Phosphorus adsorption on the surface of pumice and natural sand adsorbents

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Abstract. Climate change may cause serious implications on the fate of anthropogenic and natural chemicals in water bodies. This condition could lead health problems and environmental destruction. Phosphorus (P) from domestic wastewater released to the water body without proper treatment could lead to eutrophication. Therefore, it is crucial to remove phosphorus from domestic wastewater. Adsorption technology using locally adsorbent materials is a promising alternative method to remove P because of its low cost and effectiveness. In this study, a combination of pumice and sand was investigated to remove phosphorus from the solution. The aim of this study was to study the capacity of local sand and pumice from East Nusa Tenggara (ENTP) to adsorb phosphorus. These adsorbents were characterized using X-ray diffraction, FTIR and XRF followed by isotherm and kinetic adsorption experiments. The results showed that the adsorption of P in these local materials followed the Langmuir model and the P adsorption capacity was 0.07825 mol g⁻¹. The adsorption kinetics followed the second order. Thus, natural pumice can be potentially used as an adsorbent for treating domestic wastewater.

1. Introduction
Phosphorus (P) is a macronutrient that is essential for living organisms, particularly for plant growth and controlling factor for plant productivity [1]. However, the high concentration of phosphorus in the water body could lead to environmental problems. Phosphorus from land released to water could be caused by climate change. In the last fifty years, the extensive application of phosphorus in industry and agriculture has increased phosphorus concentration in the environment. The high concentration of phosphorus released to the aquatic environment could result in deterioration of aquatic environment notably eutrophication which can break the ecosystem such algal bloom, reduced fish population and loss of species [2, 3]. According to Government of Indonesia Regulation No.82/2001, the admissible water quality standard of total phosphorus with provision for irrigation, cultivation of fresh water fish and livestock is 0.2 mg L⁻¹. Thus, it is necessary to treat phosphorus before this compound is released to water body due to its harmful effect to the environment.

In the last two decades, there were various treatment methods that have been developed for phosphorus removal including biological treatment [4, 5] and physiochemical methods [6-9]. In general, chemical and biological methods have several weaknesses such as high cost of chemicals, side effect polluted product, instability and inefficient [2, 10]. Therefore, it is crucial to find effective and low-cost methods for phosphorus removal.

Adsorption is a method that widely used for removing phosphorus because of its cost-effectiveness, design flexibility, low energy consumption and operational simplicity. Ahmed, Ashiq [3] stated that
adsorption is considered as good potential alternative treatment methods due to more effective and low-cost methods for phosphorus removal in comparison with other methods. In adsorption method, adsorbents play an important role to effectively remove phosphorus from wastewater. In recent years, many adsorbents have been investigated to remove phosphorus such as zeolite, biochar, clay composite, carbon supported with zero-valent iron, acid mine, fly ash, and red mud. The selection of adsorbent is generally depended on low-cost materials with high removal capacity as well as the abundance of adsorbent material in the location. As a type of volcanic rock material, pumice has high porosity, large surface area and light weight. The skeleton structure of pumice mainly consists of silica which can allow water and ions to interact in the crystal structure [11]. Therefore, pumice is potentially used as alternative material for pollutant removal from wastewater.

This study aims to investigate the capacity of local sand and pumice to adsorb phosphorus to solve environmental and health problems because of climate change effect.

2. Methods

2.1. Media characterization
Sand was taken from Takari in Kupang District and the pumice was obtained Tuamese Village, Biboki Anleu Sub district, The District of North Center Timor (Timo Tengah Utara). This research investigated the sand media (50%) mixed with pumice (50%). Characterization of adsorbent has been reported in previous paper [12]. The summary of media characterization is shown in Table 1.

| Parameters             | Media     |
|------------------------|-----------|
|                        | Sand      | Pumice    |
| Organic matter (%)     | 3.1       | 10.9      |
| H₂O (%)                | 1.6       | 1.1       |
| pH                     | 8.05      | 8.17      |
| CEC (cmol(+) kg⁻¹)     | 47.76     | 50.88     |
| Functional groups      | Si-O-Si; O-H | Si-O-Si; O-H |
| Main elements          | CaO, SiO₂, Fe₂O₃, CaO, Fe₂O₃, TiO₂ | Al₂O₃, K₂O |

2.2. Isotherm adsorption capacity study
The isotherm adsorption was carried out by weighing 0.5 g of sand 50% mixed with pumice 50% and the weighed samples were placed in the containers. Each container was added with 20 ml of PO₄-P solution with various concentrations (0; 0.01; 0.02; 0.04; 0.06; 0.08; 0.1; 0.2; 0.4; 0.6; 0.8; 1; 2; 5; 10; 20; 40; 60; 80; 100) and shaken for two hours. The filtrates were collected in the containers and analysed for PO₄-P using molybdenum blue methods with spectrophotometry according to standard methods for examination of water and wastewater [13].

