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ENHANCEMENT OF PHOSPHOROUS REMOVAL FROM WASTEWATER USING MURUNKAN CLAY MIXED MEDIA

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ABSTRACT

Phosphorous (P) in wastewater is a primary source of P entering lakes and streams, contributing to water pollution. Hence, it must be treated before being released into the environment. This study aimed to quantify the adsorption characteristics of phosphorous in a batch experiment using 5 and 10 g/l Murunkan clay with varying concentrations of PO_4^{3-}-P and to quantify phosphorous leaching and assess the efficiency of absorptivity of Murunkan clay in a leaching column experiment using a mixture of clay and sand at ratios of 20:80, 30:70, 40:60 and 0:100 as controls. Murunkan clay is a promising P adsorbent naturally found in Murunkan, Mannar district, Sri Lanka. The adsorption isotherm had a better fitted Freundlich model than Langmuir. Batch experiments reveal that phosphorous adsorption on clay increases with increasing soil-solution ratio. The leaching column test reveals that Murunkan clay positively impacts P adsorption, as more than 99.75% of applied P was adsorbed. Moreover, the maximum amount of Murunkan clay needed to adsorb 60 mg of P is less than 262.6 g, corresponding to a 20:80 clay–sand mixture. Extensive research is recommended, as it enables scaling down the size of treatment plants, ensuring that a greater amount of phosphorous is adsorbed, minimizing water pollution.

Keywords: Adsorption, Batch experiment, Leaching column, Murunkan clay, Phosphorous

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INTRODUCTION

Phosphorus has been identified as a potential environmental risk to waterways from different sources, mainly contributing to eutrophication (Benzizoune et al., 2004; Turner et al., 2013; Youcef et al., 2014; Bensafia and Remini, 2014). This curbs water uses for fisheries, recreation, and industry due to the increased growth of undesirable algae and aquatic weeds, followed by oxygen shortages resulting from the death and decomposition of living beings (Kovar and Pierzynski, 2009). It has been reported that an increasing number of surface waters have been facing periodic and massive harmful algal blooms (e.g., *cyanobacteria* and *Pfiesteria*), which lead to fish kills, the unpalatability of drinking water, the development of carcinogens during water chlorination, and human neurological impairments (Kovar and Pierzynski, 2009). A critical P concentration of 0.02 to 0.035 mg. L^{-1} can trigger eutrophic effects in lakes (Heckrath et al., 1995). Beira Lake in Sri Lanka has been polluted with sewage and industrial waste (Perera et al., 2014); Gregory Lake in Nuwara Eliya has also been contaminated with runoff from agricultural fields.

Both natural and anthropogenic sources of P contribute to P enrichment in water resources. These include weathering of rocks, bank erosion during flood conditions, soil erosion, wastewater treatment plants, runoff from fertilized lands and croplands, failing septic systems, runoff from animal manure storage areas, disturbed land areas, and drained land wetlands, water treatment, and commercial cleaning preparations. Studies show that P pollution is common in graywater. Graywater sources include household activities such as kitchen, bathroom, or laundry activities (Al-Gheethi et al., 2019). The chemical compounds available in graywater are produced from household chemicals, washing, piping, and cooking (Eriksson et al., 2002). Graywater contributes to approximately 50% of the total organic load and approximately 66% of the phosphorous load in domestic wastewater (UNESCO, 2003). There is no limit on phosphorus levels in wastewater, but the proposed limit has been set at 0.7 mg. L^{-1} in Sri Lanka (Dissanayake et al., 2007).

Graywater can be treated in various ways: gardening, wastewater ponds, biological treatment, membrane technology, biotretention (Davis et al., 2006), and constructed wetlands, as it can be assimilated and released by vegetation and microorganisms or by sorption to the media (Johansson, 2002). Moreover, substrates such as natural materials, industrial byproducts, and artificial products that can remove P from wastewater have been investigated (Johansson, 2002). Murunkan clay (MC), a naturally occurring clay found in the Murunkan region, Mannar District, Sri Lanka, has also been identified as a promising P adsorbent (Jayawardana et al., 2015). X-ray diffraction analysis indicates that MC is rich in montmorillonite (MMT), an aluminosilicate clay mineral that belongs to smectite clay (Adikary et al., 2015) and generally belongs to a group of Grumosols. The general formula of montmorillonite is $(Na, Ca)0.3(Al, Mg)2Si_4O_{10}(OH)_2$, nH_2O (Wanasinghe and Adikary, 2017).

