Comparable Influencing Factors to evaluate the Phosphate Removal on the Batch and the fix-bed Column by Converter Slag

ABSTRACT
The influencing factors to remove phosphate were evaluated by converter slag (CS). Experiments were performed by batch tests using different CS sizes and column test. Solutions were prepared at the different pH and concentrations. The maximum removal efficiency was obtained over 98% with the finest particle size, CSa, within 2 hours in batch tests. The removal efficiency was increased in the order of decreasing size with same amount of CS for any pH of solutions. The adsorption data were well fitted to Freundlich isotherm. From the column experiment, the specific factors were revealed that the breakthrough removal capacity (BRC) x_{b}/m_{c}, was decreased by increasing the influent concentration. The breakthrough time, t_{b} was lasted shorter as increasing the influent concentration. The pH drop simultaneously led to lower BRC drop during the experimental hours. The relation between the breakthrough time and the BRC to influent concentration was shown in the logarithmic decrease. Results suggested that the large surface area of CS possessed a great potential for adsorptive phosphate removal. Consequently particle size and initial concentration played the major influencing factors in phosphate removal by converter slag.

Key words: converter slag, Phosphate removal, Adsorption isotherm, Breakthrough time, Breakthrough adsorption capacity

1. Introduction
Phosphorus is a very important element for growth of organisms in most ecosystems. Efforts to reduce phosphorus concentrations in aqua systems have mainly concerned with improving the water quality in water body. Once released in exceed concentration into the water body, excessive amounts of phosphate supply to water bodies may cause eutrophication and subsequent deterioration of water quality. Even the trace amount of phosphate in municipal wastewater and industrial wastewater is often responsible for algae blooming in stagnant water bodies. Removal technologies such as various biological removal, constructed wet lands, chemical precipitation using coagulant, adsorption by activated carbon and fly ashes have been employed to
remove effectively from wastewater systems. Of those technologies some biological treatments and wetland systems cannot be applied for the stringent guidelines.

In a batch study, the maximum fluoride removal was achieved within the pH range 5.0-7.0, taking about 2 hour to attain equilibrium. They reported that the equilibrium time did not depend upon the initial fluoride concentration. The breakthrough time and exhaustion time decreased with increasing flow rate, decreasing bed depth and increasing influent fluoride concentration (Chen et al. 2011). The dynamic adsorption capacity calculated from the breakthrough curves progressively decreased with the increases in the face velocity, suggesting that the effect of intrataparticle diffusion and possibly the rate of adsorption as the rate-limiting mechanism were increasingly more profound for a chemical filter-type adsorbent configuration (Shiue et al. 2011). Phosphorus was removed by natural sorbents but these materials were less efficient than mineral-based sorbents. The evidence suggested that a soluble amorphous tricalcium phosphate was formed in the mineral-based sorbents (Gustafsson et al. 2008). Researchers found that pH and temperature play a major role in orthophosphate uptake with ordered meso-porous silica (Delaney et al. 2011). The removal of phosphate was performed using the modified fly ash by sulphuric acid, resulting increase of the specific area. Both adsorption and precipitation contributed to the removal of phosphate but precipitation was a major mechanism of phosphate removal. The results showed that pH in ranging of 5-9 did not significantly affect the removal of phosphate and the removal efficiency increased with the increase with the increase of adsorbent dosage (Xu et al. 2010). Major factors including the initial phosphate concentration, adsorption kinetics, temperature, and pH were investigated. Peat was effective in phosphate removal from wastewater, especially at its low concentrations as low as 1-2 mg/L. The adsorption on peat decreased with increasing temperature and was the highest at pH 6.5. The results suggested that peat with large surface area possessed great potential for its use as substrate bed material for adsorptive phosphate removal from wastewater (Xiong and Mahmood 2010). The adsorption capacity was found to increase as temperature was increased, indicating that the sorption of phosphates onto hydroxalite was endothermic. Surface hydroxyl groups played an important role in phosphate adsorption (Peleka and Deliyanni 2009). The phosphate removal was better achieved by Fe²⁺/H₂O₂ than by Fe³⁺ alone or ferric coagulation. The dominant mechanism was considered chemical co-precipitation for phosphate removal in presence of Fe²⁺/H₂O₂ (Li et al. 2009). Investigation of phosphate adsorption onto aluminium oxide hydroxide was performed to estimate the adsorption isotherms, the adsorption rate and adsorption selectivity. The phosphate adsorption onto aluminium oxide hydroxide was influenced by pH in solution; the optimum pH for the amount adsorbed was at pH 4, ranging with pH from 2 to 9. The results indicated that the hydroxyl groups on aluminium oxide hydroxide have selective adsorption capability for phosphate and could be used for the removal of phosphate (Tanada et al. 2003). The pH decrease was appeared in all blast furnace slag samples as a function of phosphate addition. The calcium concentration was decreased as a function of phosphate concentration in the furnace slag. They suggested that Ca-P precipitation was the major phosphate removal mechanism with the furnace slag. The complex speciation of Ca-PO₄ data revealed the formation of amorphous calcium phosphates and/or octacalcium phosphate as the major phosphate removal mechanism (Johansson and Gustafsson 2000). The influence of pH, temperature, agitation rate, and dosage of blast furnace slag on phosphate removal was investigated by conducting a series of batch adsorption experiments. Precipitation was the predominant mechanism rather than weak physical interactions between adsorbent and phosphate (Oguz 2004). The influence of steel slag was investigated in a series of batch experiments. They found that the phosphate removal efficiency depended on pH, initial phosphate concentration, adsorbent dose and temperature. Phosphate removal increased with the increasing temperature, adsorbent dose and decreasing initial phosphate concentrations by steel slag (Xiong et al. 2008) and by peat (Xiong and Mahmood 2010).

