (WTB binder type, model 720, German) for twenty-four hours. The experiment was kept at 8 pH using NaOH. The solutions were filtered with a 0.45 µm filter membrane and the filtrates analyzed for phosphorus (APHA, AWWA and WEF, 1998).

Statistical Validity of Data: For all treatments in the experiment, four replicates were used. The data used in all the discussion are the mean values of the four

replicates. ANalysis of VAriance (ANOVA) and Regression analysis was performed.

For ANOVA statistical test, a single test was performed to see if there are significant difference on phosphorus sorption between the three grain sizes (1-2 mm, 2-4 mm and 4-8 mm) of the Moshi Pumice substrate at 95% Confidence Interval (0.05 probability level).

Linear Regression analysis was used for determining the relationship between, the amount of phosphorus sorbed by the substrate and phosphorus concentration, the amount of phosphorus sorbed by the substrate and temperature and the amount of phosphorus sorbed by the substrate and time.

RESULTS AND DISCUSSION

The physical properties and chemical composition of the substrates are presented in Table 1 and Table 2, respectively.

Table 1: Physical Characteristics of Moshi Pumice Substrate

| Average particle diameter (mm) | Specific surface area, (mm ² /g) | Porosity | Particle density (kg/m ³) | pH |
|--------------------------------|---|----------|---------------------------------------|-----|
| 1 | 13.35 | 66% | 2617 | 7.9 |

Table 2: Chemical Composition of Moshi Pumice Substrate

| Al ₂ O ₃ % | CaO % | MgO % | Fe ₂ O ₃ % | MnO % | (Na ₂ O + K ₂ O) % | SiO ₂ % | P ₂ O ₅ % | TiO ₂ % | LOI % |
|----------------------------------|-------|-------|----------------------------------|-------|--|--------------------|---------------------------------|--------------------|-------|
| 19.2 | 1.3 | 0.69 | 5.13 | 0.05 | 6.7 | 61.9 | 0.04 | 0.51 | 4.4 |

As presented in Table 1, the analyzed physical properties of the substrate were specific surface area, porosity, pH and Particle diameter and density. The specific surface area and porosity are an indirect measure of the surface available for the adsorption of phosphorus although it depends also on the density of the active sites on the material.

As presented in Table 2, the analysis shows that Moshi Pumice substrate has high levels of Al and Si. The high levels of Al and Si are the positive indicator of its potential for phosphorus precipitation.

The phosphorus sorption isotherms obtained for different Moshi Pumice grain sizes are presented in Figure 1. Above 400 mg P/L, the sorption curves showed no significant change indicating that the maximum sorption capacity of the substrate has been reached. According to this analysis, the maximum sorption capacities for the substrate were 2500 mg P/Kg, 2200 mg P/Kg and 2100 mg P/Kg for the grains 1-2 mm, 2-4 mm and 4-8mm, respectively.

