



Comparative study of phosphorus sorption characteristics and behaviours of Kilimanjaro-Pumice and Rungwe-Pumice wetland soils

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Abstract

Kilimanjaro-Pumice and Rungwe-Pumice soils are potential media for phosphorus removal in constructed wetlands. The characteristics and behaviours of these soils in phosphorus sorption were carried in batch experiments at laboratory scale by which three varied sizes of Kilimanjaro-Pumice and Rungwe-Pumice soils were tested. For the phosphorus sorption isotherms, the findings reveal that Kilimanjaro soil has high ability in sorbing phosphorus compared to Rungwe-Pumice soil. The capacities for the Kilimanjaro-Pumice and Rungwe-Pumice soils in phosphorus sorption were 2.50 and 2.20 grams Phosphorus per kilogram of soil, respectively. For finer (1-2mm) and courser (4-8mm) particle sizes; about fifty percent of sorption in Kilimanjaro soil occurred in the 18th and 20th hour, correspondingly, while for Rungwe-Pumice soil, it occurred in the 17th and 18th hour, correspondingly. They were no significant influence of temperature on sorption of phosphorus for the finer particle when compared to 2-4mm and 4-8mm particle sizes. Both Kilimanjaro-Pumice and Rungwe-Pumice soils have good capacity in reducing phosphorus from wastewater. They are suggested to be utilized as constructed wetlands soils for removal of phosphorus.

Keywords: Constructed wetland, phosphorus, sorption, wastewater.

Introduction

Phosphorus is a vital nutrient in living things. Nevertheless, discharges of phosphorus in excess are pollute the environment. The phosphorus concentrations above permissible discharge limits are connected to rapid increase of algae (algal-blooms) that cause the eutrophication in surface water bodies. The phenomenon happens while surface waters become overly enriched with phosphorus and/or nitrogen. This promotes the growth of algae and plants which that afterward they die and decompose. Decomposition of dead algal and plant blooms is associated with abrupt dropping levels of dissolved oxygen in those waters as the result it causes death of aquatic living organisms. Due to this fact, wastewater treatment is compulsory to reduce the levels of pollutants to permissible discharge limits^{1,2}.

Furthermore, many wastewater treatment technologies have been developed to control discharge levels of phosphorus by which one of the methods is the use of constructed wetlands. Constructed wetland systems are becoming important wastewater treatment method globally, since they have the capacity to retain and cycle phosphorus^{2,3}.

Phosphorus elimination or reduction in constructed wetlands mostly takes place by plant uptake and sorption. Sorption of Phosphorus in soils of constructed wetlands takes place by processes such as chemical bonding and adsorption. Retention of phosphorus in the soil via chemical bonding is influenced by

physico-chemical characteristics of the soil such as Iron (Fe), Magnesium (Mg), Aluminium (Al), Calcium (Ca), specific surface area and porosity and the physico-chemical environment such as pH, redox potential and dissolved ions^{3,4}.

Wetland soils such as gravel, clay and soil are usually not capable for constant removal of phosphorus in wastewater. For long-term investigations i.e. above five years, the reduction of phosphorus over 20% in wetlands is rarely reported. For achievement of high removal in phosphorus, a variety of soils that are rich in minerals have been tested. Those soils include natural soils that are rich in metal oxide, granite, by-products from mining production, limestone and slags⁴ by which among them have very high capacity in sorption of phosphorus².

Kilimanjaro-Pumice and Rungwe-Pumice are soils that have abundance of minerals required for retention of phosphorus through sorption process². Research findings have revealed that Kilimanjaro-Pumice soil has higher potential in reduction of phosphorus than gravel, clay soil, and granite⁵. However, slight is known about the phosphorus sorption characteristics and behaviours of Kilimanjaro-Pumice and Rungwe-Pumice soils².

Materials and methods

Soil origin: The soils used in this study were Kilimanjaro-Pumice and Rungwe-Pumice. Kilimanjaro-Pumice is the soil from Moshi region in Tanzania. It is a volcanic and porous soil found adjacent the slopes of Mountain Kilimanjaro. Rungwe-

Pumice is the soil from Mbeya region in Tanzania. The soil is also a volcanic and porous material found adjacent to slopes of Mountain Rungwe. Rungwe-Pumice soil is light in weight and colour when compared to Kilimanjaro-Pumice soil².

Determination of soil characteristics: Determination of soil characteristics involved determination of composition, porosity, surface area and density of Kilimanjaro-Pumice and Rungwe-Pumice soils. The compositions of the Kilimanjaro-Pumice and Rungwe-Pumice soils were examined by instrument known as XRF (X-ray fluorescence). Soil particles were reduced to sizes of less than four hundred and twenty micrometer and they were dried-up at a temperature of 105°C in an oven to remove moisture. The dried sample was mixed with NaBH₄ (sodium boro-hydride). The mixed content was liquefied to get the specimen to be examined by XRF technique. The densities of the soils were established by water displacement method. Brunauer Emmett and Teller (BET) method was used to establish the specific surface area and porosity of the soils and the particle diameters used ranged from 125µm to 420µm^{2,5}.