In early research on phosphate removal for the column study, Breakthrough data of phosphate on dust and cake
were predicted by the dynamic model based on the surface diffusion. The simplified model on the linear driving force could not predict the breakthrough curves from the column of cake slag properly, particularly at low concentrations. They noted that the adsorption capacities of dust and cake of slag were much higher than that of a sandy loam soil. Thereby they implied that slag from steel industries were good candidate adsorbent for phosphate removal (Lee et al. 1997). It is necessary to mention that cost effective removal technology using solid wastes such as fly ash, slag and cement instead of expensive coagulants have been applied for the removal of phosphate. The significant factors to remove phosphate were solute concentration, acidic pH and higher temperature rather than particle size in column study (Agyei et al. 2002). The effect of solution pH and initial concentration for the removal of phosphate was investigated by converter slag and cinder with column study. The influence of initial pH on phosphate removal by converter slag was significant at the beginning of experiment (Yang, et al. 2009). Other papers with column study to remove pollutants in aqueous phase were reported using GAC (Shiue, et al. 2011) and graphite (Goshadrou and Moheb 2011). A comprehensive series of column tests were performed to determine the breakthrough curves, and the effects of the feed flow rate, initial dye concentration, and adsorbent dosage on adsorption process were studied. The results showed that the breakthrough time increased in proportion to the increase in the dose of adsorbent, but decreased with increase in flow rate and initial dye concentration (Goshadrou and Moheb 2011). Study was performed using column experiments, and batch tests were performed under a range of conditions to assess the effect of solution pH, filtration rate, initial ammonium concentration on the performance and capacity of the zeolite in ammonium removal. The breakthrough product made from modified zeolite filtering media would have high ammonium removal efficiency (Li et al. 2011). The removal of CD(II) from industrial wastewater by macrofungas Pleurotus platytopus was investigated in a fixed bed column. Experiments were conducted to study the effect of important parameters such as bed depth and flow rate. Under optimized conditions in batch study, the major water quality parameters of effluent such as pH, TDS, COD and colour were measured. The adsorption followed the Freundlich isotherm model and the kinetic constant (Kf) related to adsorption capacity was found to be higher for real wastewater over distilled water spiked samples. Kinetic study showed that the rate limiting step was the chemisorption (Vimala et al. 2011). Phosphate removal by nanocomposite slag was evaluated with several variables, contact time, pH and temperature. Phosphate adsorption was performed at the very early experimental hour within 30 minutes. The adsorption capacity was risen as temperature increases. The adsorption data obtained were fitted both Langmuir isotherm and Freundlich isotherm(Islam, et al. 2014).

