Recovery oriented phosphorus adsorption process in decentralized advanced Johkasou

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ABSTRACT

Decentralized advanced wastewater treatment using adsorption and desorption process for recovery and recycling oriented phosphorus removal was developed. Adsorbent particles made of zirconium were set in a column, and it was installed as subsequent stage of BOD and nitrogen removal type Johkasou, a household domestic wastewater treatment facility. The water quality of the effluent of adsorption column in a number of experimental sites was monitored. The effluent phosphorus concentration was kept below 1 mg l^{-1} during 90 days at all the sites. Furthermore, over 80% of the sites achieved 1 mg l^{-1} of T-P during 200 days. This adsorbent was durable, and deterioration of the particles was not observed over a long duration. The adsorbent collected from each site was immersed in alkali solution to desorb phosphorus. Then the adsorbent was reactivated by soaking in acid solution. The reactivated adsorbent was reused and showed almost the same phosphorus adsorption capacity as a new one. Meanwhile, the desorbed phosphorus was recovered with high purity as trisodium phosphate by crystallization. It is proposed as a new decentralized system for recycling phosphorus that paves the way to high-purity recovery of finite phosphorus.

Key words | adsorption and desorption, decentralized advanced Johkasou, eutrophication, phosphorus recovery, phosphorus removal

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INTRODUCTION

In enclosed water bodies such as lakes and inland seas, water bloom and red tide have occurred with increases in nutrient salts such as nitrogen and phosphorus. Because of high proportion of domestic wastewater in pollution load, advanced treatment of domestic wastewater is required. Johkasou, a decentralized on-site wastewater treatment system, has become a centre of attraction because of low initial and running cost and high BOD and nitrogen removal efficiency (Watanabe *et al.* 1993; Ebie *et al.* 2002; Nakagawa *et al.* 2007). However, phosphorus is one of the rate-limiting factors for the growth of toxic algae. At this point of view, the importance of phosphorus removal from wastewater has been recognized.

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Recently, phosphorus resources depletion is also another important issue. Phosphorus is an essential nutrient, which cannot be substituted by any other element and is therefore a major component of fertilizers. World fertilizer consumption has increased almost six-fold from 1950 to 1995, and the supply of mineral phosphorus is anticipated to be exhausted globally in the mid-21 century (Steen 1998). Therefore, it is important to address not only phosphorus removal but also phosphorus recovery.

In order to remove phosphorus from wastewater, traditional chemical precipitation such as polyaluminium chloride (PAC) method (Boisvert *et al.* 1997) and enhanced biological phosphorus removal process have been used. These processes remove phosphorus from liquid to sludge. However, phosphorus recovery from the sludge is inefficient compared with recovering from liquid. Phosphate recovery system has been also developed such as magnesium ammonium phosphate (MAP) method (Jaffera *et al.* 2002). However, these methods can applied only in large scale systems treating wastewater containing high phosphorus concentration, and recovery ratio is not so high. The other weak points are difficulty of operation of crystallization process and insufficient removal of phosphorus to descharge to the natural environments. So far, the recovery oriented phosphorus removal process in decentralized system has not been developed.

One of the promising technologies for phosphorus removal and recovery from wastewater is the adsorption/desorption process because of its high phosphorus removal ability in the wide range of the phosphorus concentration. In this study, therefore, the recovery and recycling oriented adsorption/desorption phosphorus removal process in the small decentralized domestic wastewater treatment system "Johkasou" was developed and evaluated.

MATERIALS AND METHODS

Characteristics of phosphorus adsorbent

Phosphorus adsorbent used in this study was made of zirconium (supplied from Japan EnviroChemicals, Ltd.). The principle of the phosphorus adsorption is ion exchange. Although this particle adsorbs PO_4^{3-}, F^-, SO_2^-, Br^-, NO_2^-, Cl^-, and NO_3^-, the specificity to phosphorus is quite high. Influence of other ion on phosphorus adsorption is almost nothing. The shape of this adsorbent is spherical and particle diameter is 0.7 mm. The specific gravity is about 1.0 and the surface area is around $150\,m^2\,g^{-1}$. The phosphorus adsorption capacity of this adsorbent had been determined about 8 mg-P g-adsorbent^{-1} in the condition of neutral pH. The adsorbed phosphorus can be desorbed by soaking in alkali solution. Then the adsorbent is reactivated by using acid solution. This adsorbent can be used repetitively after reactivation.

