

Research Article

The Simultaneous Recovery from Stock Raising Drainage of Phosphorus and Potassium

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Abstract

Zirconium-based adsorbent having 150 μm ~300 μm of diameter made by using the biomass which was not used at room temperature. Phosphorus adsorption was performed using fluidized bed reactor of lab scale for the biological treatment water of stock raising using this adsorbent. The quantity of adsorption was 0.9 mol/kg, and consecutive treatment was possible until during 10days which achieved 80% removal rate. Desorption operation allowed adsorption repeatedly. In addition, the desorption rate was 90%. Simultaneous recovery of phosphorus and potassium can be possible by use treatment water for desorption.

Keywords: Adsorption; Biomass; Phosphorus; Stock Raising Treatment Water; Zirconium

Introduction

The phosphorus resources would be exhausted in the near future. Japan imports all phosphate rock, so must think about correspondence toward the future now. Recovery of phosphorus from waste water is necessary. Around thirty years ago, it was a problem to influence eutrophication than exhausted, so the many removal methods were examined [1,2]. The physico-chemical removal method has a chemical precipitation method [3], crystallization method, the adsorption method. The cost for phosphorus removal of chemical precipitation method is cheaper, but the disposal of sludge is necessary. The crystallization can recycle phosphorus as manure material. The hydro-oxapatite crystallization is applied to secondary treatment water [4]. As to the manure effect of the deposit were argued. The MAP (Magnesium ammonium phosphate) method is suggested for phosphorus of the high concentration such as the anaerobic digestion liquid [5]. Magnesium ammonium phosphate contains nitrogen and phosphorus in three major manure ingredients. They are good methods, but the HAP and MAP crystal method can anticipate only the use as the manure in recycling. The adsorption method can satisfy its demand.

Its adsorbed phosphorus selectively and can get phosphorus of the high concentration by desorption operation. Sodium

phosphate becoming the industrial raw materials is made from a discrete liquid by adding sodium hydroxide for reproduction of the adsorbent [6]. Zirconium has affinity to phosphorus and fixed on ferrite as adsorbent. High performance of the adsorbent was shown by batch processing for the artificial waste water [7].

The target waste water assumed stock raising drainage. The waste water contained higher concentration of phosphorus and potassium, the potassium are resources that would be exhausted as well as phosphorus, so it aimed to simultaneously recovery of both materials.

Materials and Method

Preparation of adsorbent

Crude orange waste was kindly donated by JA Saga Beverage Ltd. Approximately 100 g of orange waste was taken together with and 8 g of $\text{Ca}(\text{OH})_2$ and crushed into small particles by were combined using a Hitachi VA-10 juice mixer for about 15 min at room temperature. The crushed orange waste suspension was transferred into to a beaker, mixed with a large volume of deionized water and stirred for 24 hr at 200 rpm. After stirring, the suspension was repeatedly rapidly washed by means of decantation with deionized water until a neutral pH was attained. Finally, the suspension was filtered to obtain a wet gel, which was dried at 70 °C for about 48 h. This is referred to as Saponified Orange Juice Residue (SOJR) hereafter. The dried gel was further ground into small particles. The specific surface area of this gel was measured

as 7.25 m²/g using Belsorp 18PLUS-SP (BEL Japan INC), and the leading principal pore size was found to be mesoporous with an average pore diameter of 14.3 nm. The SOJR thus

prepared was further modified by loading with Zr (IV) to facilitate phosphate adsorption. Approximately 3 gm of SOJR was equilibrated with 500 ml of 0.1 M zirconium at pH 2.11 for 24 hr. The mixture was then filtered, washed with deionized water, dried in vacuum and sieved to obtain the adsorption gel was sieved to produce a particle size fraction between 75 and 150µm for the adsorption test. The amount of zirconium loaded on the SOJR was calculated from the difference in the metal concentration in the solution before and after loading.