The objective of this research was to evaluate the significance of influencing factors of converter slag for removing phosphate. In batch experiments, the maximum phosphate adsorption kinetics, solution pH, different sizes, initial phosphate concentration were evaluated. Subsequently, three columns with the different initial concentration were conducted to investigate the breakthrough time and breakthrough adsorption capacity whether those are fitted to arithmetic or logarithmic relation.

2. Materials and methods

2.1 Materials

Waste converter slag (CS) used was a by-product derived from iron ore industry, Pohang city Korea. The converter slag was examined by X-ray diffraction spectroscopy. The result of analysis by XRD was illustrated in the previous reference(Lee and Lee, 2007). The chemical compositions are composed as follows; FeO 23.86%, CaCO3 38.68%, SiO2 12.71%, MgO 11.15%, MnO 2.17%, Al2O3 2.308%, others are less than 1.0%. The slag grain were available in four different sizes, 0.075-0.15 mm (CSa), 0.15-0.425mm (CS b), 0.425-2mm (CSc) and 2-4.75mm (CSd), respectively. Slag samples were washed with distilled water and dried at 105˚C for 24 hours before every experiment. The
phosphate stock solution containing 1,000 mg/L was prepared by anhydrous KH₂PO₄ in distilled water.

2.2 Batch experiments for phosphate adsorption

Batch experiments were employed to verify the effect of changing pH of solution, adsorption capacity and size effect during experimental hours. The phosphate adsorption capacity was examined using two batch equilibrium techniques as described below. The first adsorption experiments were performed at 3mg/L to understand the removal kinetics for the grain size effect of different weight and to find out adsorption kinetics. Various masses (1, 3, 5, 7, 10, 25, 50 g) were used for CSa and CSb. Several masses (10, 25, 75, 100, 150 g) were used for CSc and CSd. The second adsorption experiments were performed to verify the effect of pH solution and the intensity of solution concentration using 100g of CSa with several pH (7, 7.5, 8, 8.5) in 250mL glass Erlenmeyer flasks containing 100mL of different phosphate solution (1, 3, 5, 10mg/L). All converter slag in Erlenmeyer flask was shaken in a constant temperature shaker (SI-900R, JEIO Tech, Korea) at 20°C with 120rpm. The measurement of changing pH was employed using a pH meter (Orion 4STAR, Thermo) and phosphate was analysed by DR4000 Spectrophotometer at the given experimental intervals for every experiment.

2.3 Continuous column experiment

Column studies were conducted using three HDPE tubes of 7.5cm ID and 36cm of packed height of 45cm height. The column was filled by 2,780g of CSd with 53% porosity. The solution was fed through the bottom of vertical column by a peristaltic pump (Masterflex Variable-speed Digital Drive, Cole-Parmer) with a head (L/S Easy-load II, Cole-Parmer). The flow rate was 40mL/min, 21min of retention time, 1.026m/h of line velocity and 2.85/h of specific velocity. Each tube was fed 10, 30 and 50 mg/L of influent concentration, respectively. The effluent samples were intermittently collected at time intervals until the column reached a concentration greater than 95% of the feed concentration.