MMT clay has been widely used for different purposes, such as desalination and ion removal of polluted municipal wastewater (Almeida et al., 2009; Akpomie and Dawodu, 2016). In many other studies, MMT has been modified with either an acid or a base to increase removal efficiency (Tor 2006; Wang and Wang, 2008; Almeida et al., 2009; Akpomie, and Dawodu, 2016). Acid-modified montmorillonite was used in permeable reactive barriers to remove arsenic from groundwater, achieving more than 88% removal efficiency (Luo et al., 2016). Research conducted at the Rajarata University of Sri Lanka (RUSL) indicates that MC enhances P removal by 80% (Jayawardana et al., 2015).

Over the years, it has been identified that phosphorous sorption to the substratum is one of the vital removal mechanisms (Richardson, 1985). Drizo et al. (2002) described the P sorption capacity of the substratum as a finite process, an essential parameter for P – removal. Hence, it is crucial to consider when selecting substrates as potential media in filter-based and constructed wetlands (Drizo et al., 2002). Hence, this study aimed to quantify the adsorption characteristics of phosphorous in batch experiments and quantify the phosphorous leaching in column studies in different mixed media with varying ratios of clay/sand to find the most efficient clay mixture to be used in constructed wetlands and permeable reactive barriers.

METHODOLOGY

Soil collection and preparation

MC soil samples were collected from the Murunkan area in the Mannar district, Sri Lanka. The collected MC sample was brought to the lab, air dried, crushed and sieved through a 2 mm sieve. River sand was collected, washed, air dried, and sieved through a 2 mm sieve.

Analysis of physicochemical parameters

The air-dried, 2 mm sieved clay samples were analyzed for pH, electrical conductivity (EC), and total dissolved solids (TDS) using a multiparameter analyzer. Cation exchange capacity (CEC), available phosphorous, and total organic carbon content (TOC) were determined by the ammonium acetate method (Chapman, 1965), Murphy and Riley calorimetric method (Murphy and Riley, 1962), and Walkley and Black method (Walkley and Black, 1934), respectively. Particle density (PD), bulk density (BD), porosity, and pore volume (PV) were found separately by standard methods for clay–sand mixtures.

Bulk density

The literature value of the bulk density for clays was taken as the bulk density of clay for column compaction before column saturation. According to extensive research, the bulk density of Grumosol in the Mannar District is 1.45 g cm^{-3} (Sobana et al., 2014). The actual bulk density of each mixed media was found after column saturation by measuring the actual volume of mixed media.

Particle density

Particle density was measured to determine the porosity and find the mixed media's pore volume. The particle density of mixed media was determined using the pycnometer. Mean values of the particle density of the mixed media were obtained by averaging the values of the three replicates. Porosity and pore volumes were then calculated.

Porosity and Pore Volume

The porosity of the soil was calculated using the following expression:

$$Porosity = 100 \times \left(1 - \frac{bulkdensity}{particledensity}\right) \tag{1}$$

Pore Volume

The pore volume of the column was calculated using the following expression:

$$Porevolume = Volumeofthecolumn \times porosity \tag{2}$$

Phosphorous adsorption efficiency and adsorption percentage

Phosphorous adsorption efficiency (P adsorbed per unit weight of soil) and P adsorption percentage (ratio of adsorbed P to added P in %) were determined using batch experiments with 16 mg. L^{-1} of P by changing the amount of clay to 1, 2, 4, 8, 10, 20, 40, and 80 g. L^{-1}, while the rest of the parameters, such as contact time (3 hours), pH (neutral pH), and temperature (room temperature), remained constant.

Phosphorous Adsorption Isotherms

To determine the P sorption isotherms for Murunken clay, three replicates of 5.0 g and 10.0 g air-dried soil samples were equilibrated with 100 ml deionized water with concentrations of 2, 4, 8, 16, 32, and 64 ppm phosphorous. The P-solutions were prepared by using KH_2PO_4 and shaking for 3 hours at 275 rpm followed by one hour of settling time. Samples were filtered through Whatman No. 42 filter paper to obtain a clear solution. Phosphorus in the supernatant was then determined calorimetrically by the Murphy and Riley calorimetric method (Murphy and Riley, 1962). The amount of P adsorbed was calculated as the difference between the amount of P added and that remaining in the solution using the principles of mass balance. P-adsorption isotherms were developed for the amounts of P adsorbed in mg by a gram of MC (Ulmanu et al., 2003).