Experiments designed for the assessment of behaviors in phosphorus sorption: Artificial wastewater containing phosphorus solution was prepared in laboratory. Known concentrations of phosphorus solution and known weight of pumice soils were placed 300ml glass bottles. Experiments were conducted in batch at room temperature. In order to avoid the alteration of materials, the bottles were placed on a shaker revolving at 25rpm. For each experiment for the study of phosphorus sorption behaviors, one experiment was conducted and 4 samples were examined. The examination involved the determination of, isotherms for sorption of phosphorus, capacity of soils in sorption of phosphorus, variation of phosphorus sorption with time, influence of temperature on the sorption of phosphorus².

Determination of isotherms for sorption of phosphorus: 12 samples of varying concentration (0, 2, 4, 8, 16, 20, 40, 80, 160, 320, 600 and 1200mgP/L) were placed in 200ml phosphorus solution in 300ml glass bottles. Pumice soils of 8gm each with varying particle sizes (1-2mm, 2-4mm, and 4-8mm) were placed in the same solution. Then the bottles with mixture of phosphorus solutions and pumice soils were positioned on a slow revolving shaker which rotates at 25 revolutions per minute for 24 hours and incubated in 30°C water bath. The pH was maintained at 8. After that the solutions were screened using a 0.450µm screen and the liquid part were examined for the phosphorus².

Determination of variation of sorption with time: Four bottles were filled with 200ml solutions which each hold 20.0 mg of phosphorus per litre and 8gm of soils. The particle sizes employed were 1-2mm and 4-8mm. After that the bottles containing a mixture of phosphorus solution and pumice soils were positioned on the slow revolving shaker and incubated in 30°C water bath. The time was changed from 1 to 300 hours.

The pH was maintained at 8. After that the solutions were screened using a 0.450µm screen and the liquid part were examined for the phosphorus².

Determination of influence of Temperature on sorption of Phosphorus: 24 glass bottles of 300ml volume were used. Each particle size (i.e. 1-2mm, 2-4mm, and 4-8mm) were placed in 200ml phosphorus solution that hold a concentration of 20 mg/L. This experimentation was carried out in the incubator set at varying temperatures of 21°C, 35°C, 40°C and 45°C for 24 hours. The pH was maintained at 8. After that the solutions were screened using a 0.450µm screen and the liquid part were examined for the phosphorus².

Examination of Ortho-Phosphate Phosphorus (PO₄-P): Ascorbic Acid Method according to standard methods for examination of wastewater was used to determine phosphorus concentrations in the solution⁶.

Sorption Isotherms: Isotherms are lines drawn on a graph or plot linking all points of equal or constant temperature. Phosphorus sorption isotherms are useful to quantify phosphorus sorption processes by soils or soils⁷. They are usually measured by mixing a known amount of soil or soil with a solution containing a range of known phosphorus concentrations. Soil solutions are equilibrated (by shaking) for 24 hours at a constant temperature. The difference in amounts of phosphorus sorbed and recovered in solution at each concentration after equilibrations are considered to be phosphorus sorbed by soil or soil⁶. The phosphorus sorption isotherms were described using Freundlich and Michaelis-Menten Models. A best-fit model can be predicted using linear regression correlation coefficient values. High correlation coefficient values (0.85 – 1) confirm the applicability of the model for design calculations^{2,8-11}.

Freundlich Sorption Model: This model is helpful in explaining sorption isotherms for batch experiments. It can stand for nonlinear sorption behaviours¹². The equation by *Freundlich* model is shown in equation (1)¹².

$$Q = KC^{1/n} \quad (1)$$

Where: Q = amount sorbed (mg/g), K = Freundlich constant (indicator of the sorption capacity), C = concentration in solution phase, mg/L, n = Freundlich constant (indicator of the sorption intensity).

Michaelis-Menten Sorption Model: This model was taken on to demonstrate the phosphorus sorption as a function of time⁶. The equation by *Michaelis-Menten* is shown in equation-(2)¹³.

$$Q_{(t)} = (Q_{\max} * t)/(k + t) \quad (2)$$

Where: Q_(t) = amount of sorbed phosphorus (mg P/Kg soil) at time t, Q_{max} = the maximum phosphorus sorption at a certain

phosphorus loading (mg P/Kg soil), t = incubation time (hour) and k = constant, when fifty percent (50%) of the maximum sorption occur.

In order to establish the constants Q_{max} and k , the Line weaver Bulk method was employed to transform soil-sorption data into linear (linearise). If the sorption data tag along *Michaelis-Menten* Model then a graph of reciprocal of Q_t against a reciprocal of t (time) as the result Y-intercept is represented by $(1/Q_{max})$, X-intercept by $(-1/k)$, and slope by (k/Q_{max}) .

