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Preparation of phosphate sequestration agent from waste paper sludge using granulation and calcination

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ABSTRACT : *Paper sludge (PS) is generated as an industrial waste during the manufacture of recycled paper products, and amounts discharged globally are increasing annually. On the other hands, phosphate is usually considered as the limiting nutrient with respect to the eutrophication of natural bodies. In this study, paper sludge was converted into an effective phosphate sequestration agent through granulation and calcination. PS was granulated with distilled water using pan granulator (40 rpm) at 30 – 50 °C with the angle of 30 – 45 °, and the sludge can be granulated at 40 - 50 °C with the angle of 37.5 – 45 ° for less than 10 min. The particle shapes of granulated sludge can be kept after calcination at 800 °C, and the product, which was granulated at 40 – 50 °C with the angle of 45 °, indicates strong porous structure. The product has phosphate removal ability for water purification, due to the formation of calcium phosphate minerals.*

KEYWORDS: *Paper sludge, Phosphate removal, Granulation, Calcination, Recycle*

I. INTRODUCTION

During the manufacture of recycled paper, paper sludge is discharged as an industrial waste. Over 3 million tonnes of sludge is discharged per year in Japan, and approximately 8 and 2 million tonnes are discharged in the United States and the United Kingdom, respectively [1 - 3]. These amounts are increasing annually. Although a small part of paper sludge is used as a soil improver and fertilizer in agriculture [4 - 8], most of the paper sludge is usually disposed of in open dumps or in landfills after incineration. Recently, reduction of available landfill space increasing costs of land disposal of waste in industrial countries necessitates other means for the disposal of waste paper sludge. An economically valuable solution to this problem should include utilization of the waste materials as new products for other applications rather than disposal in a landfill.

Phosphate is usually considered as the limiting nutrient with respect to the eutrophication of natural water bodies. Therefore, water treatment facilities remove phosphate from the wastewater before it is returned to the environment. Various techniques have been used for phosphate removal. Among these, chemical precipitation, adsorption, and biological methods have been applied successfully. Adsorption is a comparatively more useful and more efficient technique for removing phosphate [9]. Because recycling and reuse of wastes are energy efficient, environmentally friendly, and cost-effective, phosphate adsorbents can be produced from many raw materials, such as industrial and agricultural wastes, at low cost. For example, coal fly ash [10, 11], slag [12], red mud [13], alum sludge [14], cow bone [15], peat [16], oyster shell [17], scallop shell [18], wheat straw [19], and iron oxide tailings [20] have been used to remove phosphate. Paper sludge varies in composition from mill to mill, but is composed generally of organic fibers (cellulose, hemicelluloses, and/or lignin) and inorganic fillers and coating materials such as kaolinite ($Al_2Si_2O_5(OH)_4$), limestone ($CaCO_3$) and talc ($Mg_3Si_4O_{10}(OH)_2$); the level of potentially toxic components normally is extremely low [21, 22].

In our previous studies, it was confirmed that paper sludge ash, produced from paper sludge by incineration for energy recovery in the manufacturing process, has a high affinity for phosphate and heavy metals in aqueous solution [23 – 26]. In addition, paper sludge calcined at 800°C showed good removal ability for phosphate ion, fluoride ion, and heavy metal ions to develop an active phase for removal [27 – 30]. Furthermore, paper sludge can be granulated using distilled water, and calcined paper sludge granules (ø2 - 4 mm), which keep the shape strongly, can be prepared without chemical binder [31]. Therefore, paper sludge is expected to be converted into the particles with phosphate removal properties after appropriate heat-treatment via granulation. The present study describes the preparation of phosphate sequestration agent particles from waste paper sludge by granulation and calcination with the goal of developing original ways of utilizing waste paper sludge for water purification.