Stock raising drainage

Phosphorus-containing waste solution was collected from a secondary effluent of piggery wastewater treatment plant (Saga Livestock Research Institute, Japan). The effluent was analyzed and the composition of the secondary effluent is shown in Table 1. Total Organic Carbon (TOC) was also measured using a TOC analyzer (Shimadzu-TOC-V, Japan). As can be seen from Table 1, a relatively high concentration of phosphorus in the effluent necessitates treating the waste solution before discharging it to the environment.

Characteristics of adsorbent

As for the sedimentation rate, the density and particle size were measured using Andreasen pipet, pycnometer and a laser-style particle size meter respectively.

Adsorption and desorption test

The continuous adsorption test for phosphate removal was carried out in a transparent glass fluidized bed - reactor 2 cm inner diameter, 10 cm long plexiglass tube was fused to a 6 cm inner diameter, 5 cm long tube to form the 150 ml reactor body (Figure 1). Approximately 5g of the Zr-SOJR was first soaked in deionized water to facilitate swelling and then packed into the reactor. The phosphate solution (from the secondary effluent) was fed through the bottom of the column at a desired flow rate using an Iwaki model PST-100N peristaltic pump. The pH of the solution was adjusted to 3 with H₂SO₄. At set time intervals, Samples were using a Biorad Model 2110 Fraction Collector at definite time intervals in 8 ml plastic tubes using a Biorad Model 2110 Fraction Collector, and were analyzed for the residual concentration of phosphate. After complete adsorption, an elution test was carried out by percolating 0.2 M NaOH solution at the same flow rate. All the experiments were carried out at 30 °C. To recover phosphorus as solid at the time of the adsorbent reproduction, high concentration magnesium was added to the eluted solution after precipitation, the solution was filtered and the filtrate and filter cake were analysed by ICP-

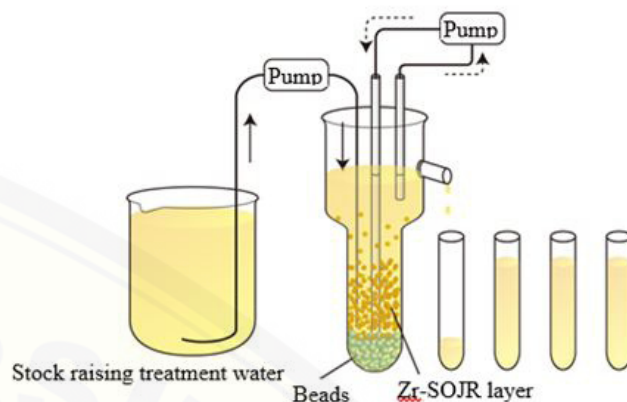


Figure 1: Experimental set up.

Solidification of the phosphorus solution

A concentrate method of desorption liquid by heating was suggested to solidify as sodium phosphate [8]. This study used higher potassium concentration in the effluent of adsorption. Potassium and phosphorus react and generate phosphorus acid magnesium potassium when it adds magnesium because pH of the desorption liquid is high. Therefore, its dissolved sodium hydroxide in processing water and used it for desorption operation. The reaction is thought about as follows [9]. In addition, as for the treatment water potassium concentration was 207 mg/dm³ and the magnesium concentration was 37.4 mg/dm³.



Results and Discussion

Characteristics of adsorbent

The characteristic of this adsorbent is made without adding heat, on the other hand, many adsorbents need heating to over 400 °C [10,11]. It examined a particle size and density and the relations with the sedimentation rate in Table 1. The separation of effluents and adsorbent becomes easy when particle size larger than 150µm. It used to the adsorbent more than 150µm in the following experiments from a result of Table 1.

	density (g/cm ³)	Mean diameter (µm)	Settling rate (cm/s)
>300µm	1.53	568	9.34
150-300µm	1.67	324	3.85
<150µm	1.72	106	0.44

Table 1: Relationship between diameter and settling rate.