Advanced Johkasou with phosphorus adsorption process

Phosphorus adsorption process was installed as subsequent stage of a BOD and nitrogen removal type Johkasou, a household wastewater treatment facility, to remove and recover the phosphorus (Figure 1). The phosphorus adsorption column was constructed as downflow reactor and some part of the effluent of the column was used for backwash of the adsorbent. The volume of the adsorbent particles was 60 L which was decided based on the phosphorus adsorption capacity and phosphorus load. The SV (Space Velocity) was approximately $1\,h^{-1}$. This system was installed in 30 sites in Tsuchiura, Japan. The effluent and influent, which was effluent of the Johkasou, of phosphorus adsorption column were collected and phosphorus concentration was measured to evaluate the performance of this phosphorus adsorption process.

The adsorbent was collected when the effluent phosphorus concentration of the column was over $1\,mg\,l^{-1}$ which was target water quality of advanced Johkasou

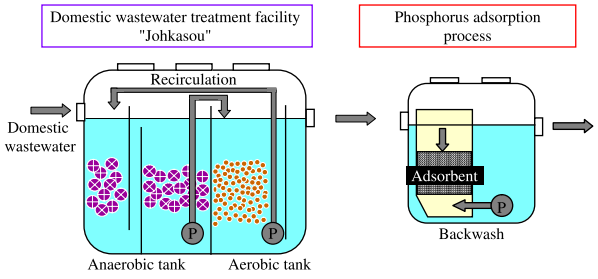

Figure 1 | Combination process of BOD and nitrogen removal type Johkasou and phosphorus adsorption column.

system. The collected adsorbent was moved to desorption process as below. After reactivation process, the adsorbent was replaced in the original experimental site, and the ability of phosphorus adsorption of the used adsorbent was monitored.

Desorption and reactivation of adsorbent and recovery of phosphorus

The adsorbent was collected from each experimental site when the effluent phosphorus concentration was over 1 mg l^{-1} and immersed in 7% sodium hydroxide solution to desorb phosphorus. The adsorbent was reactivated by soaking in 1% sulfuric acid. Meanwhile the desorbed phosphorus in desorption solution was crystallized in the low temperature concentrator in vacuo. The temperature was 50°C and degree of vacuum was −90 kPa. The recovered phosphorus from desorption solution was dried up at room temperature.

RESULTS AND DISCUSSION

Performance of the phosphorus adsorption process

BOD and nitrogen removal efficiencies were high in the Johkasou systems and effluent water quality was below BOD 10 mg l^{-1} and T-N 10 mg l^{-1}. Although phosphorus concentration of effluent of Johkasou was ranged from 1 to 10 mg l^{-1} (Figure 2), phosphorus adsorption column following the Johkasou removed phosphorus effectively and effluent phosphorus concentration was decreased to 1 mg l^{-1} or less. Time courses of the influent and the effluent phosphorus concentration in some experimental sites are shown in Figure 2. The high phosphorus removal ability of the column was confirmed in spite of variation of influent phosphorus concentration. During 90 days operation, effluent phosphorus concentration was kept below 1 mg l^{-1} at all the sites. Furthermore, over 80% of the experimental sites had achieved 1 mg l^{-1} of effluent phosphorus concentration during 200 days.

The phosphorus adsorption column must be backwashed to detach the biofilm even if the BOD concentration of the influent of the column is below 10 mg l^{-1}. Backwashing with effluent of the column once a day worked well and no clogging was observed in all experimental sites. This adsorbent was durable, and deterioration of the particles was not observed over a long duration.

Efficiency of desorption process and performance of reactivated phosphorus adsorbent

The adsorbent was collected at breakthrough point, 1 mg-P l^{-1}, and the collected adsorbent were immersed in desorption solution (7% sodium hydroxide) to desorb phosphorus. To optimize desorption process, desorption characteristics were investigated in desorption column. The effect of SV was investigated ranged from 1 to 20. In this desorption process, phosphorus concentration in