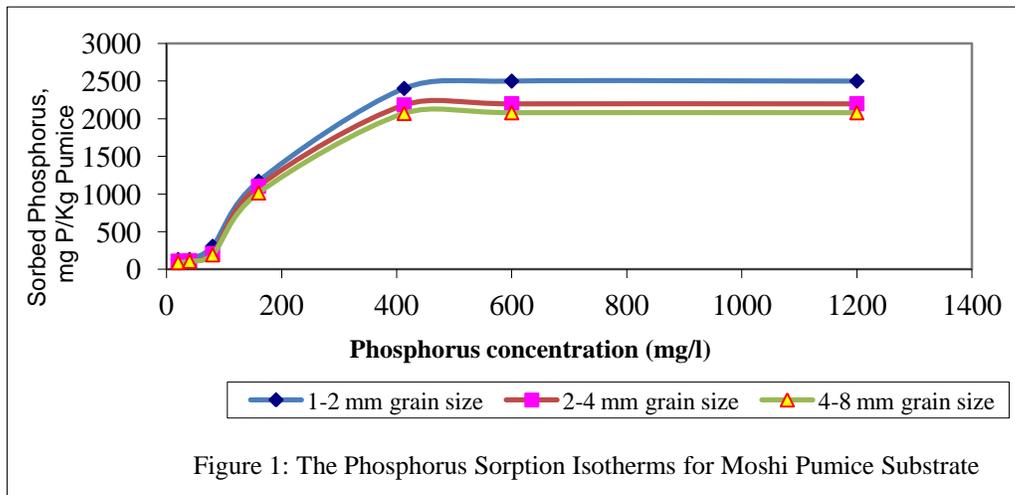


Figure 1: The Phosphorus Sorption Isotherms for Moshi Pumice Substrate

The tabulated value of F at 95% Confidence Interval is 4.3. The calculated F value ($F = 192397.43$) exceeds this tabulated F value ($F = 4.3$) at 95% Confidence Interval. So there is a significant difference between in phosphorus sorption between Moshi Pumice grains (i.e. 1-2 mm, 2-4 mm and 4-8 m).

Freundlich model is useful for describing physical sorption. The model can represent non linear sorption of phosphorus from solution. The model equation is exponential and is represented by equation (1) (Volesky

$$Q = KC^{\frac{1}{n}} \dots\dots\dots (1)$$

where, Q = the amount sorbed C = equilibrium concentration, mg/L K = dimensionless Freundlich constant, indicator of the sorption capacity. n = dimensionless Freundlich constant, indicator of the sorption intensity. The sorption (Q) to concentration (C) relationship by Freundlich model is presented in Figure 2 and equations 2-4.

$$1 - 2mm : \text{Log}(Q) = 0.807 \text{Log}(C) + 1.169$$

$$R^2 = 0.945 \dots\dots\dots (2)$$

$$2 - 4mm : \text{Log}(Q) = 0.887 \text{Log}(C) + 0.916$$

$$R^2 = 0.944 \dots\dots\dots (3)$$

$$4 - 8mm : \text{Log}(Q) = 0.989 \text{Log}(C) + 0.626$$

$$R^2 = 0.952 \dots\dots\dots (4)$$

Sampling during the first day and increasing the incubation time to 360 hours obtained a curve. Figure

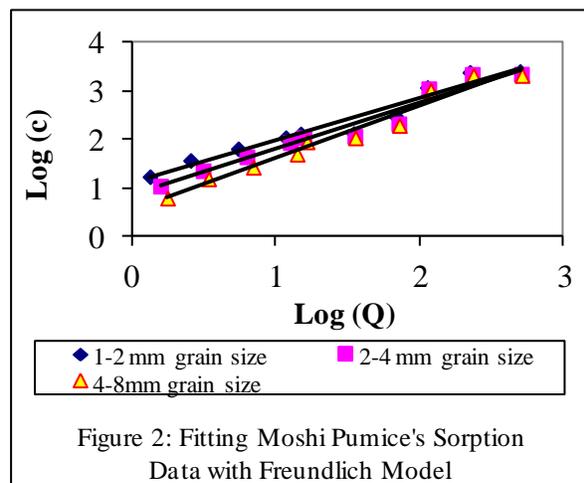


Figure 2: Fitting Moshi Pumice's Sorption Data with Freundlich Model

Since the relationship of Log (Q) & Log (C) is linear with a maximum of $R^2 = 0.9$, it indicates that the Freundlich model fitted all the sorption isotherms data quite satisfactorily hence the correlations are acceptable and the model can be use in prediction and verification of the amount of phosphorus sorbed at any equilibrium concentration.

Under the same conditions, the difference between the phosphorus sorption behaviours of the fine and coarse grain is attributed to the large sorbing surface area of the finer medium and the more easily released metal ions in the finer medium. This can be verified by equation 2 where by the grain 1-2 mm has the highest sorption capacity coefficient ($k = 14.76$) compared to the others.