Statistical validity of data: The statistical tests that performed include ANOVA, Student t-test and Regression analysis. At each experiment/test, four replicates were used. Student t-test and ANalysis of VAriance (ANOVA) was executed at a probability level of 0.05 (95% Confidence Interval) to check if there is considerable variation in averages concentrations of sorbed phosphorus. ANalysis of VAriance (ANOVA) was used for detecting significant difference among the three chosen particle sizes of each soil. Student's t-test was used to detect if there is considerable variation in phosphorus sorption among Kilimanjaro and Rungwe soils. Linear Regression analysis was engaged in order to establish a correlation between; the amount of sorbed phosphorus and the concentration of remaining phosphorus in the solution, the amount of sorbed phosphorus and temperature and the amount of sorbed phosphorus and the

time spent. The data used in all the discussion are the mean values of the four replicates².

Results and discussion

Physico-chemical Characteristics of the Soils: Chemical characteristics of the pumice soils are shown in Table-1 while physical characteristics of the same soils are shown in Table-2.

The analysis in Table-1 demonstrates that Kilimanjaro-Pumice when compared to Rungwe-Pumice soils has elevated levels of Magnesium (Mg), Aluminium (Al), Calcium (Ca), and Iron (Fe). The elevated levels of the mentioned minerals in Kilimanjaro-Pumice soil are the affirmative sign of its ability for sorption of phosphorus².

The analysis in Table-2 illustrates that Rungwe-Pumice soil when compared to Kilimanjaro-Pumice soil has high specific surface area and porosity values. Porosity, specific surface area and the density of the active sites on the soil are indirect gauge of the surface present for the phosphorus adsorption².

Isotherms for sorption of phosphorus by the Kilimanjaro-Pumice Soil: The isotherms for sorption of phosphorus found from the three particle sizes of Kilimanjaro-Pumice are shown in Figure-1².

Table-1: Chemical Characteristics (Composition) of Kilimanjaro-Pumice and Rungwe-Pumice Soils.

Material Name	Al ₂ O ₃ %	CaO %	MgO %	Fe ₂ O ₃ %	MnO %	Na ₂ O %	SiO ₂ %	P ₂ O ₅ %	TiO ₂ %	K ₂ O %	LOI %
Kilimanjaro-Pumice ⁵	19.2	1.3	0.69	5.13	0.05	3.12	61.9	0.04	0.51	3.58	4.4
Rungwe-Pumice	17.8	1.13	0.39	3.38	0.2	4.58	61.2	0.20	0.87	6.50	3.6

Table-2: Physical Characteristics of Kilimanjaro-Pumice Soil Compared to Rungwe-Pumice Soil.

Material Name	Soil particle diameter (mm)	Soil particle density (g/cm ³)	Specific surface area, (mm ² /g)	Soil Porosity	Soil pH
Kilimanjaro-Pumice ⁵	1.000	2.617	13.350	66%	7.9
Rungwe-Pumice	1.000	2.246	15.250	69%	8.5

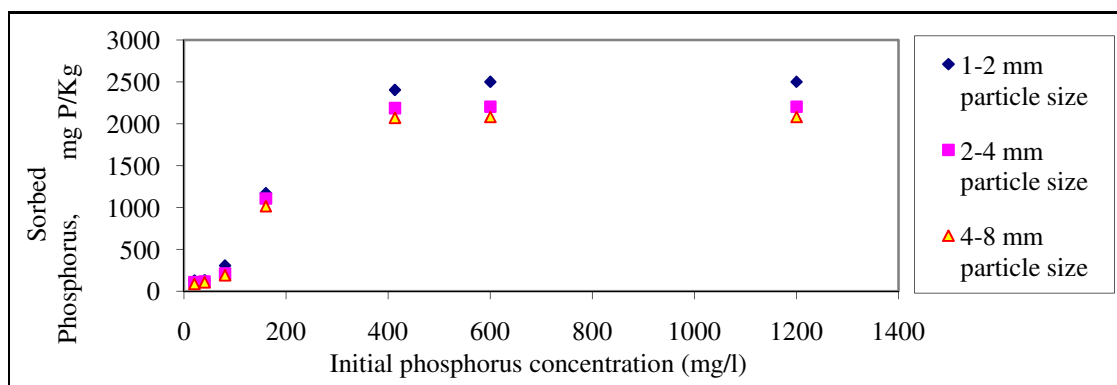


Figure-1: Isotherms for Sorption of Phosphorus by Kilimanjaro-Pumice Soil.