3. Results and discussion

3.1 Effect of particle size and weight

The removal efficiency was more than 80% in 2 hours with CSa, 8 hours with CSb. The final removal efficiency was 94% for CSa, 90% for CSb, 81% for CSc and 73% for CSd, respectively. It was increased as the surface area increase as the particle size was fine. Those were not exactly proportional to the particle size. The amount of phosphate adsorbed increased with the adsorption time for all experiments. The kinetic constants for the different weight of every size of converter slag were calculated to elucidate the adsorption rate using the formula of the first-order reaction as shown in Table 1. The removal rates increased as decreasing size and increasing weight at a given experimental hour.

The increasing values of removal kinetic appeared to correspond to the order of increasing the weight of converter slag. It must be pointed out that the removal kinetic constants were correlated to the increasing weight of the given any size of converter slag. The contribution of removal kinetic appears to be relatively highly relevant and dependant on particle size which means smaller size contributed the larger adsorption surface area. However the relation between size and weight for every size of converter slag is not exactly correlated. The rate constants for same amount (10, 25, 50g) of CSa and CSb were much higher than those of CSc and CSd. It

| Table 1. Removal kinetic (hr⁻¹) for different size and varying weights of converter slag. |
|------------------------------------------|------------------------------------------|------------------------------------------|------------------------------------------|------------------------------------------|------------------------------------------|------------------------------------------|------------------------------------------|------------------------------------------|------------------------------------------|
| CSa  | 1g    | 3g    | 5g    | 7g    | 10g   | 25g   | 50g   | 75g   | 100g   | 150g   |
| -    | 0.024 | 0.032 | 0.036 | 0.041 | 0.044 | 0.052 | 0.056 | -     | -      | -      |
| CSb  | 0.023 | 0.030 | 0.034 | 0.036 | 0.039 | 0.047 | 0.052 | -     | -      | -      |
| CSc  | -     | -     | -     | -     | 0.011 | 0.012 | 0.013 | 0.014 | 0.015 | 0.016  |
| CSd  | -     | -     | -     | -     | 0.011 | 0.012 | 0.013 | 0.015 | 0.016 | 0.017  |
was much influenced by increasing converter slag weight 10g to 50g for CSa and CSb as small size comparing with CSc and CSd. Also the removal rate can be compared that the rate kinetic increased twice higher at 50 g than 1g of CSa and CSb. However the rate kinetic did not change much for any weight of CSa and CSb. Comparing the rate kinetic for small size and big size, the rate of small size revealed four times higher than that of small size. However it was not different appearance though increasing converter slag weight 10g to 50g for CSa and CSb as large size. It was increased as increasing for low weight of converter slag such as 1g to far up 50g of CSa and CSb. The increasing weight contributed to increase the rate kinetic for CDa and CDb as small size. It was not much increased even though the weight of converter slag increased 10g to 150g for CSa and CSb as large size. Therefore it was found that the removal rate was highly affected by adsorbent size, on the other hand increasing weight did not much contribute the kinetic rate for CDc and CDd as bigger size. The smaller the particle size led the higher final pH of solution. It seems that surface area increased as small particle. The removal rate efficiencies of phosphate removal from aqueous solution were found to increase as increase of surface area of particle.

### 3.2 Adsorption isotherms

The equilibrium data is important to analyse fitting classic adsorption isotherm equation. The Langmuir and Freundlich adsorption isotherm models were utilized to describe the equilibrium data. The Langmuir isotherm model is based on that the phosphate adsorption occurs on a solid surface by monolayer adsorption, which is expressed following equation (1).

$$ q_e = \frac{bq_mC_e}{1+bC_e} $$

(1)

Where, $q_e$ is the amount of phosphate adsorbed at equilibrium (mg/g), $C_e$ is phosphate concentration in equilibrium (mg/L), $q_m$ is maximum phosphate adsorption capacity on converter slag (mg/g), and $b$ is a constant related to phosphate on converter slag (L/g). The Freundlich equation is represented by following equation (2).

$$ q_e = K_FC_e^{(1/n)} $$

(2)