Generally, adsorption is depicted using Freundlich and Langmuir adsorption isotherm models, which relate the quantity of contaminant adsorbed in the solid phase q_e and the concentration of the remaining solution in the bulk phase C_e . These are related through the well-known adsorption isotherm Freundlich equation as follows:

$$q_e = KC_e^n \tag{3}$$

where:

q_e = the amount of adsorption (adsorbate per unit mass of adsorbent)

K = distribution coefficient

n = correction factor

C_e = the equilibrium or final adsorptive concentration

Additionally, the equation for the Langmuir adsorption isotherm model is as follows:

$$q = \frac{Ckx}{1+kx} \tag{4}$$

where:

q = the amount of adsorption - adsorbate per unit mass of adsorbent (mg/kg)

k = Langmuir coefficient – related to bonding energy (L/mg)

x = the equilibrium or final adsorptive concentration (mg/L)

C = maximum sorption capacity (mg/kg)

Soil column preparation

Batch experiments were followed by column studies with a mixture of different proportions of clay and sand in ratios of 20:80, 30:70, and 40:60. Since MC expands upon the addition of water and has a high water holding capacity, sand was mixed with MC in different ratios to conduct column studies by facilitating fluid flow and avoiding clay clogging. Columns of 100% sand were used as the control. Columns were made using PVC pipes covering the bottom with a muslin cloth. Sand and clay mixtures were then packed to a bulk density of 1.45 g cm^{-3} to a height of 30 cm in PVC pipes with a 6.2 cm internal diameter, as shown in Fig. 1. Mixed media were divided into six portions, and each part was packed to a height of 5 cm to ensure uniformity in compaction of the mixture throughout the columns. Columns were then left to saturate for 24 hours from the bottom with deionized water by allowing the water to rise. Bottom-to-top saturation of columns was performed to prevent entrapped air. Excess water was then allowed to drain, and the columns were finally arranged in a vertical setup supported by plastic funnels at the bottom to facilitate leachate collection. Before starting the column experiment, each column was flushed with deionized water to ensure that no phosphorous was left in the mixed media.

The basic arrangement of the column with the collecting flask is shown in Fig. 1a and 1(b). Table 1 shows the basic physical parameters of the columns.

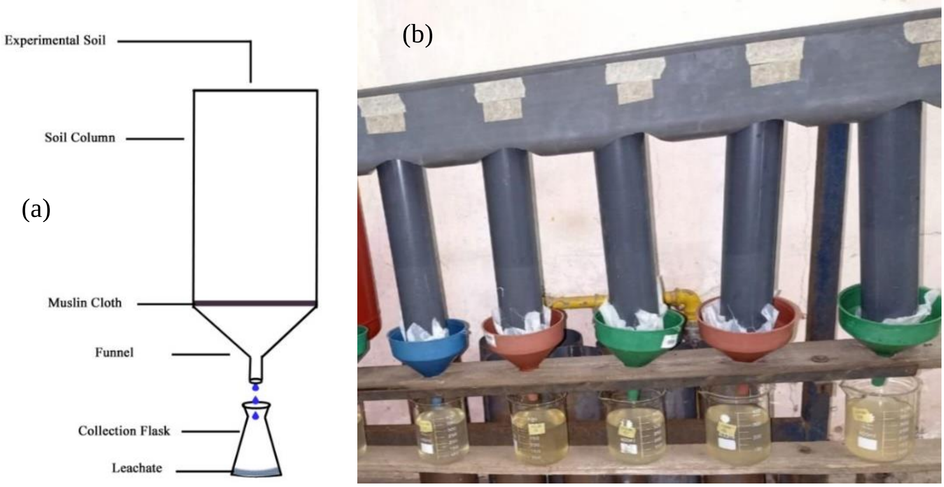

Figure 1: Arrangement of the soil column for the leaching column experiment. (a): schematic diagram of a typical column; (b): laboratory arrangement of the columns

Table 1: Basic properties of the experimental columns

Parameter	Values			
Ratio clay/sand	0:100	20:80	30:70	40:60
Height of the column (cm)	30	30	30	30
Cross-sectional area of the column (cm^2)	30.2	30.2	30.2	30.2
Bulk density of the mixed media (DB) ($g.cm^{-3}$)	1.48	1.45	1.42	1.40
Particle density of the mixed media (DP) ($g.cm^{-3}$)	2.61	2.52	2.46	2.45
Pore Volume (cm^3)	385	387	399	402

Application of phosphorous and leachate experiment

Each column was then supplemented with 15 mg, 30 mg, and 60 mg of KH_2PO_4, equivalent to fertilizer rates of 50 kg ha^{-1}, 100 kg ha^{-1}, and 200 kg ha^{-1} of phosphorous. The experimental design contains three treatments with 3 different mixtures of clay/sand ratios (20:80, 30:70, and 40:60) and 0% clay as a control (clay/sand is 0:100). Each with three replicates resulted in a total of 36 columns for analysis.