3 presents the effect of incubation time on the sorbed phosphorus at different grain sizes of Moshi Pumice

substrate. For each case concentration of 20 mg/l of phosphorus was added.

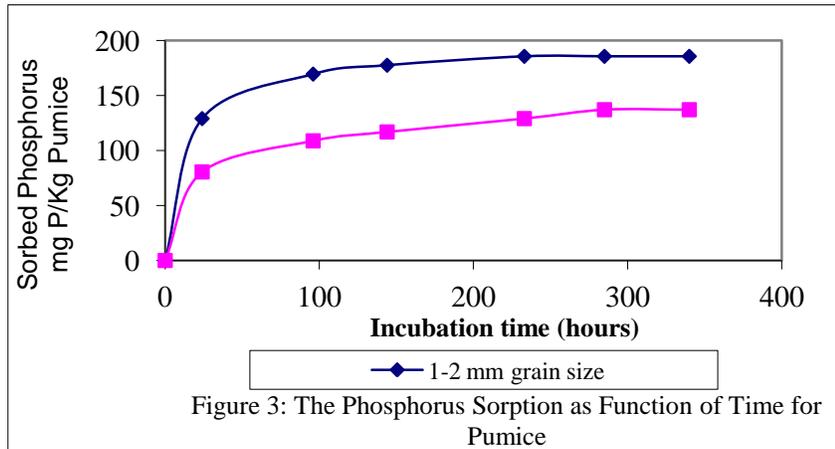


Figure 3: The Phosphorus Sorption as Function of Time for Pumice

Michaelis-Menten equation was adopted to express the phosphorus sorption as a function of time. The model equation is presented by equation (5).

$$Q_{(t)} = (Q_{max} * t) / (k + t) \dots(5)$$

Where, t = incubation time (hr). $Q_{(t)}$ = the amount of sorbed phosphorus (mg P/Kg substrate) at time t. Q_{max} = the maximum phosphorus sorption at a certain phosphorus loading (mg P/Kg substrate). k = constant, when 50% of the maximum sorption occur.

To determine the constants k and Q_{max} , the Lineweaver-Bulk analysis method of linearizing substrate-sorption data was used. When the sorption

activity follows Michaelis-Menten Model, a reciprocal plot of $1/Q$ vs $1/t$ is made. From this plot; Y-intercept = $1/Q_{max}$, X-intercept = $-1/k$, and slope = k/Q_{max} . The $1/Q$ - $1/t$ relationships by Lineweaver-Bulk analysis method for the 1-2 mm and 4-8 mm grain sizes of the substrates are presented in Figs 4, while the Q - t relationships by Michaelis-Menten model for the same grain sizes are presented in equations 6-7.

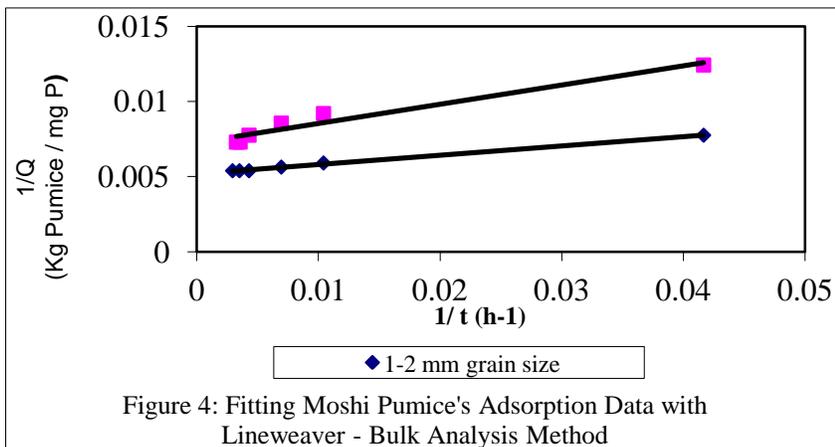


Figure 4: Fitting Moshi Pumice's Adsorption Data with Lineweaver - Bulk Analysis Method