Effects of pH

Figure 2 shows that effects of equilibrium pH on treatment with SOJR and Zr-loaded SOJR. SOJR did not show anionic adsorption, and the phosphorus concentration did not change to pH 5. The concentration decreased at further high pH and became approximately 0 when pH 10. Raw piggery water contains high in Ca Mg, NH₄, So Suzuki et al. increase by aeration in raw piggery waste water as act decarbonation, and made MAP particle. The major cation concentration is higher, Ca = 123, NH₄ = 253 mg/L, Mg = 22.5 mg/L in this study. With pH increases, that concentration decreased to Ca = 3.19, NH₄ = 4.95 and Mg = 0.696 mg/L. The decrement which was higher than a decrement of phosphorus was seen. It was thought that it was caused by the formation of the cation and phosphorus complex materials. It adjusted pH of solution to 2 in the following experiments from a result of Figure 2 and Figure 3.

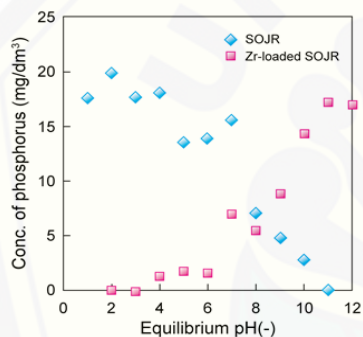


Figure 2: Effects of pH on phosphorous concentration with and without adsorbent in batch treatment.

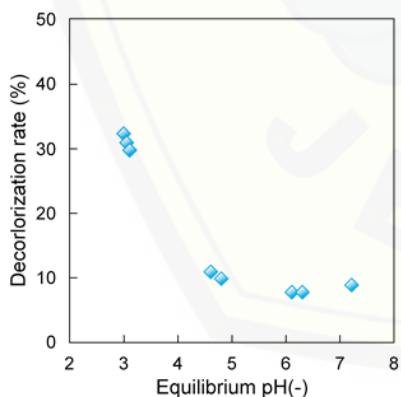
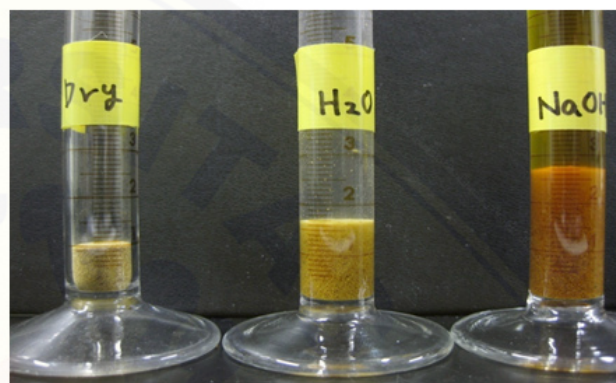


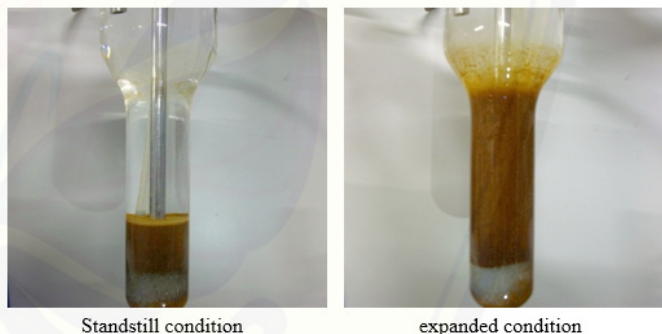
Figure 3: Effects of pH on decolorization rate.

Continuous treatment

Photograph 1 shows about dry condition, in the water condition and in the alkaline solution condition respectively. The reproduction of adsorbent assumes that it used the sodium hydroxide of 0.2 - 0.5 M. The volume of adsorbent expanded in a process of the desorption from adsorption, therefore a reactor was selected with a fluid bed type. The un-flow and flow condition are showed in Photograph 2.



Photograph 1: Adsorbent volume swells in water and alkali solution.



Photograph 2: Up-flow condition in reactor.

It shows the result of adsorption of the second treatment water from stock raising in Figure 4. There are many reports for raw water [12,13], but there are only a little for after the biological treatment water the removal rate maintained 80% by the first and second adsorption operation until 10 days and 14 days. By the adsorption experiment, I handled 8.3 dm³ treatment water in total, and the quantity of phosphorus adsorption were 0.81 mol/kg and 0.95 mol/kg for the first operation and second operation respectively.