Water was added with 0.2 pore volume, 77 ml, 77.4 ml, 79.8 ml, and 80.4 ml for columns with 0:100, 20:80, 30:70, and 40:60 clay:sand mixtures, respectively. Water was added stepwise until the phosphorous in the leachate was < 1% of the initial amount of phosphorous applied.

Leachate collection and measurement of PO_4^{3-}-P concentration in leachate

The volume of water leached to the drainage flask was measured, followed by each water application of 0.2 pore volume. The leachate samples were filtered, and 5 ml of the filtrates were taken for phosphorous analysis. Phosphorous in the clear supernatant was analyzed calorimetrically using the molybdenum – blue method (Murphy and Riley, 1962).

RESULTS AND DISCUSSION

Physicochemical properties of Murunkan clay

Table 2 shows the measured physicochemical properties of the Murunkan clay soil samples used for the experiments.

Table 2: Physicochemical properties of Murunkan clay

Physicochemical Properties of Murunkan Clay at 27°C	Measured Values
pH	8.4 ± 0.4
EC	114.5 ± 3 µs.cm^{-1}
TDS	49.8 ± 1.4 mg.L^{-1}
CEC	41.2 ± 2.1 cmol. kg^{-1}
Available P	7.9 ± 0.3 mg.kg^{-1}
Organic matter	0.4%

According to Table 2, MC has comparatively higher CEC, pH, and EC values, which are usually close to 3.2 cmol kg^{-1}, pH of 6.37, and 0.03 dS m^{-1} of EC, respectively, in soils found in the dry zones of Sri Lanka (Sanjeevani et al., 2013). Furthermore, these values were higher than general values reported in the literature for soils with different minerals, such as kaolinite and illite, indicating a higher accumulation of dissolved salts and higher salinity in the selected Grumusols (Sanjeevani et al., 2013).

The diameter of MMT particles is extremely small compared to their length; hence, an extremely high average length/diameter ratio called the aspect ratio of 200/500 is achieved. This high aspect ratio results in a higher surface area (Subasinghe et al., 2020). For example, a smaller mass, such as 1 g of nanoclay, has a surface area of more than 750 m^2. Fine-grained clay particles result in an increased surface area per unit mass. Increased accessibility of the clay surface to P enhances the amount of adsorbed P, as it is predicted that phosphorous is fixed by adsorption on the surface of the clays (Pissarides et al., 1968). Fine particle sizes, such as 1 nm – 2 nm in diameter, produce a high surface area that can adsorb a considerable amount of positive ions, which could finally result in significant levels of electrical conductivity.

Soil organic matter (SOM) has been identified as one of the vital factors affecting P adsorption-desorption processes by different mechanisms. Having less organic matter content in MC increases the P adsorption capacity. According to the literature, the presence of organic matter is a reason for reduced P adsorption due to direct competition between organic ligands and phosphates for sorption sites of the adsorbent media, similar to the competition that can be seen in the presence of Al and Ca as well (Nurhajati, 2002). According to Yang et al. (2019), the addition of organic matter reduces the strength of P adsorption, thereby enhancing phosphorous availability. Another study claims that adsorbed P increased when SOM was removed from Andisol (Hiradate and Uchida 2004), which indicates that SOM inhibits P adsorption by occupying sites that could otherwise be used to adsorb P (Yang et al., 2019). The binding of OM depends on the type of organic matter and the clay minerals that are available for those to bind with. However, P chemistry in the soil is uncertain due to several reasons, such as continual uptake by plants and microorganisms, weathering and decaying processes, strong interaction with other organic and inorganic substances, slow reaction rates (Isirimah et al., 2003), Fe and Al oxides (Nurhajati, 2002), ionic strength, hydraulic conductivity (Del Bubba et al., 2003) and land utilization type. Hence, studying more on soil chemical, physical, and mineralogical properties is essential to enhance the reliability of predicting P adsorption capacities (Moazed et al., 2010).