Where $q_e$ is the amount of phosphate adsorbed on the solid phase (mg/g), $C_e$ is the equilibrium phosphate concentration in solution phase (mg/L), $K_F$ is an indicator of the adsorption capacity and $1/n$ is the heterogeneity factor which has a lower value for more...
Table 2. The KF and $1/n$ values for the Freundlich isotherm and regression coefficients of equation

<table>
<thead>
<tr>
<th>Size</th>
<th>KF</th>
<th>$1/n$</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSa</td>
<td>5.80</td>
<td>0.36</td>
<td>0.95</td>
</tr>
<tr>
<td>CSb</td>
<td>1.70</td>
<td>0.42</td>
<td>0.99</td>
</tr>
<tr>
<td>CSc</td>
<td>2.91</td>
<td>0.37</td>
<td>0.92</td>
</tr>
<tr>
<td>CSd</td>
<td>1.52</td>
<td>0.32</td>
<td>0.95</td>
</tr>
</tbody>
</table>

heterogeneous surfaces. Application of the Freundlich equation to the data is illustrated graphically in Figure 1. Adsorption constants for Freundlich isotherm were illustrated in Table 2. However, result of Langmuir isotherm was negligible. Linearized forms of Freundlich isotherm for the phosphate adsorption on converter slag were shown in Figure 1.

The KF and $1/n$ values for the Freundlich isotherm and regression coefficients by equation (2) were shown in Table 2. The correlation coefficients ranging were from 0.92 to 0.99. The constant $n$ for $n>1$ indicates favourable adsorption. Higher adsorption capacity of CS was likely related to the higher surface area of CS. It can be postulated that the removal kinetics were greater at high concentration with bigger size of CS and greater at lower concentration with smaller size of CS.

3.3 Removal characteristics by column experiment

The characteristics of breakthrough curves strongly depended on operating concentration. The effect of phosphate concentration was explored at 10, 30 and 50 mg/L at constant flow rate as described in the experimental conditions. The volume of solution treated before breakthrough point was considerably reduced by increasing the influent concentration as shown in Figure 3 which implied breakthrough time was reached faster at low influent concentration. The initial pH of solutions were prepared at pH 7, the pH drop was appeared slowly for 10 mg/L as shown in Figure (2A) in long time, however it was appeared fast drop in a short time for 50 mg/L as shown in Figure (2C). For the results, the sharp drop of pH led to commonly the high efficiency of phosphate removal on high influent concentrations. The corresponding results appeared to the order of increasing of phosphate influent concentration. The increase of influent phosphate concentration led to shorter breakthrough time and sharp drop of pH of effluent.

The final solution pH reached at 9.7 for 10mg/L, 9.2 for 30mg/L and 8.6 for 50mg/L with the initial pH of
Table 3. Breakthrough time and breakthrough adsorption capacity for the different influent concentrations by column experiments

<table>
<thead>
<tr>
<th>Influent Concentration (mg/L)</th>
<th>10</th>
<th>30</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Breakthrough time(hr)</td>
<td>1.432</td>
<td>499</td>
<td>312</td>
</tr>
<tr>
<td>Breakthrough Adsorption Capacity(mg P/g CS)</td>
<td>3.543</td>
<td>2.436</td>
<td>1.722</td>
</tr>
</tbody>
</table>

7.0. The sharp decrease in pH at the initial run time for 50mg/L however gradual decrease of pH was revealed as experimental time for 10mg/L. The removal trend does not exactly controversial proportion to the pH drop of solution throughout run time shown in Figure 2. It seems that the slow decrease of removal induced gradual drop of pH at 10mg/L of phosphate solution, however faster pH drop with higher concentration at 50mg/L was appeared than any other concentration.