When the concentration in the equilibrated solution was 1000 - 1200 mg P/L, the particle size 1-2mm sorbed a large amount of phosphorus (about 2500mg P/Kg Kilimanjaro-Pumice) compared to 2-4mm and 4-8 mm particles which sorbed about 2200 and 2100mg P/Kg, respectively. It can be seen from the phosphorus sorption curves that the phosphorus sorption for all particle sizes was not increasing in phosphorus concentration that ranges between 1000 and 1200mg P/L, signifying that the capacity in phosphorus sorption has been attained.

Results on statistical check for significance difference on sorption of phosphorus between Kilimanjaro-Pumice Particle Sizes: At 0.05 probability level, the computed value of F (F = 192397) surpasses the value of F that is obtained from the statistical table (F = 4.3) and it even surpasses the tabulated value of F (F = 16.4) found at 0.01 probability level. Therefore, there is a very highly significant difference among the three Kilimanjaro-Pumice particle sizes².

Freundlich Model: The relationship of Q (sorption) and C (concentration) by this model is as shown in equations 3-5 and Figure-2.

$$1 - 2 \text{ mm: } \text{Log} (Q) = 0.81 \text{ Log} (C) + \text{Log}(k) = 1.17 \quad (3)$$

$$R^2 = 0.95$$

$$2 - 4 \text{ mm: } \text{Log} (Q) = 0.89 \text{ Log} (C) + \text{Log} (k) = 0.92 \quad (4)$$

$$R^2 = 0.94$$

$$4 - 8 \text{ mm: } \text{Log} (Q) = 0.99 \text{ Log} (C) + \text{Log}(k) = 0.63 \quad (5)$$

$$R^2 = 0.95$$

Due to the fact that a plot in Figure-2 gives a linear relationship and the correlations, R^2 (equations 3-5) are acceptable (above 0.7), it is evident that the model fitted acceptably all the data for the sorption isotherms and can be helpful in design computations of constructed wetlands. Coefficient $k = 14.76$ in equation (3) shows that the 1-2 mm grain size has the highest capacity in sorption of phosphorus compared to the others, signifying that for the same conditions, the finest particle size sorbs the largest amount of phosphorus².

Isotherms for Sorption of Phosphorus for the Rungwe-Pumice Soil: The isotherms for sorption of phosphorus which are found from the three particle sizes of Rungwe-Pumice are demonstrated in Figure-3. When the concentration in the equilibrated solution was 500-600mg P/L, the 1-2mm particle sorbed a large amount of phosphorus (approximately 2240mg P/Kg) compared to 2-4mm and 4-8mm particles which sorbed around 2200 and 2100mg P/Kg, respectively. It can be seen from the phosphorus sorption curves that the phosphorus sorption for all particle sizes was not increasing in phosphorus concentration between 500 mg P/L and 600 mg P/L indicating that its sorption capacity has been reached².

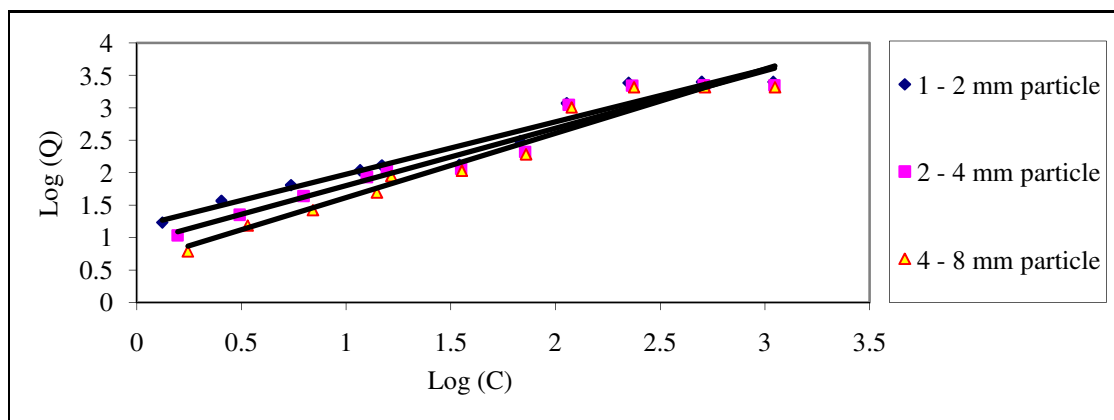


Figure-2: Inserting Sorption Data in the Freundlich Model for Kilimanjaro-Pumice soil.