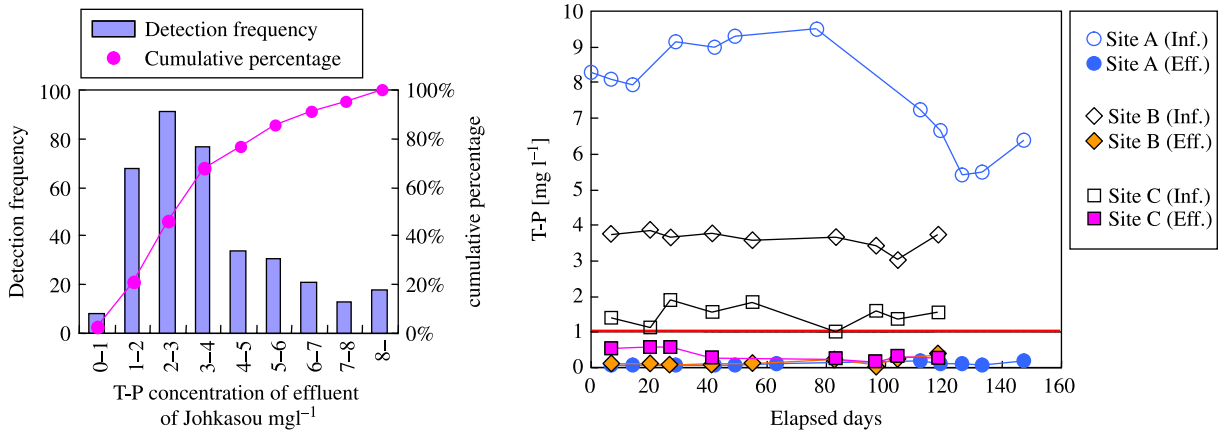

Figure 2 | Histogram of the effluent phosphorus concentration of Johkasou and performance of the phosphorus adsorption process.

desorption solution was immediately increased and saturated in 2 hrs. SV did not affect final concentration of desorbed phosphorus (data not shown). However, low SV, below 5 h^{-1}, caused coagulation in the column. Because no coagulation was observed in the condition of SVs 10 and 20 h^{-1}, this range of SV should be optimum.

The phosphorus concentration in desorption solution was also affected by the volume of desorption solution. In case of use of small volume of desorption solution, phosphorus concentration was high but desorption efficiency was low. Whereas, large volume of desorption solution led high desorption efficiency and low phosphorus concentration. In the condition of 3 L L-adsorbent^{-1}, 80% desorption efficiency was obtained and phosphorus concentration achieved to 2,500 mg l^{-1} (Figure 3).

However, 20% of phosphorus still remained in the adsorbent, and it must affect phosphorus adsorption capacity of the adsorbent after reactivation. The volume of desorption solution should not increase because the phosphorus concentration in desorption solution must affect phosphorus crystallization efficiency. Although reuse of once-used desorption solution increased phosphorus concentration in desorption solution from 2,500 to over 4,000 mg l^{-1}, desorption efficiency decreased to 60%. Therefore, a two-step desorption process was developed (Figure 4). In this process, the first step is crude desorption and the second step is finishing. Thus, the new desorption solution was used for second step, and once-used desorption solution was used for first step. In this two-step desorption process, desorption efficiency was increased from 80% to 95% and phosphorus concentration was 2,500 mg l^{-1} without increase of volume of desorption solution.

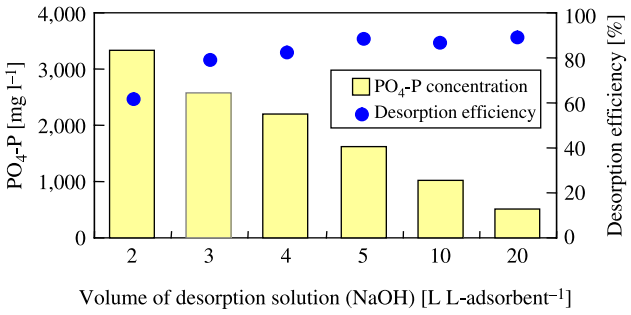

Figure 3 | Effect of desorption solution volume on phosphorus concentration in desorption solution and desorption efficiency.

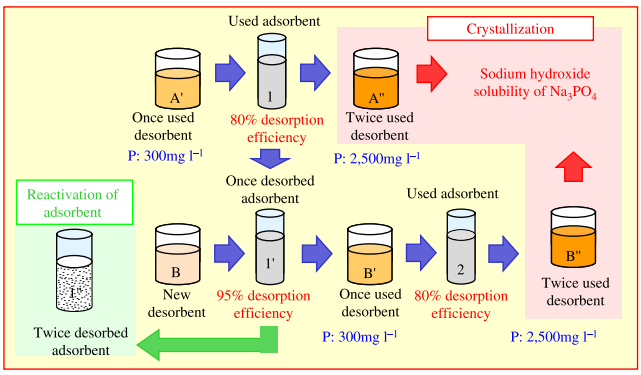

Figure 4 | Two-step desorption process to increase desorption efficiency and phosphorus concentration.

