Performance efficiency of sand media amended with biochar for phosphorus removal using column filtration

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Abstract. Increase of phosphorus concentrations from wastewater could cause a significant impact on water quality deterioration. Thus, it is crucial to regulate nutrient concentrations from wastewater effluents before the effluents are discharged to the environment. Establishment of wastewater treatment is one of the solutions. This study investigated the efficiency of column filtration using sand media amended with biochar to remove phosphorus in the laboratory scale. The experimental design consisted of 6 packed columns based on the proportion of biochar in the sand media (0 – 25%). The columns were fed with 100 mL phosphate solution (10 mg/L) at the flow rate of 66.6 mL/h. The same steps were also performed using a combination of PO$_4^{3-}$-P (10 mg/L) and NH$_4^+$-N (10 mg/L) solution. The results showed that phosphate concentration in the outflow decreased smoothly and in line with the increase of biochar percentage in the sand media. Removal efficiency of PO$_4^{3-}$-P ranged from 60.9 – 80.9 % and 35.9 - 44.2 % for media loaded PO$_4^{3-}$-P and combination of PO$_4^{3-}$-P and NH$_4^+$-N (1:1). It means that the availability of biochar in the media influenced the amount of phosphorus adsorbed into media.

1. Introduction

Currently, East Nusa Tenggara Province (ENTP) is facing water shortage problems due to polluted water from both point and non-point sources (discharge from drainage, run-off, unsealed septic tanks, domestic wastewater effluent, etc.). Decline in the water quality in some water resources in ENTP is mainly caused by the increase of population and urbanization. Domestic wastewater contributed approximately 60% of water pollution [1]. Discharging untreated domestic wastewater could increase concentrations of nutrients (N and P) into the water body. This condition could cause pollution of water bodies leading to environmental and human health problems.

Phosphorus is a limiting nutrient in most surface water and excess of phosphorus leads to acceleration of eutrophication processes [2]. Awual and Jyo [3] reported that the concentrations of phosphorus in water body should be less than 10 µg/L to preserve surface water from eutrophication. Thus, it is important to find a proper treatment to reduce phosphorus concentrations from domestic wastewater to meet admissible level of water body systems.
Conventional methods for treating wastewater, such as activated sludge and membrane bioreactors, cannot be applied in ENTP because of high operational and investment costs. Filtration is a potential alternative method due to its cost-effectiveness. In this technology, the media plays a crucial role in phosphorus removals [4]. Phosphorus removal takes place via several mechanisms i.e. sorption on the media, plant and microbial uptake and sedimentation [5, 6]. The selection of media is based on the capacity of media to bind phosphorus since sorption is one of the most important mechanisms of phosphorus removals [7].

Materials used as a media for phosphorus removal are classified into three categories; natural materials, industrial by-products, and man-made products [6]. In general, natural materials such as a variety of sands, gravels and soils which are locally available have been utilized as a filter media. In the sand media, phosphorus compounds are primarily bound with calcium (Ca), aluminum (Al) and iron (Fe), depending on the pH value [8]. Adsorption of phosphorus into iron and aluminum oxides took place at pH level higher than 6. In this pH condition, precipitation could occur when phosphate ions react with calcium ions. The precipitation of iron phosphates and aluminum phosphates mainly take place at pH levels lower than 6 [6].

Biochar, the porous solid carbon obtained from pyrolysis of biomass, is an attractive option of media for phosphorus removal due to its large surface area and microporosity [9]. Therefore, sand media should be amended with other material such as biochar that could improve phosphorus removal in filtration system. Based on laboratory experiments, Kizito, et al. [10] found that biochar from corn cob and wood was significantly higher phosphate removal (>71%) than gravel media. Trazzi, et al. [11] reported that biochar prepared from Miscanthus giganteus biomass had higher P adsorption (15.5 mg g\(^{-1}\)) compared to sugar cane biomass (12.8 mg g\(^{-1}\)). Wang et al. [12] investigated P adsorption from biochar blended with calcium with various mass ratios and concluded that the 2:1 mass ration had the highest adsorption capacity (314 mg g\(^{-1}\)). Since the findings showed a better performance of biochar in removing phosphorus, it is necessary to utilize biochar as a media amendment in filtration systems. The objective of this study was to investigate the efficiency of biochar amended in the sand media filters in removing phosphorus.

2. Methods

2.1. Media characterization
The sand was bought from local store and biochar was made with slow pyrolysis method from Eucalyptus plants. The physical and chemical parameters of the media measured included porosity, pH, cation exchange capacity (CEC) and organic matter. Displacement methods were used to determine porosity and bulk density [13]. The pH was determined in 0.01 M CaCl\(_2\) solution using pH meter based on procedure number C2B/2 and CEC was determined using the silver thiourea method [14]. The organic matter (OM) was determined by weighing after igniting the media at 550°C for 4 hours in the furnace.