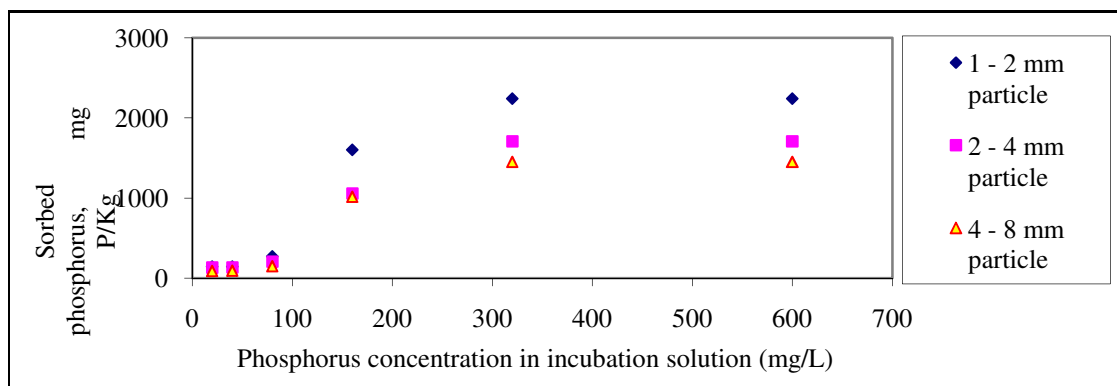


Figure-3: The Isotherms for Sorption of Phosphorus for the Rungwe-Pumice Soil.

Statistical Test for Significance Difference on Phosphorus Sorption between Rungwe Soil Particles: At 95% Confidence Interval, the computed F-Statistic value (11.23) surpasses the F-Statistic value (4.3) that is found in statistical table, therefore there is a considerable variation among all tested particles of Rungwe soil².

Freundlich Model: The relationship Q (sorption) to C (concentration) by this model is as shown in Figure-4 and equations 6-8.

$$1 - 2 \text{ mm: } \text{Log}(Q) = 0.66 \text{ Log}(C) + \text{Log}(k) = 1.45 \quad (6)$$

$$R^2 = 0.86.$$

$$2 - 4 \text{ mm: } \text{Log}(Q) = 0.75 \text{ Log}(C) + \text{Log}(k) = 1.24 \quad (7)$$

$$R^2 = 0.91.$$

$$4 - 8 \text{ mm: } \text{Log}(Q) = 0.82 \text{ Log}(C) + \text{Log}(k) = 1.02 \quad (8)$$

$$R^2 = 0.87$$

The relationship given by a plot in Figure-4 is linear and the correlations, R² are satisfactory. Coefficient k=28.60 in equation (6) shows that the 1-2mm grain size has the highest capacity in sorption of phosphorus compared to the others, signifying that for the same conditions, the finest particle size sorbs the largest amount of phosphorus.

For the similar environment, the differentiation in the sorption behaviors between the 1-2mm and 4-8mm soil particles is attributed by (1) the easily released metallic ions in the finer soil (2) the big surface area of finer soil for phosphorus sorption. Additionally, the difference among their capacities in phosphorus sorption is attributed by comparatively higher total metal content found in Kilimanjaro-Pumice soil².

Statistical Test for Significance between Kilimanjaro-Pumice and Rungwe-Pumice Soils: Since our calculated t-value (t = 27.3) exceeds tabulated T-values (T = 2.45 and T = 5.96) at 95% and 99.9% Confidence Intervals, respectively, then the difference between means concentrations of phosphorus sorption between the two soils is very significant. Therefore under the same conditions Kilimanjaro-Pumice soil sorbs significantly more phosphorus than Rungwe-Pumice soil².

Variation of Phosphorus Sorption with Time: Figures-5 and 6 show the influence of retention time on the sorption of phosphorus by comparing two particle sizes (1-2mm and 4-8 mm) of Kilimanjaro-Pumice and Rungwe-Pumice soils, respectively².

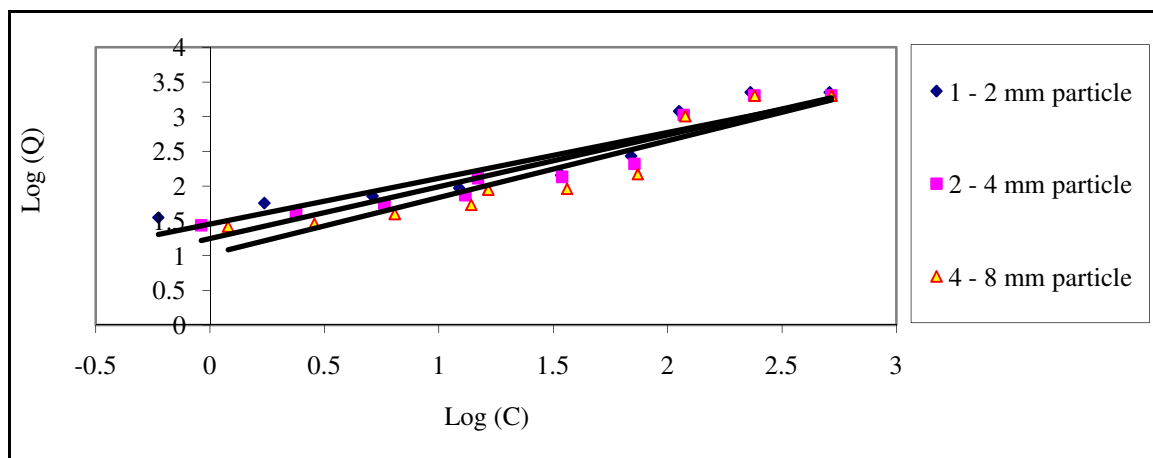


Figure-4: Fitting Rungwe-Pumice's Sorption Data with Freundlich Model.