Adsorption of phosphorous on Murunkan clay

Adsorption of P with MC dosage

The batch experiments show the adsorption of different amounts of phosphorus with varying quantities of MC. Fig. 2 shows the percentage of P adsorption with an initial concentration of 16 mg. L^{-1} of phosphorous increases with increasing MC dosage. The results indicate that the adsorption percentage gradually increases with MC as the number of adsorption sites increases. Hence, increasing the clay content with a fixed amount of initial phosphorous increases the amount of phosphorous adsorbed as more MC contains more surface area and high surface reactivity.

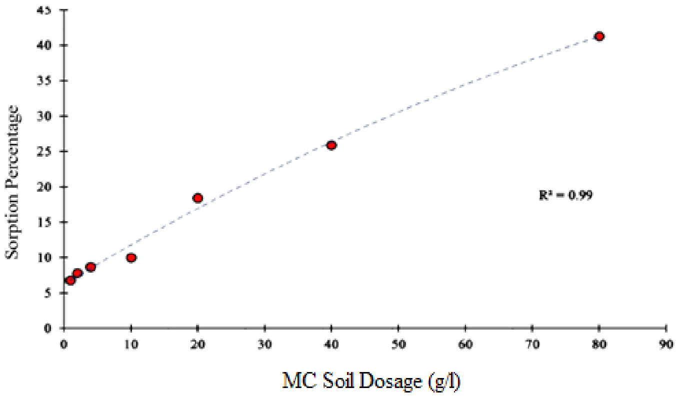

Figure 2: Adsorption with MC dosage

Adsorption of phosphorous with varying initial concentrations of P

Fig. 3 also suggests how P adsorption is affected by the initial concentration. Based on the experiments, 5 g MC in 100 ml of DW (1:20 clay: solution) shows more P adsorption than 10 g MC in 100 ml DW (1:10 clay: solution) ratio, accounting for 50 g and 100 g soils, respectively, in 1 L of distilled water. These results coincide with the results obtained by Fuhrman et al. (2005) on soils found in Oklahoma, USA, which suggests more significant adsorption of P when there is a broader soil/solution ratio. Furthermore, Fuhrman et al. (2005) suggest that there is a significant difference between wider soil:solution ratios vs. narrower soil/solution ratios, and this finding is strengthened by Chapman et al. (1997), who reported that the amount of P extracted per gram of soil with varying vigor of shaking increased with a wider soil/solution ratio (Barrow and Shaw, 1979).

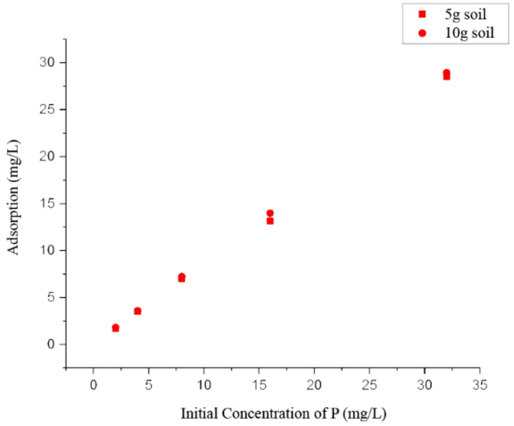

Figure 3: Adsorption efficiency with different P concentrations

Adsorption Isotherms

The adsorption isotherm in Fig. 4 shows the distribution of the dissolved contaminant phosphate phosphorous (PO_4^{3-} - P) between the solid and liquid phases by a set of mathematical relationships at a constant temperature. These models are highly dependent on certain assumptions, including the heterogeneity of the surface of the adsorbent, the interaction between the adsorbent species, interparticular diffusion, and the coverage type (Patel, 2019).

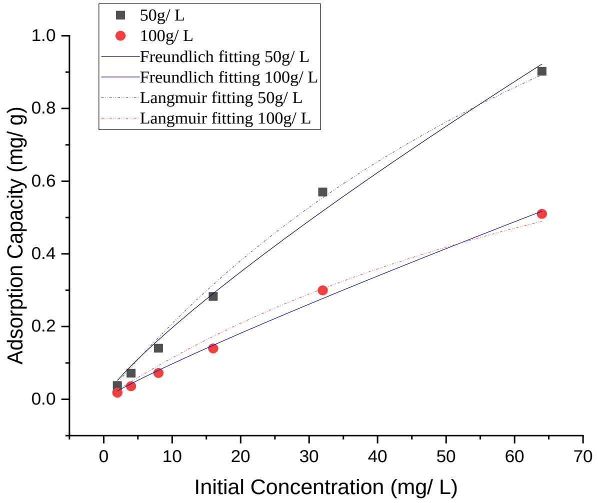

Figure 4: Isotherm models - Freundlich and Langmuir for 50 g/L and 100 g/L MC/sand ratios