II. MATERIALS AND METHODS

Sample: Paper sludge (PS) from a paper company in Japan was used as the starting material. Raw PS is aggregate blocks, and for this experiment, the PS was dried at 80 °C overnight, milled and sieved for particle size less than 250 µm. The chemical composition of the PS is listed in Table 1. The PS contained 4.3 % moisture, organic components such as cellulose fibers (29.0 %), and inorganic components (66.7 %), predominantly CaO (29.7 %), SiO_2 (15.5 %), and Al_2O_3 (15.6 %). The moisture and organic contents in the PS were determined by differential thermal analysis (DTA) / thermo-gravimetry (TG) (TG8120, Rigaku, Japan) in the temperature range 20 - 1000 °C at a heating rate of 10°C/min in flowing air. The inorganic elements in the PS were determined by X-ray fluorescence (XRF) (Primini, Rigaku, Japan).

Table 1. Chemical composition of paper sludge (wt.%)

Moisture	Organic content	Inorganic content							
4.3	29.0	CaO	SiO_2	Al_2O_3	MgO	Fe_2O_3	Cl	SO_3	P_2O_5
		29.7	15.5	15.6	4.1	0.7	0.1	0.4	0.2

Granulation and calcination : Preparation procedure of calcined PS particle in this experiment is shown in Figure 1. A pan granular (DPZ-01R, As One, Japan) with a diameter of 300 mm and depth of 120 mm was used for granulation of paper sludge. The pan speed was fixed at 40 rpm, and the granulation time is 10 min. The temperature of the pan is 25 - 50 ºC and pan angle are 30 - 45 º. Initially, distilled water was sprayed using a handheld sprayer on the granulator surface and powder PS were added to form a wet bed. 1 - 3 grams of powder PS was used, and the addition of distilled water to rotation pan granulator was used as they helped information of granules. After the granulation process, the samples were first dried in a drying oven at 80 ºC for 4 h, the obtained PS particles were calcined at 800 °C for 1 h in an electric furnace under air atmosphere and then cooled to room temperature to obtain the calcined product.

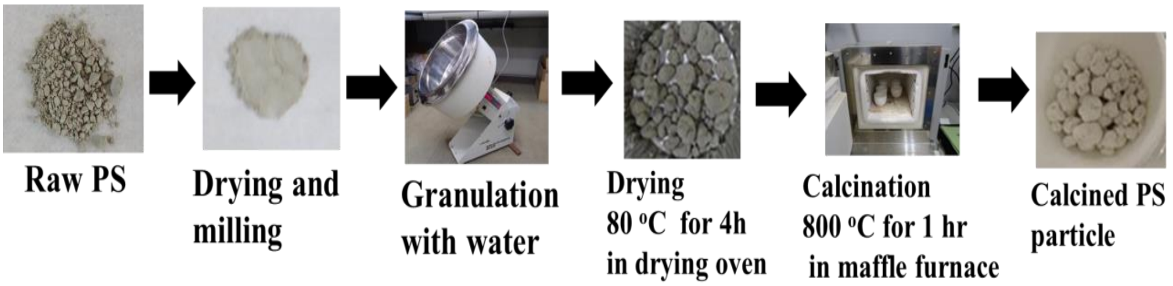

Figure 1. Preparation procedure of calcined PS particle in this experiment.

The mineralogical compositions of raw PS and the product were determined by powder X-ray diffraction (XRD) (miniFlex600, Rigaku). The morphologies of the product were analyzed using an optical microscope (VHX-5000, Keyence) and scanning electron microscope (JSM-6510A, JEOL). The particle distribution of the product was measured using 4 sieves to separate the particle into 5 groups (< 0.5 mm, 0.5 - 1 mm, 1 – 2 mm, 2 – 4 mm, > 4 mm). The strength of the product particle in water was examined as follows; 0.2 g of the products obtained on various conditions were added into 20 mL of distilled water in 50 mL of the centrifuge tube, and then the tube was shaken with a reciprocal shaker (SR-1, TAITEC) at 60 rpm for 1 h. After shaking, the particle shape was observed.