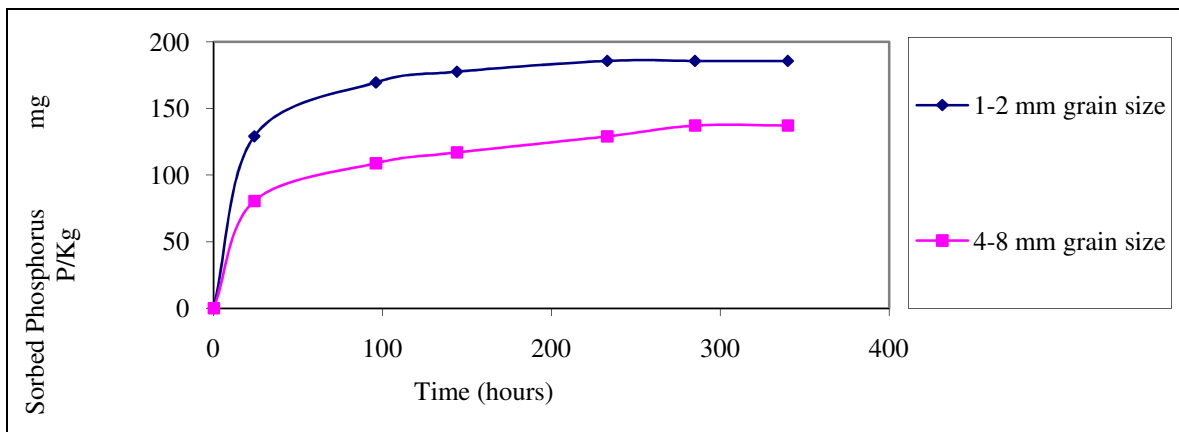


Figure-5: Variation of Phosphorus Sorption with Time for Kilimanjaro-Pumice Soil.

Michaelis-Menten Model: The relationship between $1/Q$ and $1/t$ by Lineweaver-Bulk method for the 1-2mm and 4-8mm particle sizes of the soils are shown in Figures-7 and 8, whereas the relationship between Q and t by Michaelis-Menten are shown by equations 9 - 12.

Equations by Michaelis-Menten for the Kilimanjaro Soil:

$$1 - 2 \text{ mm: } Q_{(t)} = (192 * t)/(12 + t) \quad R^2 = 0.99. \quad (9)$$

$$4 - 8 \text{ mm: } Q_{(t)} = (137 * t)/(17 + t) \quad R^2 = 0.96 \quad (10)$$

Equations by Michaelis-Menten for the Rungwe Soil:

$$1 - 2 \text{ mm: } Q_{(t)} = (204 * t)/(11.0 + t) \quad R^2 = 0.98. \quad (11)$$

$$4 - 8 \text{ mm: } Q_{(t)} = (145 * t)/(12.5 + t) \quad R^2 = 0.93 \quad (12)$$

From equations 9-12, the maximum sorption for Kilimanjaro-Pumice when phosphorus concentration in the solution was 20 mg P/L was 192 and 137mg P/Kg for the particles 1-2mm and 4-8mm, respectively and was 204 and 149mg P/Kg for the Rungwe-Pumice soil of the same particle sizes. Fifty percent of the sorption in Pumice soil from Kilimanjaro happens in the eightieth (18th) and twentieth (20th) hours for finer (1-2mm) and course (4-8mm) particle sizes, respectively, while in Rungwe-Pumice soil, the fifty percent of phosphorus sorption happens in 17th and 18th hour, respectively. It takes about 233 hours for the

1-2 mm Kilimanjaro-Pumice particle size and 192 hours for Rungwe-Pumice of the same size to attain to the highest sorption value when the concentration in the solution was 20mg P/L. From this experiment, it is clear that Rungwe-Pumice soil has higher phosphorus sorption rate (i.e. phosphorus removal rate) than Kilimanjaro-Pumice soil. The higher sorption rates of Rungwe-Pumice soil compared to the Kilimanjaro-Pumice soil might have been contributed by the higher porosity value of the Rungwe-Pumice².

Influence of Temperature on Sorption of Phosphorus: The results are shown in Figure-9 and Tables-3 and 4. These findings reveal that, the sorption of phosphorus diminishes with decrease in temperature where by finer soils has smaller influence of temperature. By looking Table-3, when temperature was reduced from 45^oC to 21^oC for the Kilimanjaro-Pumice soil, phosphorus sorption reduced by 33 percent and 57 percent for 1-2mm and for 4-8mm particles, respectively. While for Rungwe-Pumice soil, a similar reduction of temperature led to a decline in sorption of phosphorus by 25 percent and 62 percent for the same particle sizes, respectively. For both soils, a graph in Figure-9 presents the relationship which is linear. Elevated temperatures raise the action of the metal ion and thus raise the movement rate of metal ion².