Table 3: Adsorption isotherm parameters for the Langmuir and Freundlich models

Model	**Langmuir**		**Freundlich**	
Equation	$q = \frac{Ckx}{1+kx}$		$q_e = K C_e^n$	
Plot	Adsorption capacity		Adsorption capacity	
Dosage	50 g/L	100 g/L	50 g/L	100 g/L
C	3.32409 ± 0.046	1.27753 ± 0.042	79013 ± 0.068	91143 ± 0.031
k, *K*	0.001	0.001	0.03251 ± 0.009	0.01164 ± 0.001
Reduced Chi-Sqr	5.17273E-4	4.34782E-4	0.00178	9.25855E-5
R-Square (COD)	0.99515	0.98855	0.99859	0.99745

The data show a fit with the Freundlich model with an R^2 value of 0.99 for both soil dosages and slightly lower R^2 values for the Langmuir model. Phosphorous adsorption data fitted to the Freundlich model gave an adsorption maximum of 79013 mg kg^{-1} and

91143 mg kg^{-1} for soil dosages of 50 g L^{-1} and 100 g L^{-1}, respectively, indicating a high phosphorous fixing ability of MC.

Generally, the characteristics of P adsorption are heavily influenced to different degrees by specific soil properties such as pH, soil organic carbon (SOC), $Al_{sat,}$ exchangeable Ca, and clay content (Moazed et al., 2010). Since MC contains Al ions, phosphorous adsorption can also be due to its phosphate formation, as Idris and Ahmed (2012) suggest that higher values of P adsorption in soils with elevated amounts of Fe and Al might be due to the formation of their respective metal phosphates. In addition, various studies have shown that aluminosilicate clay minerals have a crucial role in P sorption by soils. These clay minerals have positive surface charges, leading to greater anion exchange capacity, which brings a greater affinity for PO_4^{3-} ions.

Breakthrough curve of P leaching

Comparison of the rate of leaching losses in the columns

MC has a high water holding capacity; hence, leaching losses were delayed with increasing MC percentage in the mixed media. The MC used in this study contains a higher percentage of MMT clay minerals (Adikary et al., 2015). It is generally perceived in layers and sheets as a 2:1 mineral, comprising octahedral and tetrahedral sheets of hydrogen, oxygen, aluminum, and silicon (Subasinghe et al., 2020). Layers are held in clay crystallite as interlayer cations by Van der Waals forces, electrostatic forces, or hydrogen bonds. MMT is also identified as a mineral that expands upon water absorption (Adikary et al., 2015); hence, sand was mixed to avoid clogging of clay and delayed leachate collection to facilitate faster leaching.

As a result, faster leaching was observed in the column with 100% sand, followed by the columns with the mixed media of 20:80 MC/sand ratio, as the amount of sand used was high in that mixture. The slowest leaching was seen in the 40:60 MC-sand mixed media, as the clay content was the highest in those columns.

Comparison of PO_4^{3-}- P adsorption with different P dosages

As shown in Fig. 5a, columns with ratios of 20:80 clay–sand mixed media treated with the three different amounts of phosphorous reached a maximum cumulative concentration of 0.85 mg. L^{-1} PO_4^{3-}- P regardless of the amount of P treatment. The cumulative concentration of PO_4^{3-}- P increased from 0.08 mg. L^{-1} at 0.2 PV and increased to 0.8 mg. L^{-1} by the end of 1.8 PV. Columns filled with 30:70 clay–sand mixture media treated with the three different phosphorous dosages reached a cumulative concentration of 0.82 mg. L^{-1} PO_4^{3-}- P regardless of the amount of P treatment, as shown in Fig. 5b. The cumulative concentration of PO_4^{3-}- P increased from 0.06 mg. L^{-1} at 0.2 PV and increased to 0.82 mg. L^{-1} by the end of 1.8 PV. Similar to the above two columns, the columns with 40:60 clay–sand mixed media treated with the three different amounts of phosphorous reached a cumulative concentration of 0.76 mg. L^{-1} PO_4^{3-}- P regardless of the amount of treatment, as shown in Fig. 5c. The cumulative concentration of PO_4^{3-}- P increased from 0.08 mg. L^{-1} at 0.2 PV and rose to 0.76 mg. L^{-1} by 1.8 PV. There was no significant difference between the values of cumulative concentrations with different phosphorous treatments. The columns filled with 40:60 clay–sand contain more clay than those with 30:70 and 20:80 clay–sand. Hence, it shows that the amount of clay used in all the columns experimented with different ratios of clay: sand can adsorb more phosphorous than 60 mg, which is equivalent to 200 kg ha^{-1}, or more than the maximum amount of PO_4^{3-}- P that could otherwise be adsorbed by 20: 80 clay: sand mixed media.