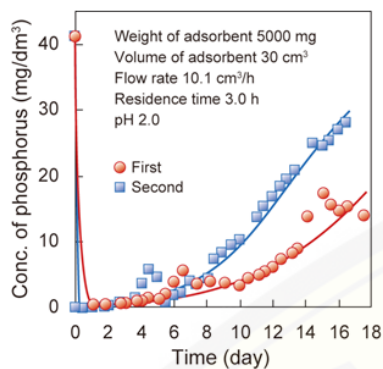


Figure 4: Adsorption of the second treatment water from stock raising.

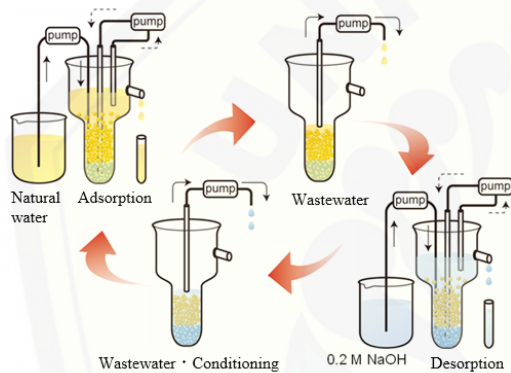


Figure 5: Experimental procedure adsorption and desorption.

When adsorbent have reached the saturation, it revitalizes adsorbent by 0.2M alkali solution. Afterwards, its repeated adsorption operation. Specifically, its repeated inflow-standstill-separation using second treatment water and alkaline solution like the sequencing batch method in Figure 5. It shows the result of desorption in Figure 6.

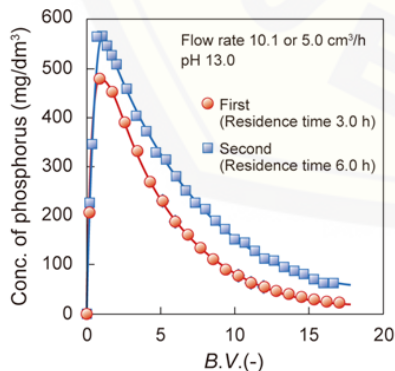


Figure 6: Relationship between bed volume (Treatment volume/adsorbent volume).

Approximately 500 cm³ of 0.2 M NaOH solution was feed by the desorption experiment, and the phosphorus desorption rate was 56% and 94% for first and second operation respectively. In addition, the phosphorus concentration of desorption liquid was 238 mg/dm³ with 163 mg/dm³ for first and second operation respectively. As a result, phosphorus was concentrated to 4 times and 6 times for first and second operation, respectively.

Solidification of the phosphorus solution which desorbed

In Figure 7 the ingredient of the solid was estimated from a decrement in a liquid. As a result, potassium magnesium phosphate was generated, and pH after the equilibrium decreased to 10.0.

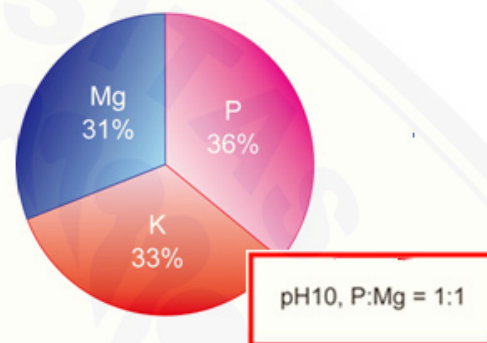


Figure 7: The estimate of the ingredient of the solid.

Conclusions

Zirconium-based adsorbent having 150µm~300µm of diameter made by using the biomass which was not used at room temperature. Phosphorus adsorption was performed using fluidized bed reactor of lab scale for the biological treatment water of stock raising using this adsorbent. The quantity of adsorption was 0.9 mol/kg, and consecutive treatment was possible until during 10 days which achieved 80% removal rate. Desorption operation allowed adsorption repeatedly. In addition, the desorption rate was 90%. Simultaneous recovery of phosphorus and potassium can be possible by use treatment water for desorption. Both phosphorus and potassium were thought dry resources in the near future. That is why this technique is effective.

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