2.2. Column experiment
The column experiment was carried out in the laboratory using glass columns with inner diameter = 2.5 cm and height = 50 cm (Figure 1). There were six columns (BCR00% - BCR25%) representing the six types of media based on biochar content amended in the sand media with 5% increment of biochar (Table 1). The columns were filled with 1 cm layer of gravel (10 – 20 cm) at the bottom. The sand media or sand media amended with biochar were added into following layer to the height of 38 cm. To compact the sand layer, 50 g iron weight was dropped 10 times from 15 cm height. Finally, 1 cm of gravel was placed to ensure that all water was equally distributed and to maintain biochar floatation. The media introduced in the columns were in wet conditions.
Table 1. Characterisation of media in the column filtration

| Parameters | Media          |
|------------|---------------|
|            | BCR00%  | BCR05%  | BCR10%  | BCR15%  | BCR20%  | BCR25%  |
| Porosity (%) | 42.61±0.13 | 40.19±1.51 | 39.65±1.18 | 38.07±0.55 | 36.95±1.84 | 36.63±1.58 |
| pH         | 6.79±0.02  | 6.81±0.01  | 6.88±0.01  | 6.95±0.01  | 7.06±0.02  | 7.19±0.02  |
| OM (%)     | 0.59±0.04  | 1.47±0.09  | 2.32±0.12  | 3.56±0.17  | 4.85±0.16  | 5.67±0.56  |
| CEC (meq/100g) | 5.73±0.54 | 6.85±0.54  | 7.55±0.30  | 8.37±0.27  | 9.23±0.35  | 10.21±0.13 |

CEC = cation exchange capacity
OM = organic matter

2.3. Chemicals
All chemicals were analytical grades. Phosphate solution (PO\(_4^{3-}\) = 10 mg/L) was made up by dissolving 43.9 mg KH\(_2\)PO\(_4\) into 1 L volumetric flask. Ammonium solution 10 (NH\(_4^+\) = 10 mg/L) was made up by 38.19 mg NH\(_4\)Cl into 1 L volumetric flask. The sample stocks were stored at 4°C in the fridge.

2.4. Sample collection and analysis
This column experiment was divided into two parts according to the effluents used: (1) the experiment using phosphate (PO\(_4^{3-}\)) solution and (2) the experiment using a combination of phosphate (PO\(_4^{3-}\)) and ammonium (NH\(_4^+\)) solution. Measurements of phosphate concentrations were carried out on inflow and outflow. For the first five days, each column was loaded daily with 50 ml deionized (DI) water at a flow rate of 16.6 mL/h. The outflow was collected daily in 100 ml beaker glass and stored in fridge at 4°C until analyzed. The outflow collected from the column was determined phosphate concentration using a molybdenum blue method and measured using a spectrophotometer at a wavelength of 880 nm. This step intended to obtain the information of leachable phosphorus in the media using DI water.

After feeding with 50 ml DI water for the first five days, 50 ml of phosphate solution 10 mg/L was allowed to percolate through the column at the same as the previous flow rate for the second five days. Each day, the outflow was collected in 100 ml beaker glass for further phosphate determination. Then, the concentrations of phosphate from both inflows and outflows were determined using a spectrophotometer with a wavelength of 880 nm. This step aimed to determine phosphate accumulated in the media after percolation with 50 ml of PO\(_4^{3-}\) (10 mg/L) during 5 days loading. The accumulation of phosphate in the media was determined by calculating the difference between the concentration of phosphate before and after percolation. The same steps of column experiment as above were also performed using a combination of PO\(_4^{3-}\) (10 mg/L) and NH\(_4^+\) (10 mg/L) solution. This step intended to enlighten the influence of NH\(_4^+\) ion in phosphate adsorption. Spectrophotometer (molybdenum blue method) was used to measure phosphorus concentration at 880 nm. All the column experiments were conducted in duplicate.

2.5. Data Analysis
Data were analysed using the SPSS 21 to perform all statistical tests. The ability of each treatment to remove PO\(_4^{3-}\) was conducted by determining inflow and outflow concentrations of PO\(_4^{3-}\). Percentage removal efficiency was calculated as \(\% R = \frac{C_{in}-C_{ef}}{C_{in}} \times 100\%\) where \(C_{in}\) and \(C_{ef}\) are inflow and outflow of the parameters measured. The mean and standard deviation for each dataset were determined. One-way ANOVA followed by Tukey HSD posthoc tests were applied to identify the differences among treatments for removing PO\(_4^{3-}\) as well as to determine which treatments were significantly different. We used a significant level (\(\alpha = 0.05\)) in all cases.
3. Results and Discussion

The results are demonstrated in three sections. First, the outflow concentrations of $PO_4^{3-}$-P when loaded with DI water are introduced. Second, the efficiencies of the experimental column containing sand media amended with various proportions of biochar for phosphorus removal are presented. Finally, the effect of $NH_4^+$-N on phosphorus removal in experimental column containing sand media amended with biochar is explained. Discussion is presented in each relevant section.