The data were analysed using Langmuir adsorption isotherm with assumption monolayer adsorption sites. The formula (1) of Langmuir isotherm is presented below [14]:

\[ q = \frac{bKC}{1 + KC} \]  

(1)

Where q is the quantity of PO₄-P adsorbed per gram of media (mg g⁻¹), C is the equilibrium concentration of PO₄-P (g m⁻³), K is the affinity of the contaminant, b is the maximum amount of PO₄-P that can be adsorbed onto absorbent. The adsorption energy (ΔGo) was calculated using thermodynamic formula [15]. The formula was presented (2) below

\[ E_{ads} = -\Delta G_{o} = RT \ln K \]  

(2)
Where $R$ is the gas constant, $T$ is the temperature in Kelvin and $K$ is thermodynamic equilibrium constant.

2.3. Kinetic adsorption

In this study, 0.5 g of sand 50% mixed with pumice 50% was added into containers and 20 ml of PO$_4$-P solutions were added into the containers. The samples were shaken in the mechanical shaker for 0; 1; 2; 4; 6; 8; 10; 15; 30; 45; 60; 90; 120; and 150 minutes. The samples then were filtered using filter Whatman 42 and the filtrates were collected in the containers. Finally, the PO$_4$-P concentrations were determined using molybdenum blue methods [13].

3. Result and discussion

3.1. Isotherm adsorption

The isotherm pattern of sand 50% + pumice 50% in the solution in varied initial PO$_4$-P concentrations is shown in Figure 1. It is presented that at low concentrations, there is a significant increase in adsorption on the media. The PO$_4$-P began to reach equilibrium where the phosphate slowly reached a saturated state or close to strong adsorption capacity (SAC). The equilibrium of each variation of the media reached the SAC state when the concentration of PO$_4$-P 2.5 mg L$^{-1}$.

![Figure 1. Langmuir Isotherm adsorption of pumice 50% and sand 50%.

3.2. Energy and adsorption capacity

From linier Langmuir model, it can be seen that there was a strong relationship between Ce/qe and Ce. This means that PO$_4$-P adsorption isotherm in the three media provided a good picture relationship with regression coefficient close to 1. Table 2 shows that the adsorption capacity and adsorption energy were 0.0783 mol g$^{-1}$ and 26.47 KJ mol$^{-1}$, respectively. The obtained adsorption energy was in line with the adsorption energy reported by Anshar et al. [16]. Based on the adsorption energy, our results were categorized into the chemical bond because adsorption process is greater than 20 KJ mol$^{-1}$. The CaO, Fe$_2$O$_3$ and Al$_2$O$_3$ could be the main contributor for PO$_4$-P adsorption in the pumice and sand adsorbent.
Figure 2. Linier model of Langmuir Isotherm adsorption from pumice 50% and sand 50%.

Table 2. Isotherm adsorption of combination of sand (50%) and pumice (50%)

| Adsorbent          | Coefficient correlation ($R^2$) | Adsorption capacity ($b$) mol g$^{-1}$ | Equilibrium constant (K) | Adsorption energy ($\Delta G$) KJ mol$^{-1}$ |
|--------------------|----------------------------------|----------------------------------------|---------------------------|---------------------------------------------|
| Pumice 50% and    | 0.989                            | 0.0783                                 | 40.803                    | 26.47                                       |
| Sand 50%           |                                  |                                        |                           |                                             |

Figure 3. Adsorption kinetics of PO$_4$-P from pumice 50% and sand 50% based on order reactions (a) pseudo first order (b) pseudo second order.
3.3. Kinetic adsorption
The results of adsorption kinetics of PO₄-P were shown in Figure 3. There are two types of models developed to investigate the order of adsorption kinetics. The linear regressions ($r^2 = 0.96$) were better found in the pseudo second order compared to pseudo first order. Our results showed that the fast adsorption processes occurred in the first 4 minutes and slowly increased after 6 minutes. The equilibrium was reached within 45 minutes. Yan et al. [17] reported that the fast adsorption might be due to electrostatic reactions which resulted in rapid transportation of PO₄-P onto surface adsorbent. The slow adsorption could be attributed to ion and ligand exchange mechanism during adsorption processes.

4. Conclusion
Based on the results, the adsorption pattern of sand (50%) and pumice (50%) followed the Langmuir isotherm with adsorption energy 26.47 KJ mol⁻¹. Based on adsorption energy, the adsorption of PO₄-P in the media was classified as chemisorption. For adsorption kinetics, our results showed that the adsorption of PO₄-P in the sand and pumice adsorbents were linear in pseudo second order. It can be concluded that pumice can be used as a potential material for removing phosphorus leading to reducing serious health and environmental problems due to climate change effect.

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