Experimental and Modeling Column Study of Phosphorus Removal by Permeable Reactive Materials
Osama Eljamal¹, Ahmed M.E. Khalil², Nobuhiro Matsunaga³

Department of Earth Science and Technology, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasugakoen, Kasuga-shi, Fukuoka, 816-8580, Japan.

Abstract—This study evaluates the performance of permeable reactive materials for phosphorus removal from water by experimental and model development. A one dimensional solute transport model that describes adsorption process in porous media by mass transfer equation and surface area reduction was developed. Validity of the model was evaluated using several data sets from batch and column experiments. The marble dust, standard sand and volcanic ash were utilized as permeable reactive barriers and porous materials inside packed columns in this research. It was found that the calcium (Ca) content was the most important characteristic of the permeable reactive materials and a factor determining their phosphorus removal efficiency. A high Ca content material showed higher removal capacity of phosphorus. The results of this study demonstrated that the marble dust sorbent has a high efficiency to remove phosphorus from aqueous solution. Comparing the performances of three packed columns filled up with different combinations of the three investigated materials, the differences in permeability played an important role in the treatment residence time and its ensuing effect on the removal efficiencies of phosphorus from water. A combination of 70% marble dust and 30% volcanic ash (as porous packed layers in one column) made a reasonable compromise between high steady phosphorus removal efficiency (~80%) and longevity (over 180 days). A suggestion/recommendation in conclusion was proposed based on these results.

Keywords—column experiment, marble dust, phosphorus, reactive material, solute transport model.

I. INTRODUCTION

Phosphorus (P) is one of the most essential nutrients of non-renewable resource that can be found in wastewater or surface water. Its presence in water (in forms of orthophosphates, polyphosphates and organic phosphates [1, 2]) originates from different sources such as fertilizers and animal feed run-off (from agriculture wastewater [3]), detergents (from industrial wastewater [4]), and sewage water [5]. Up to now, the main source of phosphorus is mostly obtained from mined rock phosphate. The available rock phosphate reserves are expected to finish within 100 years [6]. However, the estimated amount of phosphorus contained in wastewater and sewage systems corresponds to about 40–50% of phosphorus ore [7]. At the same time the release of phosphorus from wastewater, agricultural areas runoff and landfill leachate into resource water reserves constitutes the main risk for reduced water quality. This excessive release (at phosphate concentrations > 0.1 mg/L [8]) is known to cause environmental problems such as massive algae bloom and eutrophication, which are harmful for the aquatic life and lead to the instability of ecosystem.

For the aforementioned problems, many and different techniques were evolved to remove and recover phosphorus from water bodies. Technologies such as biological phosphorus removal process [9, 10], constructed wetlands, crystallization [11], chemical precipitation and adsorption [12, 13], presented in vast studies [14, 15], offered significant treatment of phosphorus-contaminated water. Because of mud problem of precipitation [16], inefficiency and high cost of reverse osmosis [17] and drop in performance (at low P concentrations) of biological methods, the adsorption technique stands as a prominent and promising method among all other methods. The importance of this method is more clear in every research after research, starting from using natural reactive materials to improve the phosphorus removal efficiency by adsorption, including: limestone, shale, slag, iron rich gravel, zeolite, calcite and other artificial materials [18], then recently bimetallic nanoscale zerovalent iron adsorbed phosphorus with high kinetic rates and adsorption capacity [19], and zerovalent iron was used in column studies supported on sand bed for this purpose [20]. The phosphorus adsorption is controlled by the value of pH and the respective adsorptive surface area [21]. Larger surface area of small particle size can increase phosphorus adsorption rate and capacity. However, small particle size presents usually low permeability, which rapidly leads to the clogging of porous media.

In order to reduce the negative effects of overloading the ecosystems with phosphorus as well as recycling of phosphorus and reducing the high costs of mining and processing of phosphorus, it is necessary to investigate various techniques and materials that could contribute to the removal and recycling of phosphorus. Adam et al. [22] reported that the natural reactive
materials of shellsand and filtralite were studied for their adsorption capacity to adsorb phosphorus by conducting batch and column experiments and found that the phosphorus removal rate of 92% and 91% was measured in the columns of shellsand and filtralite, respectively. It was also reported that zeolite and pelleted clay, used as natural reactive materials either alone or in combination with soils, alum, calcite and dolomite, was found to improve the phosphorus adsorption capacity [23]. As far as the authors know, materials such as volcanic ash in combination with marble dust were not been used by other researchers in column studies to treat phosphorus.