3.1. Concentration of $PO_4^{3-}$-P loaded with DI water

The results showed that outflow concentration of $PO_4^{3-}$-P in six types of column filtration media using 50 ml of DI water for five days ranged from 0.014 mg/L to 0.112 mg/L (Figure 2). The lowest concentration of $PO_4^{3-}$-P was found in the media without addition of biochar (BCR00%) meanwhile the highest concentration was in the media with 25% of biochar (BCR25%). This is noted that increasing percentage of biochar amended in the sand media led to increasing $PO_4^{3-}$-P concentrations in the outflow. The availability of phosphorus in the biochar varies depending on the feedstock [15]. This suggested that biochar used in this study influenced the availability of loosely bound phosphorous in the media. The biochar utilized in this experiment was produced from hardwood and this type may contain small amount of loosely bound phosphorus compound. In addition, the outflow concentrations of $PO_4^{3-}$-P decreased over time because the leachable phosphorus has been released from the media.
Figure 2. PO$_4^{3-}$-P concentrations in six types of media loaded with 50 ml of DI water for five days.

3.2. Efficiencies of sand media amended with biochar in column experiment loaded with PO$_4^{3-}$-P

When the column filtrations were loaded with PO$_4^{3-}$-P 10 mg/L, the PO$_4^{3-}$-P concentration in the outflow decreased ranging from 1.50 mg/L – 3.56 mg/L (Figure 3). The decrease of outflow phosphate concentration was in line with the increase of biochar percentage in the sand media. Figure 3 also shows that the removal efficiencies of PO$_4^{3-}$-P ranged from 60.9 – 80.9 %. Sand media amended with 25% of biochar (BCR25%) was the highest removal efficiency; meanwhile, pure sand media (BCR00%) performed the poorest efficiency. This means that the availability of biochar in the media increased the amount of phosphorus adsorbed into media. This result indicated that the higher percentage of biochar on the media, the higher the phosphate absorbed by the media, leading to an increase of phosphorus removal. This was in line with the results obtained by Yao, et al. [16] stating that biochar was able to adsorb PO$_4^{3-}$-P from aqueous solution. Yao, et al. [16] pointed out that the abundance of colloidal and nano-sized periclase (MgO) on biochar’s surface may influence the increased phosphate removal since this periclase was able to bind phosphate strongly in aqueous solution.
Figure 3. PO$_4^{3-}$-P concentration in six types of media loaded with the 50 ml of PO$_4^{3-}$-P (10 mg/L) for five days

### 3.3. Effect of NH$_4^+$-N on PO$_4^{3-}$-P removal in experimental column

This section used a combination of a phosphate (PO$_4^{3-}$-P) and ammonium (NH$_4^+$-N) solution. The purpose of this section was to explain the influence of NH$_4^+$-N ions in the adsorption processes of PO$_4^{3-}$-P in the sand media amended with biochar. The result showed that the concentration of phosphate in the outflow varied, ranging from 5.71 mg/L to 6.55 mg/L (Figure 4). The highest outflow concentration was in the pure sand media (BCR00%) and the lowest concentration was in the media with 25% of biochar (BCR25%). This is noted that the removal percentage of PO$_4^{3-}$-P in the outflow increased smoothly from 35.9% in the media without addition of biochar to 44.2% in the sand media amended with 25% of biochar.

Compared to the previous column experiment that utilized only phosphate solution, the adsorption of phosphate in this part tended to be lower. It can be inferred that there was a competition among the ions particularly PO$_4^{3-}$ and NH$_4^+$ to the surface of the media. The ability of media to adsorb nutrient elements relies on either media and nutrient types [16]. Since most biochar surfaces have negatively charged functional groups, this is obvious that biochar preferred to bind with cationic species from solution provided, resulting in the effectiveness in removing cationic species [17, 18]. In this experiment, the sand media amended with biochar were probably bound with NH$_4^+$ which had positive charges in comparison with PO$_4^{3-}$ which had negative charges.
Figure 4. PO$_4^{3-}$-P concentration in six types of media loaded with the 50 ml of combination PO$_4^{3-}$-P (10 mg/L) and NH$_4^-$-N (0 mg/L) for five days

4. Conclusion

From this experiment, it can be concluded that removal efficiencies of PO$_4^{3-}$-P loaded with PO$_4^{3-}$-P solution were in the range of 60.9 - 80.9 % meanwhile PO$_4^{3-}$-P removal efficiency for the media loaded with PO$_4^{3-}$-P and NH$_4^+$-N solution (1:1) ranged from 35.9 - 44.2 %. It means that the use of biochar from Eucalyptus plants amended in sand media in filtration system could be used for an alternative option to treat PO$_4^{3-}$-P from domestic wastewater in ENTP. The adsorption of phosphate onto surface areas of biochar depends on the types of solution poured in the sand media amended with biochar. The results showed that higher percentage of biochar in sand media provided more phosphate adsorbed into the media, resulting in the increase of phosphorus removal. However, if the solution introduced to the sand media amended with biochar contained a combination of phosphate and ammonium ions, the adsorption of phosphate was influenced by competition processes between these ions. The sand media amended with biochar could have an opportunity to bind with NH$_4^+$ which had a positive charge and also with PO$_4^{3-}$ which had a negative charge. Since domestic wastewater contains many types of pollutants, it would be better if the application of this technology considered hydraulic loading rate (HLR) and could be combined with other eco-technology such as constructed wetlands.

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