Phosphate removal: Phosphate removal ability of the product was examined using the KH_2PO_4 solution with 0.01 M and 0.1 M, assuming the fish aquarium and sewage wastewater, respectively. It is noted that the pH of each solution was adjusted to 7.5 by adding NaOH solution. 0.3 g of the product particles were added into 30 mL of the phosphate solution, and after settling for 1 day, a part of the supernatant solution (2 mL) was collected to determine the phosphate concentration using molybdenum blue method. After collecting 2 mL of the solution, 2 mL of fresh phosphate solution was added into the solution, and settle for 1 day again. This process was repeated 10 times (10 days) to estimate phosphate removal. The removal of phosphate was calculated by the difference between initial and measured phosphate concentration.

III. RESULTS AND DISCUSSION

Table 2 shows the results for granulation of PS. Granulation of PS is succeeded at the temperature over 40 ^{o}C and at the angle over 37.5 ^{o}, while that is not succeeded at 25 ^{o}C and 30 ^{o}.

Table 2 Results for granulation of PS

Temperature (^{o}C)	Angle (^{o})		
	30	37.5	45
25	X	X	X
40	X	O	O
50	X	O	O

Figure 2 shows the photos of granulated PS at 50 ^{o}C and calcined PS. The granules of PS can be observed after granulation at 37.5 ^{o} and 45 ^{o}, while the PS powder remains after granulation at 30 ^{o}, which indicates that 30 ^{o} (low angle) is not enough to granulate PS using distilled water. It is noted that the shapes of all samples keep after calcination and becomes hard with white color, which means that the granulation of PS is possible using distilled water without chemical binders.

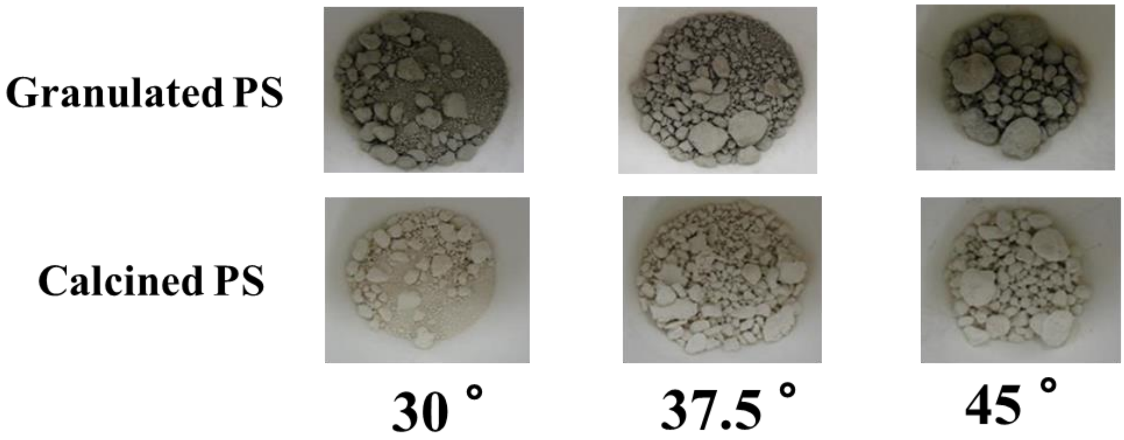

Figure 2. Photos of granulated PS and calcined PS: Granulation at 50 ^{o}C.

Figure 3 shows the particle size distribution of calcined PS after granulation at 50 ^{o}C. With increasing the angle of granulation, the particle size increases. It is noted that particle size distributions of granules above 1 mm are 92.69 % at 45 ^{o}, 49.16 % at 37.5 ^{o}, and 33.90 % at 30 ^{o}.