This study focuses on using a combination of methods, adsorption and precipitation, via constructing different configurations of volcanic ash, marble and sand layers in vertical packed column with clear objectives which are: (i) to evaluate the performance of a mixture of soils and reactive materials used in these vertical columns for removal of phosphorus; and (ii) to gain a phosphorus rich product, which can be recycled by the phosphorus industry and/or may directly be used as a fertilizer. Based on these results, optimum configuration can be selected for an efficient treatment of phosphorus-contaminated water.

II. MATERIAL AND METHOD

2.1 Reactive materials

Phosphorus stock solution was prepared by dissolving potassium dihydrogen phosphate (KH2PO4 99.5%, Kanto Chemical Co., Japan) in deoxygenated deionized water in case of batch experiments and tap water in case of column experiments. The natural reactive materials used in this study are marble dust, standard sand and volcanic ash, brought from Yuesuyey Company, Japan. These materials were directly used without further treatment. The sieve analysis showed that the particle sizes of marble dust and volcanic ash were smaller than 0.2 mm, while the particle size of standard sand was 0.15 – 0.3 mm. Table 1 shows the chemical compositions of the reactive materials in weight%.

<table>
<thead>
<tr>
<th>(%)</th>
<th>SiO2</th>
<th>CaCO3</th>
<th>Al2O3</th>
<th>Fe2O3</th>
<th>CaO</th>
<th>MgO</th>
<th>K2O</th>
<th>Na2O</th>
<th>P2O5</th>
<th>Ig-loss</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard Sand</td>
<td>92.6</td>
<td>3.7</td>
<td>0.7</td>
<td>0.5</td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.5</td>
<td>98.2</td>
</tr>
<tr>
<td>Marble Dust</td>
<td>28.1</td>
<td>70.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.4</td>
<td>98.5</td>
</tr>
<tr>
<td>Volcanic Ash</td>
<td>37.1</td>
<td>8.8</td>
<td>27.2</td>
<td>3.9</td>
<td>1.2</td>
<td>1.4</td>
<td>1.4</td>
<td>0.5</td>
<td></td>
<td>17.1</td>
<td>98.6</td>
</tr>
</tbody>
</table>

2.2 Batch experiments

Series of batch experimental tests were conducted to study the phosphorus removal/sorption rate by marble dust, standard sand and volcanic ash. KH2PO4 was dissolved in deoxygenated deionized water to prepare the standard solution of phosphorus. Glass flasks of 300 ml size were used for carrying out batch experiments. 250 ml of prepared phosphorus solution were mixed with five grams from each natural material and added into the 300 ml glass flasks. The flasks were tightly capped and mixed using an orbital shaker (NS-LR, As One Co., Japan) at 120 rpm and 25°C. 5 ml of solution were periodically withdrawn to analyse phosphorus content using spectrophotometer (DR 3900, Hach Co., USA). To ensure the accuracy of results, duplicate experiments were conducted. The amount of phosphorus removed by reactive material from the solution at equilibrium \( q_e \) (mg/g) was computed using the following equation [24]:

\[
q_e = \left( \frac{C_i - C_e}{m} \right) v,
\]

where \( C_i \) and \( C_e \) are the initial and equilibrium concentrations of phosphorus respectively (mg/l), \( v \) is the solution volume (l) and \( m \) is the mass of adsorbent (g).

2.3 Column experiments

Columns with 100 cm height and 10 cm inner diameter, made from acrylic glass, were used for carrying out column experiments. The schematic diagram of experimental column is shown in Fig. 1. The three columns were filled up with a mixture of natural materials to 90 cm height. The first column was filled up with 30% marble dust as reactive material and 70% sand as inactive material to maintain the permeability of the column; the second column was filled up with 50% marble dust and 50% sand; and the third column was filled up with 30% marble dust and 70% volcanic ash. Continuous phosphorus solution with 100 mg/l concentration was supplied to columns using a constant head feeding tank. The three columns were run in downward flow at room temperature of 25°C. The effluent from each column was collected periodically for the analysis of phosphorus concentrations using spectrophotometer (DR 3900, Hach Co., USA). Furthermore, the flow rate, pH
and hydraulic head were measured. The removal percentage of phosphorus ($R_e$) was calculated using the ensuing equation [25]:

$$R_e = \frac{C_i - C_e}{C_i} \times 100,$$

where $C_i$ and $C_e$ are phosphorus concentrations of columns influent and effluent respectively (mg/l).