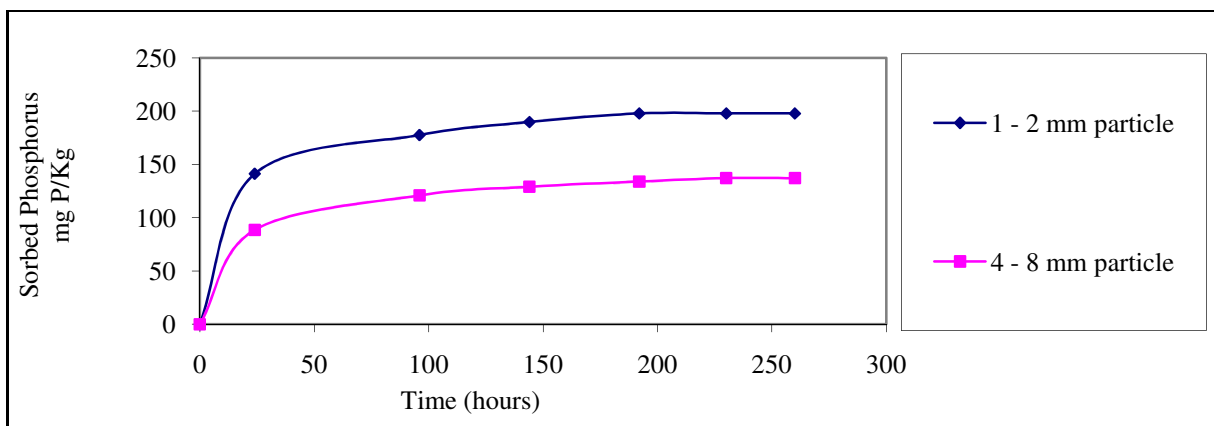


Figure-6: Variation of Phosphorus Sorption with Time for Rungwe-Pumice Soil.

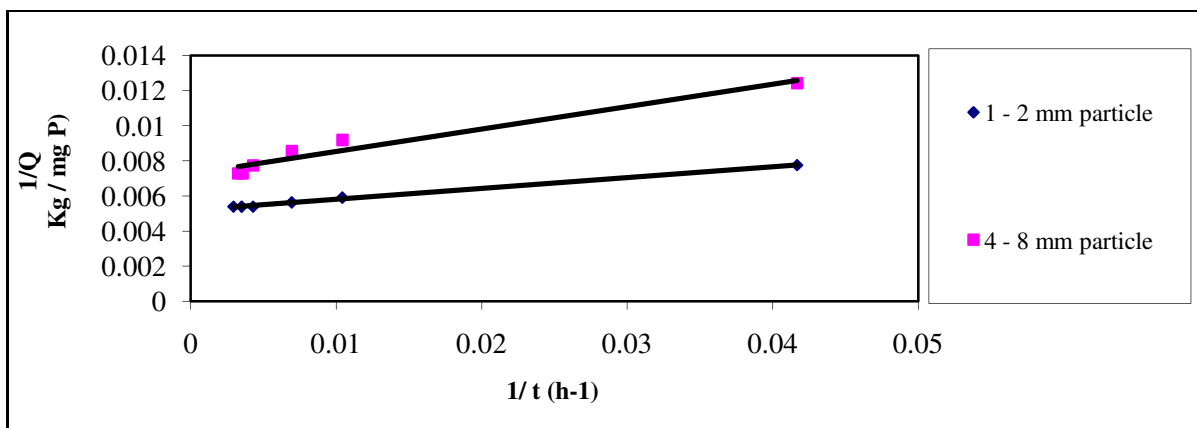


Figure-7: Fitting Sorption Data with Lineweaver-Bulk Method for the Kilimanjaro-Pumice.