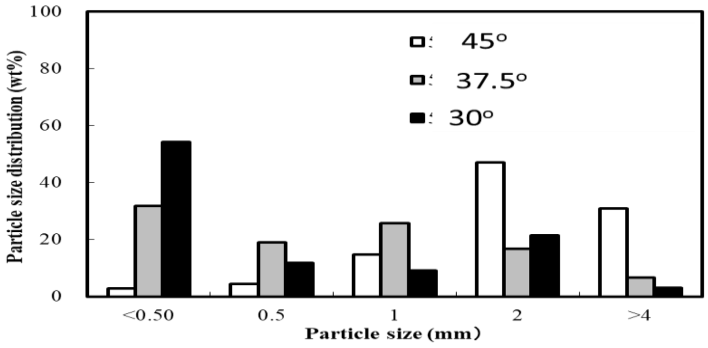

Figure 3. Particle size distribution of calcined PS: granulation at 50 ^{o}C.

Figure 4 shows the photos of calcined PS after (a), (b) granulation at 50 ºC, (c), (d) granulation at 40 ºC, and (e), (f) calcined raw PS block. The calcined samples after granulation at both 50 ºC and 40 ºC are an almost spherical shape with a smooth surface, while calcined raw PS block is an irregular shape with some deep depressions. It can be observed that all granules are the aggregates of many small crystals.

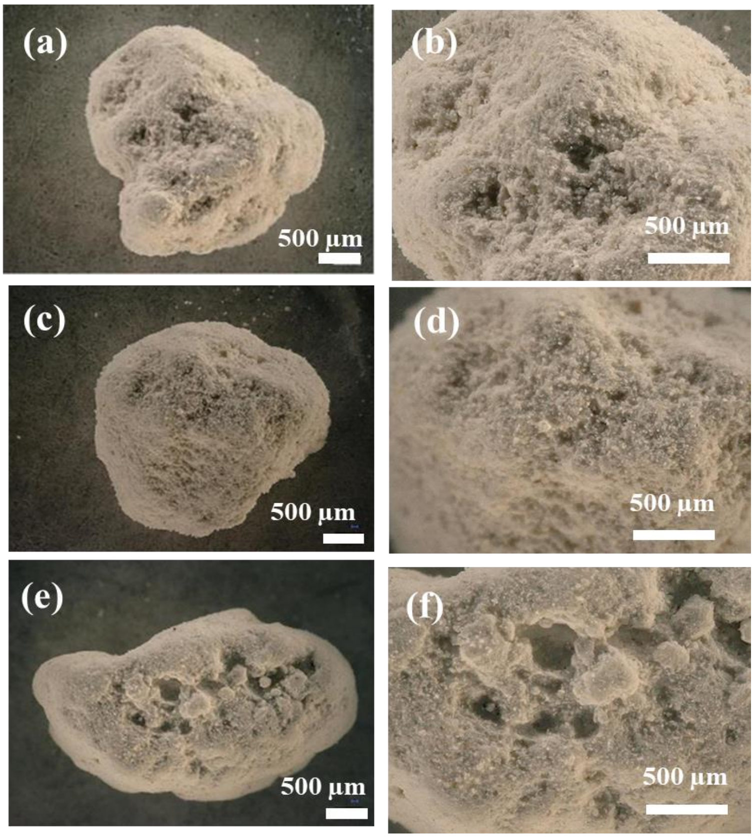

Figure 4. Photos of calcined PS after (a),(b) granulation at 50 ºC, (c),(d) granulation at 40 ºC, and (e),(f) calcined raw PS block.

Figure 5 shows the SEM photos of (a) raw PS block, (b) calcined raw PS block, and calcined PS after (c) granulation at 30 º and (g) granulation at 45 º. The SEM microphotograph of PS shows an agglomerated texture of organic fibers together with fine particles, which seem to be kaolinite and calcite, with a rough surface (Fig. 5 (a)), and calcined raw PS block composed of the large platy block with irregular size (Fig. 5 (b)). Calcined PS after granulation is the agglomerated particles with pore spaces, and that after granulation at 45 º is more filled than that after granulation at 30 º.