![Schematic Diagram of Experimental Column](image)

**FIGURE 1. SCHEMATIC DIAGRAM OF EXPERIMENTAL COLUMN**

### 2.4 Model development

#### 2.4.1 Transport model

The mass conservation equation of one-dimensional solute transport with chemical reaction term as adsorption in the porous media can be written as [26]:

$$\frac{\partial \{C_i\}}{\partial t} = \frac{\partial}{\partial y} \left( D_L \frac{\partial \{C_i\}}{\partial y} \right) - v' \frac{\partial \{C_i\}}{\partial y} + R_i,$$

where $C_i$ is the dissolved concentration of species $i$, $D_L$ is the longitudinal dispersion coefficient, $v'$ is the average pore water velocity, $t$ is the time, $y$ is the distance, and $R_i$ is the chemical reaction term. The longitudinal dispersion coefficient $D_L$ is described by Appelo and Postma [27] as: $D_L = \alpha_L v' + D_M$, where $\alpha_L$ is the longitudinal dispersivity, and $D_M$ is the molecular diffusion coefficient.

#### 2.4.2 Adsorption model

Based on the results of batch experiments of phosphorus removal, the kinetics of adsorption conform to mass transfer equation with taking into account the surface area reduction. In a subsequent step the column results were simulated with the adsorption model as the chemical reaction term ($R_e$) in the mass conservation equation of one-dimensional solute transport, which couples with the solute transport model. The mass transfer equation can be expressed as [28]:

$$\frac{dq}{dt} = \frac{k}{\rho} (C_i - q),$$

where $q$ is the adsorption concentration, $k$ is the mass transfer coefficient between dissolved and adsorbed phases and $\rho$ is the bulk density of the medium.
The surface area available for mass transfer change as adsorption occurs, which will reduce the mass transfer coefficient. Change of the surface area due to adsorption was computed using the following formula:

\[ \frac{dS}{dt} = -k_s q , \]

where \( S \) is the surface area of adsorbent material and \( k_s \) is the surface area rate constant.

The mass transfer coefficient \( k \) is normalized using the available surface area of adsorbent material as follows: \( \kappa = \kappa_s S \), where \( k_s \) is the specific mass transfer coefficient.

### 2.4.3 Coupling of transport and adsorption

The whole equations describing transport and adsorption could be solved simultaneously. The finite difference as a numerical method is used to solve model equations However, the sequential procedure is used where first the advective and dispersive transport equations are solved independently. Then the adsorption equation is solved with the concentration changes from the transport step. Fig. 2 illustrates the simulation procedure performed in advection-dispersion and adsorption model.

![Flow chart of solute transport and adsorption model](image)

**Figure 2. Flow chart of solute transport and adsorption model**

### 3.1 Model parameter

The adsorption model parameters estimated from adsorption rate determined in batch experiments. Alternatively, column experiments were used to estimate adsorption parameters by curve fitting with the transport model. The parameters of adsorption model such as specific mass transfer coefficient and surface area rate constant are displayed in Table 2. The initial value of parameters were increased and decreased by one order of magnitude in order to determine the parameter sensitivity.

The discretization of the hypothetical column, and the hydraulic parameters used for simulation of advective and dispersive transport are showed in Table 3. The discretization is chosen such as it meets numerical stability and accuracy criteria (Courant number = \( (v \Delta t) / \Delta x \leq 1 \), grid number = \( \Delta x/\alpha L \leq 2 \) [28]. The pore water velocity of the column was calculated based on the measured data.

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3.2 Result of batch experiments

The kinetic behaviour of phosphorus adsorption onto reactive materials was examined by 120-hour contact time. To facilitate calculations, marble dust was treated as a pseudo-adsorbent material. Krishnan et al. [29] reported that the kinetics of phosphorus adsorption governs the rate, which determines the residence time, and it is one of the important characteristics defining the efficiency of adsorbent. The variation of adsorption capacity of phosphorus with contact time for the adsorbents is shown in Fig. 3. The results show that the adsorption capacities of the adsorbents for phosphorus after 12 hours were 2.51 mg/g, 1.2 mg/g and 0.02 mg/g for marble dust, volcanic ash, and standard sand, respectively. The rate of phosphorus adsorption was initially rapid, but decreased with time. The initial faster rate is due to the availability of the uncovered surface area of the adsorbent, since adsorption kinetics depends on the available surface area of the adsorbent [30]. The curves for all adsorbents become nearly flat by the time of 24 hours. The final adsorption capacities of the adsorbents for phosphorus were 3.81 mg/g, 1.56 mg/g and 0.11 mg/g for marble dust, volcanic ash, and standard sand, respectively. These results demonstrate that marble dust is the most efficient adsorbent amongst the materials tested, having the potential to remove 93% of dissolved phosphorus from aqueous solution. This high removal performance can be attributed to the presence of high Ca content as indicated in Table 1, which interact effectively with phosphorus and precipitate it in form of calcium phosphate (hydroxyapatite, Ca_5(PO_4)_3OH) [14].