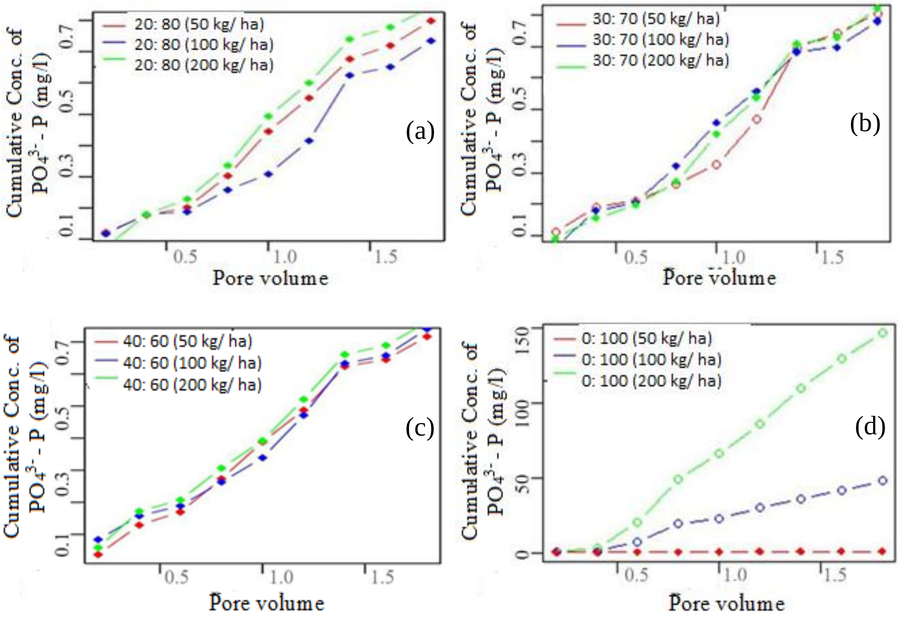

Figure 5: Cumulative concentration of PO_4^{-3} - P in the leachate of different clay, sand mixture media. (a): 20:80 clay–sand mixed media, (b): 30:70 clay–sand mixed media, (c): 40:60 clay–sand mixed media, (d): 0:100 clay–sand mixed media

Unlike the columns with different combinations of clay–sand mixtures, the columns with 100% sand treated with the three different amounts of phosphorous show significantly different amounts of cumulative concentration of $PO4^{3-}$- P in the leachate, which can be observed in Fig. 5d. The cumulative concentration of PO_4^{3-}- P treated with 50 kg ha^{-1}, 100 kg ha^{-1}, and 200 kg ha^{-1} doses reached a maximum cumulative concentration of 3.36 mg. L^{-1}, 47.95 mg. L^{-1}, and 146.71 mg. L^{-1}, respectively, at the end of 1.8 PV, while the initial $PO4^{3-}$ - P concentration for all three treatments was 0.09 mg. L^{-1} at 0.2 PV. These results prove that PO_4^{3-} - P is hardly adsorbed by sand. Although the amount of adsorbed P is less initially, the trend shows an increasing P concentration in the leachate with increasing pore volume.

Comparison of PO_4^{3-}- P adsorption with mixed media

Fig. 6a shows the cumulative concentration of $PO4^{3-}$ - P against the pore volume treated with 50 kg ha^{-1} for columns filled with 20: 80, 30: 70 and 40:60 clay: sand mixed media compared with the control. Fig. 6b compares the cumulative concentrations of PO_4^{3-} - P against the pore volume treated with 100 kg ha^{-1} for columns filled with 20: 80, 30: 70 and 40:60 clay–sand mixed media against the control. A comparison between the cumulative concentrations of PO_4^{3-} - P against the PV for columns treated with 60 mg of P equivalent to 200 kg ha^{-1} filled with 20:80, 30:70 and 40:60 clay–sand mixed media against the control is shown in Fig. 6c. Statistical analysis indicates that the cumulative phosphorus concentration of each column for each phosphorous treatment with different mixed media shows a significant difference between all the mixed media against the control. In contrast, there was no significant difference among the mixed media ($p < 0.05$). This clarifies that phosphorous is being adsorbed by clay and not being adsorbed by sand. Hence, the maximum clay–sand ratio needed to adsorb the highest fertilizer dosage (200 kg ha^{-1}) is less than 20:80.