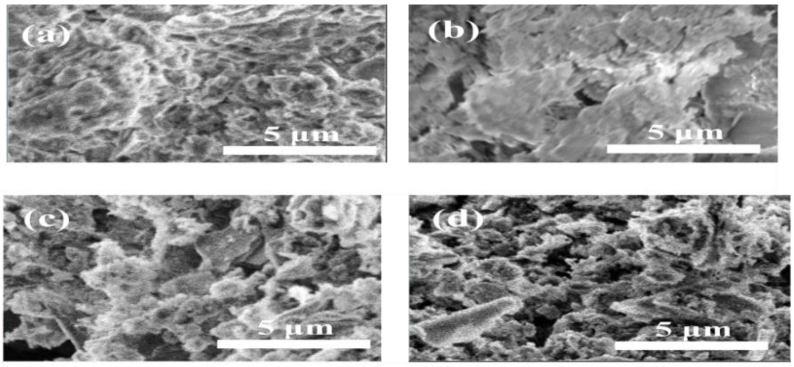

Figure 5. SEM Photos of (a) Raw PS block, (b) calcined raw PS block, and calcined PS after (c) granulation at 30 º, and (d) granulation at 45 º.

Figure 6 shows the strength of the granulated calcined PS particles and calcined raw PS block in water. Granulated calcined PS particles after granulation at the angle of 45 ° at 40 °C and 50 °C can keep the particle shape, while calcined PS after granulation at 37.5 ° collapses to be powder. It would be considered that the strength of the particle is higher by increasing the angle of granulation to be packed strongly. It is noted that large size particles of calcined raw PS brock remain to generate powder.

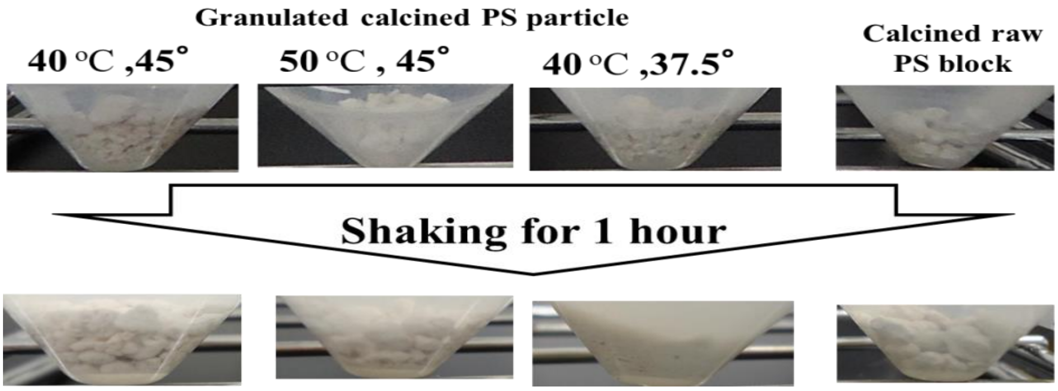

Figure 6. The strength of the granulated calcined PS particles and calcined raw PS block in water.