![Figure 3. Phosphorus adsorption capacity variation with contact time for different materials](image)
3.3 Result of column experiments

Regarding the flow rate inside columns, average flow rates of daily measurements of columns effluent volume were 20.8, 5.0 and 4.5 l/day for the first column (CI) filled up with 30% marble dust and 70% sand, the second column (CII) filled up with 50% marble dust and 50% sand and the third column (CIII) filled up with 30% marble dust and 70% volcanic ash, respectively. The flow rates of three columns are shown in Fig. 4. The first column obtained the higher flow rate that is due to the big grain size of sand, which provided an average permeability 0.0075 cm³/s, while the percentage of sand in the second column was 50% which obtained lower flow rate with an average permeability 0.0003 cm³/s. The third column was filled up with marble dust and volcanic ash, both materials with grain size smaller than 0.2 mm, which obtained lower flow rate with an average permeability 0.0002 cm³/s. The flow rate measurements through the running time of the experiments showed that there isn’t significant change in flow rate with second and third columns, while the first column showed significant increasing in flow rate may be due to high initial flow velocity (0.01 cm/s), which effect the column permeability by pushing the fine marble dust out of the column.

Concerning phosphorus removal, the developed model simulated the experimental data well. The validity of the reactive model was checked by comparison of the experimental observations data with model results. Fig. 5 shows experimental and simulation results of phosphorus concentration changes versus time for three columns. At the beginning of the experimental running time, the third column obtained the best performance, which maintained an average removal percentage 95% throughout the first 70 days, after that the performance demonstrated a fast decreasing due to the decrease in available surface adsorption area contributed to the system by marble dust (30%) as a reactive material. Whereas the second column maintained a stable performance with an average removal percentage 77% throughout the incubation period due to the availability of surface adsorption area contributed to the system by marble dust (50%). While minimum performance was obtained by the first column, which maintained an average removal percentage 27% throughout the incubation period due to its higher average value of permeability of 0.0075 cm³/s.

The three columns, filled with different percentage of marble dust as a reactive material, had shown different performances which affected mainly by the availability of marble dust as Ca sources, flow rate and residence time. An average residence time of columns was the important factor that can significantly affect phosphorus removal. The residence time was 2.8, 21.5 and 23.7 hour for first, second and third columns, respectively. Therefore the third column with high residence time (23.7 hour) at first 70 days was able to reduce the concentration of phosphorus from 100 mg/l at the inlet of the column to an average 4 mg/l at the outlet of the column.
Fig. 6 shows experimental and simulation results of vertical profiles of phosphorus concentration after 60 days for three columns. The results show that the first 15 cm of the columns I and III reached the maximum adsorption capacity, while the column II did not reach the maximum adsorption capacity at the first 15 cm due to the high availability of reactive marble dust. Also the profile shows the columns II and III still has more capacity to remove the phosphorus for the rest of column 75 cm. The vertical profile of column I kept parallel to y-axis for the rest of the column 75 cm, this means it reached the adsorption capacity in this part of the column.

The simulated results enable us to predict the long-term performance of marble dust for phosphorus removal from water as shown in Fig. 5. The longevity of the second column is high along with its high steady performance as it appears also in both Fig. 5 and Fig. 6. The combination of adsorption (by volcanic ash) and precipitation (partially by marble dust) processes prolonged the lifespan of the second column due to the difference in the kinetic rates and mechanisms of both techniques. The results showed that within the defined experimental conditions the marble dust should be able to successfully remove phosphorus from water. And the combination of marble dust mixed with volcanic ash as a support can maintain longer life for the column along with a high stable performance.
IV. CONCLUSION

This work investigated the adsorption of phosphorus by a mixture of soils with different reactive materials. For this purpose, column experiments were conducted to evaluate the performance of phosphorus adsorption as well as solute transport model was developed to perform column experiments and predict long-term performance of reactive materials for phosphorus removal. The efficiency of phosphorus removal was found affected mainly by the Ca content of reactive materials, a high Ca content material obtained higher adsorption capacity of phosphorus. The present study on the removal of phosphorus recommends and suggests that the marble dust 50% as Ca source mixed with volcanic ash 50% can be used as novel adsorbent for phosphorus removal from aqueous solution, which can maintain reasonable longevity and high steady removal performance. Furthermore, the marble dust as a waste of marble mining areas and marble industry production is not only economic adsorbent that can be used for phosphorus removal, but also at the same time their utilization solves the problem of waste residues from marble mining and industry processes.

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REFERENCES