Michaelis-Menten Model Equations for the Moshi Pumice Substrate is as described by equations 6 & 7

(1-2 mm): $Q_{(t)} = (192.3 * t) / (11.9 + t)$ $r^2 = 0.998$ (6)

(4-8 mm): $Q_{(t)} = (137 * t) / (17.4 + t)$ $r^2 = 0.956$ (7)

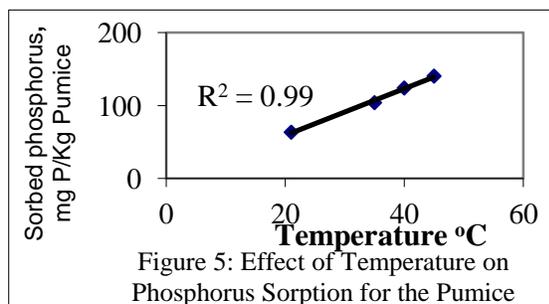
From equations 6-7, the highest phosphorus sorption of the two tested grain sizes when phosphorus

concentration in the initial solution was 20 mg P/L are 192.3 and 137 mg P/Kg Moshi Pumice for the

grains 1-2 mm and 4-8 mm respectively. It took longer time for the coarse substrate and shorter time for the fine substrate to reach sorption equilibrium. For 1-2 mm and 4-8 mm grains, 50% of the phosphorus sorption in Moshi Pumice substrate occurs in the first 18 and 20 hours, respectively. It takes about 233 hours and 285 hours for 1-2mm and 4-8 mm grains, respectively, to reach the sorption equilibrium when the phosphorus concentration in the initial solution was 20 mg P/L. The results of effect of temperature on phosphorus sorption are presented in Table 3 and Figure 5.

Table 3: Effect of Temperature on Phosphorus Sorption

| Sorbed phosphorus at different temperatures | 1-2mm | 2-4mm | 4-8 mm |
|---|-------|-------|--------|
| 21°C | 101.8 | 81.9 | 63.4 |
| 35°C | 120 | 111 | 103.9 |
| 40°C | 136.3 | 128.2 | 124 |
| 45°C | 152.5 | 144.4 | 140.3 |
| Average Decrease (%) | 33 | 43 | 57 |



These results show that the phosphorus sorption increases as temperature increases. With the treatment of 20 mg P/L in the original incubation solution, a temperature increase from 21°C to 45°C for the substrate led to an increase in phosphorus sorption of 33%, 43% and 57% for 1-2mm, 2-4mm and 4-8mm grains, respectively. The plot of sorbed phosphorus versus temperature gives a linear relationship (Figure 5). High temperatures increase the activity of the metal ion and thus increase the rate of metal ion transfer.

Conclusions and Recommendations: The grain size of the tested Moshi Pumice can influence sorption of phosphorus. The finer the grain sizes the higher the phosphorus sorption. The substrate has high sorption capacity. Since phosphorus concentrations in the sewage are normally in the range of 5-15 mg P/L (Metcalf and Eddy, 1998), the Moshi Pumice substrate will assure that a bed of the substrates can

be used for phosphorus removal in sewage for a long duration without being overloaded. From phosphorus sorption as a function of time experiment, it takes longer time (233 hours) for the coarse substrates (4-8 mm grains) and shorter time (285 hours) for the fine substrates (1-2 mm grains) to reach sorption equilibrium. Fine substrates has high removal rate. There was an effect of temperature on phosphorus sorption. Temperature has higher effect on the coarse size than the finer size. As the temperature increases the sorption of phosphorus increases. Based on the studies and tests carried out, the substrate has high potential in phosphorus removal. It can be recommended to be used as a substrate in constructed wetlands to remove phosphorus.

Acknowledgements: I would like to express my special thanks and appreciation to all those who helped me in completion of this research work. I would like to give my special thanks and appreciation to my supervisors, Prof. T.S.A. Mbwette and Prof. K.N Njau for giving me support, advice and comments during the conduct of this research.

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