The influent concentration influenced both breakthrough time and adsorption capacity as illustrated in Table 3. The breakthrough times were 1,432, 499 and 312 hours for 10, 30 and 50mg/L of the influent concentration, respectively. The adsorption capacities were 3.543, 2.436 and 1.722 mg P/g CS for 10, 30 and 50mg/L of the influent concentration, respectively. The adsorption capacity at breakthrough time was decreased as increasing the influent concentration. The adsorption capacity was correlated with logarithmic relation for the influent concentration but the breakthrough time was less logarithmic linear relation than breakthrough adsorption capacity to the influent concentration with same amount of converter slag in column as shown in Figure 3. The breakthrough adsorption capacity was mainly influenced by breakthrough time, \( t_b \) as shown in Equation (3). It depends upon breakthrough time rather than the initial concentration in column experiment. Which means \( t_b \) is the functional factor of determining breakthrough adsorption capacity. The reason of the result is that \( t_b \) is main affecting factor though the breakthrough time should be shorter as increasing the influent concentration. The increase of influent concentration leads shorter breakthrough time and higher total adsorption quantity when the total adsorption quantity stands for the column experiment.

Thereby, the breakthrough adsorption capacity was low as same as that of breakthrough time as shown in Table 3. This explains that breakthrough adsorption capacity of adsorbed phosphate quantities is decreased at higher influent concentration.

The breakthrough time was decreased as increasing the influent concentration increasing from 10 to 50mg/L. The breakthrough adsorption capacity was calculated by the Equation (3) during the continuous flow column experiment (Crittenden, et al., 1987a).

\[
\frac{x_b}{m} = \frac{x_b}{m_{cs}} = Q(C_0 - C_b) \frac{t_b}{m_{cs}}
\]

Where, \( (x/m)_b \) is breakthrough adsorption capacity (g/g), \( m_{cs} \) is weight of converter slag(g), \( Q \) is flow rate (m$^3$/day), \( C_0 \) is influent concentration of phosphate(g/m$^3$), \( C_b \) is concentration of phosphate at breakthrough point(g/m$^3$), \( t_b \) is breakthrough time(day). The flow rate, Q and the weight of converter slag, mcs was fixed. Therefore the breakthrough adsorption capacity mainly depended upon breakthrough time, \( t_b \) for this study. The results indicated that adsorption capacity decreased 3.54g P/kg adsorbent to 1.72g P/kg adsorbent by increasing the influent concentration from 10 to 50mg/L as shown in Figure 3.

Logarithmic number of adsorption capacity and logarithmic number of breakthrough time was revealed by the linear decrease as increasing the influent concentration as shown in Figure 3.

<table>
<thead>
<tr>
<th>Breakthrough Time (hr)</th>
<th>Breakthrough Adsorption Capacity (mg P/g CS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.432</td>
<td>3.543</td>
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<td>499</td>
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</tr>
<tr>
<td>312</td>
<td>1.722</td>
</tr>
</tbody>
</table>

Fig. 3. Relation between logarithmic number of breakthrough time (hour) and logarithmic number of adsorption capacity (mg P/g CS) versus different influent concentrations.
in Figure 4. The adsorption breakthrough time obtained by changing influent phosphate concentration from 10 to 50 mg/L with conditions described procedure section. A decrease in phosphate concentration led to a later breakthrough time 432, 99 and 42 hours as increasing concentration, respectively. The results were revealed that the relation between concentration and breakthrough adsorption capacity was linearly logarithmic relation.

4. Conclusions

The by-product converter slag has been applied successfully for the removal of phosphate from aqueous solution. The volume of solution treated before breakthrough time was considerably reduced by increasing the influent phosphate concentration. converter slag exhibited significant phosphate adsorption capacities. The influencing factors for the removal of phosphate by converter slag were depending on particle size, time, initial concentration and pH of solution. In batch tests, particle size and initial concentration were the main influencing factors. The maximum phosphate adsorption earned by the application of Freundlich isotherm was mainly affected by its size. In column tests, the logarithmic conversions of both the breakthrough time and breakthrough adsorption capacity were fitted linear relation with influent concentration and decreased as increasing influent concentration.

References


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