The recovered phosphorus was crystallized by use of low temperature concentrator in vacuo, and the maximum recovery efficiency achieved 95.6%. The phosphate was needle crystal and the purity was over 95%. As a result of X-ray analysis and X-ray fluorescence element analysis, the phosphate was assumed as trisodium phosphate dodecahydrate ($Na_{3.25}(OH)_{0.25}PO_4 \cdot 12H_2O$). After drying at room temperature, the recovered phosphorus from desorption solution was analyzed as fertilizer. The characteristics of the recovered phosphate are shown in Table 1. The solubility of the recovered phosphate for citric acid and water was high. It was confirmed that toxic substances such as Hg, As, Cd, Ni, Cr, and Pb met Japanese standard of fertilizer. Furthermore, effects of recovered phosphate as fertilizer was tested based on fertilizer response test. The germination rate and the fertilizer response of recovered phosphate were almost the same to chemical fertilizer, disodium phosphate.

To reduce chemical regent cost, desorption solution after crystallization was diluted by 7% and used to desorption process again. The result of the batch test showed no significant differences in desorption efficiency between diluted

Table 1 | Characteristics of the recovered phosphate

Items	Rate of content (%)				
Samples	**Moisture**	**T-P_2O_5**	**C-P_2O_5**	**W-P_2O_5**	**Na_2O**
Hydrate	53.29	17.60	17.59	17.40	25.05
Anhydrous	1.48	35.85	35.76	35.70	52.62
Disodium phosphate (control)	–	–	–	19.72	43.56

T: total; C: citrate acid solubility; W: water solubility.

used desorption solution and new one. Therefore, desorption solution after crystallization can be reused and it could reduce running cost.

After desorption process, adsorbent was washed by water and efficiently reactivated by soaking in 1% sulfuric acid. The reactivated adsorbent was refilled into the column and installed to the same experimental site. The reactivated adsorbent showed almost the same phosphorus adsorption capacity as a new one. Therefore, it is possible to reuse the adsorbent and reduce the cost.

CONCLUSION

The new decentralized recovery oriented phosphorus adsorption process was developed and evaluated in this study. High and sustainable removal efficiency was confirmed in the field test of the phosphorus adsorption column following decentralized domestic wastewater treatment facility (Johkasou). The effluent phosphorus concentration was kept below $1\,mg\,l^{-1}$ in the all experimental sites and no clogging was achieved by backwashing once a day. Because the phosphorus adsorption ability of the reactivated adsorbent was almost the same as the new one, adsorbent could be used repetitively. Effective desorption of adsorbed phosphorus was confirmed in the two-step desorption process developed in this study, and desorption efficiency was over 90%. The phosphate recovered from domestic wastewater was trisodium phosphate dodecahydrate and the purity was over 95%. This recovered phosphate could be used as fertilizer effectively. This phosphorus flow made by recovery from domestic wastewater is one of the ideal cycles.

The developed phosphorus adsorption and desorption process is enabled us to advanced removal and recovery of phosphorus from domestic wastewater to prevent eutrophication and to avoid depletion of phosphate resource. Therefore, it is proposed as a new decentralized system for recycling phosphorus that paves the way to high-purity recovery of finite phosphorus.

REFERENCES

Boisvert, J. P., To, T. C., Berrak, A. & Jolicoeur, C. 1997 Phosphate adsorption in flocculation processes of aluminium sulphate and poly-aluminium-silicate-sulphate. *Water Res.* **31**, 1939–1946.

Ebie, Y., Matsumura, M., Noda, N., Tsuneda, S., Hirata, A. & Inamori, Y. 2002 Community analysis of nitrifying bacteria in an advanced and compact Gappei-Johkasou by FISH and PCR-DGGE. *Water Sci. Technol.* **46**(11–12), 105–111.

Jaffera, Y., Clark, T. A., Pearce, P. & Parsons, S. A. 2002 Potential phosphorus recovery by struvite formation. *Water Res.* **36**, 1834–1842.

Nakagawa, G., Ebie, Y., Tsuneda, S., Matsumura, M. & Inamori, Y. 2007 Use of real-time PCR to examine the relationship between ammonia oxidizing bacterial populations and nitrogen removal efficiency in a small decentralized treatment system "Johkasou". *Water Sci. Technol.* **55**(7), 203–210.

Steen, I. 1998 Phosphorus availability in the 21st century: management of a non-renewable resource. *Phosphorus Potassium* **217**, 25–31.

Watanabe, T., Kuniyasu, K. & Ohmori, H. 1993 Anaerobic and aerobic submerged bio-filter system for small scale on-site domestic sewage treatment. *Water Sci. Technol.* **27**(1), 51–57.