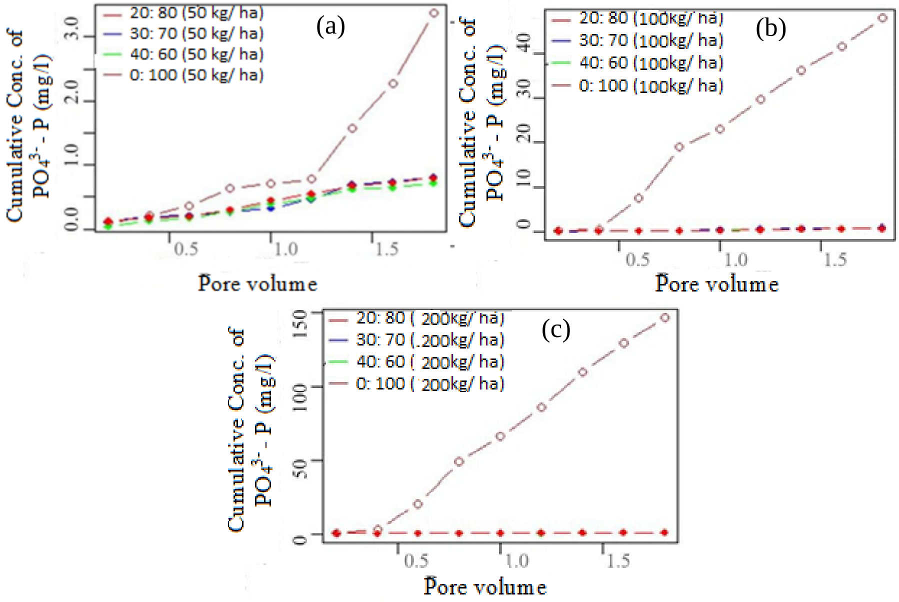

Figure 6: Cumulative concentration of PO_4^{-3} -P in samples with different MC and sand ratios treated with different fertilizer dosages. (a): 50 kg ha^{-1}, (b): 100 kg ha^{-1}, (c): 200 kg ha^{-1}

Parameters such as the volume of the substrates used (measured as the size of the column), loading rates, and retention time in the leaching column experiments were maintained according to the convenience in different studies (Johansson, 2002). As these factors influence the outcomes of the experiment, research done under different conditions makes it limited for comparison (Johansson, 2002). Table 4 shows the P values obtained from the statistical comparison of different treatments and sample comparisons.

Table 4: P - values of sample comparisons at 5% significance

	MC/Sand ratio			
	20:80	30:70	40:60	00:100
50 kg/ha	a	a	a	b
100 kg/ha	a	a	a	c
200 kg/ha	a	a	a	d

Differences between the cumulative concentrations of PO_4^{3-}- P with columns of different mixed media increase with increasing phosphorous treatment. However, it does not show any significant difference between the percentages of the clay used in the column.

CONCLUSIONS

This study was conducted to evaluate the efficiency of Murunkan clay in adsorbing phosphorous. Both batch and leaching column experiments were carried out. The Freundlich model fitted well for soil concentrations of 50 and 100 g L^{-1}.

Batch experimental results revealed that the adsorption of P increases with a wider soil:solution ratio. The 1:20 soil/solution ratio corresponding to 5 g L^{-1} shows more P adsorption than the 1:10 soil-solution ratio corresponding to 10 g L^{-1}. The column experiments proved that Murunkan clay could efficiently adsorb phosphorous in aqueous solutions. Based on this study, more than 99.75% of the applied phosphorous was adsorbed from mixed media with all the P treatments: 15 mg, 30 mg, and 60 mg of KH_2PO_4.

These results suggest that a greater amount of phosphorous can be adsorbed with a small amount of MC. Therefore, this research should be extended to find the most efficient clay percentage to adsorb a certain amount of P. Hence, small percentages of clay (below 20%) should be mixed with sand and treated with different amounts of phosphorous to evaluate the efficiency of the clay.

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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