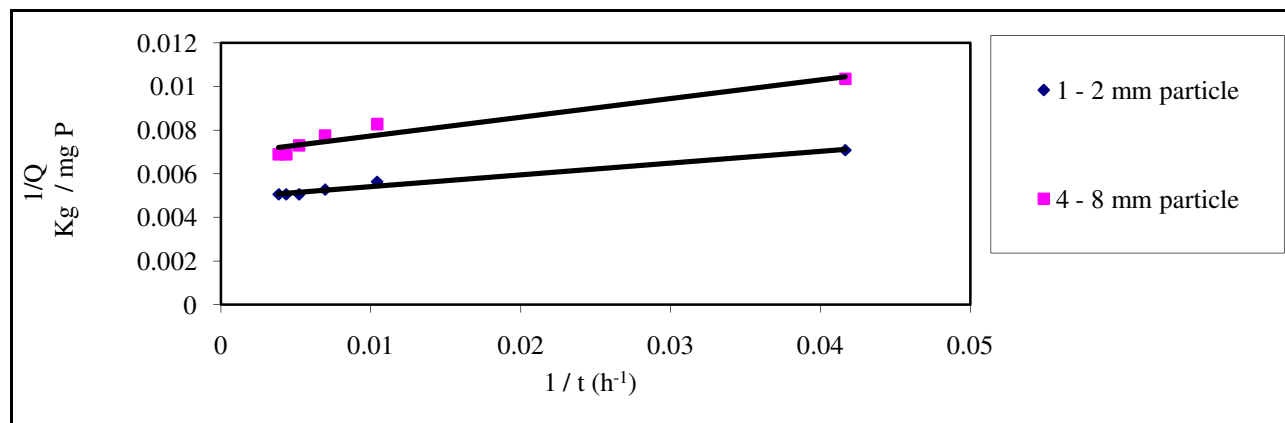


Figure-8: Fitting Sorption Data with Lineweaver-Bulk Method for the Rungwe-Pumice.

Table-3: Influence of Temperature on Sorption of Phosphorus for Kilimanjaro-Pumice.

Sorbed phosphorus (mg P/Kg) at different temperatures	1-2mm	2-4mm	4-8 mm
21°C	102	81.9	60.403
35°C	120	111	103.9
40°C	136	128	124
45°C	153	144	140.3
Average Reduction (%)	33	43	57

Table-4: Influence of Temperature on Sorption of Phosphorus for Rungwe-Pumice.

Sorbed phosphorus at different temperatures	1-2mm	2-4mm	4-8mm
21°C	163	106	68
35°C	175	131	106
40°C	197	148	140
45°C	217	181	177
Average Reduction (%)	25	41	62

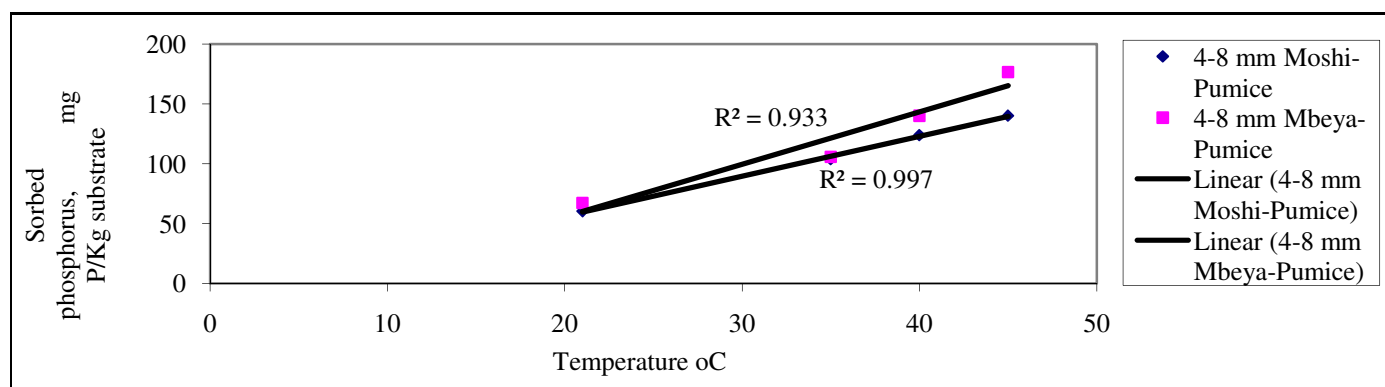


Figure-9: The Influence of Temperature on Sorption of Phosphorus for the Kilimanjaro-Pumice and Mbeya-Pumice Soils.

Conclusion

From the results presented in this research, the following are general conclusions that are drawn: (1) particles of varying sizes have an effect on sorption of phosphorus. The finer the particle sizes the higher the sorption of phosphorus, (2) Kilimanjaro-Pumice soil has higher capacity in sorption of phosphorus than Rungwe-Pumice soil, (3) given that the concentrations of phosphorus in the domestic wastewater usually range between 5 and 15 mg/L then a bed of Kilimanjaro-Pumice and Rungwe-Pumice soils when used will guarantee a removal of phosphorus in domestic wastewater for a long period without being overloaded. (4) It takes short time for the fine soils to arrive at equilibrium when compared to coarse soils, and. (5) Rungwe-Pumice soil has higher rate in sorption of phosphorus when compared to Kilimanjaro-Pumice soil.

Recommendation: Both Kilimanjaro-Pumice and Rungwe-Pumice soils have high potential in sorption of phosphorus (removal of phosphorus). They are suggested to be utilized as constructed wetlands soils to eliminate phosphorus.

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