Figure 7 shows that the change of phosphate concentration after adding the granulated calcined PS particles and calcined raw PS block in (a) 0.01 mM KH_2PO_4 solution and (b) 0.1 mM KH_2PO_4 solution. 0.01 mM P concentration solution simulates fish aquarium and 0.1 mM P concentration solution simulates sewage waste water. In the case of 0.01 mM solution, phosphate concentration decrease in first 2 days for all samples. For the calcined PS particles granulated at 40 °C, phosphate concentration in the solution increases after 2 days, and then become almost constant (0.01 mM) after 4 days, which means that the PS particle can't remove phosphate in the solution after 4 days. For calcined raw PS blocks, the phosphate concentration in the solution decreases in 5 days, then increases after 5 days and be almost constant (0.01 mM) after 8 days. The calcined PS particles after granulation at 50 °C can keep low phosphate concentration in the solution in 10 days, which means that the phosphate removal is maintained in 0.01 mM phosphate solution for 10 days. The total phosphate removals of calcined PS granulated at the temperature of 40 °C at the angle of 45 ° and 37.5 ° are 3.3 μmol/g and 2.0 μmol/g, respectively, while those of calcined PS granulated at 50 °C and of calcined raw PS block are 4.9 μmol/g and 4.6 μmol/g, respectively. In the case of 0.1 mM solution, the tendencies of all samples for phosphate concentration are almost the same. The phosphate concentration decreases initially for 1 day, then increase to 0.08 mM in 3 days, and be almost constant after 3 days. The total phosphate removals of all samples in 10 days are 30 – 40 μmol/g.

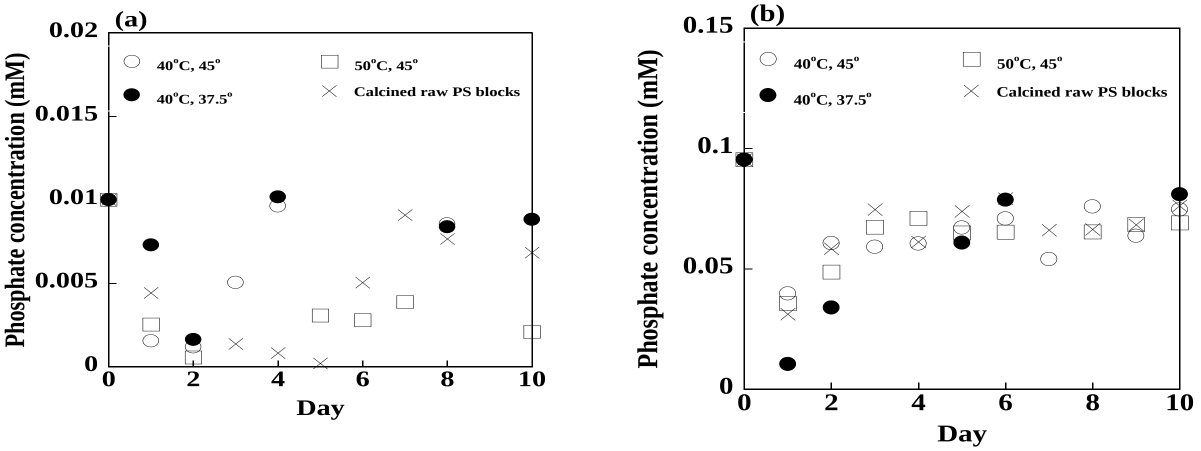

Figure 7. Change of phosphate concentration after adding the granulated calcined PS particles and calcined raw PS block in (a) 0.01 mM KH_2PO_4 solution and (b) 0.1 mM KH_2PO_4 solution.

Figure 8 shows the XRD patterns of (a) raw PS, (b) the granulated calcined PS particles and the granulated calcined PS after 10 days phosphate removal test in (c) 0.01 mM KH_2PO_4 solution and (d) 0.1 mM KH_2PO_4 solution. For raw PS, the main crystalline constituents were cellulose (with relatively broad peaks due to the low crystallinity of the fibers around 2θ = 20 °), calcite ($CaCO_3$), kaolinite ($Al_2Si_2O_5(OH)_4$) and talc ($Mg_3Si_4O_{10}(OH)_2$) (the filler and/or coating components of the paper) (Fig. 8(a)). After calcination at 800 °C, The peaks assigned to calcite and kaolinite disappeared to form amorphous $CaO\text{-}Al_2O_3\text{-}SiO_2$ (CAS) and portlandite ($Ca(OH)_2$) [29, 30] (Fig.8 (b)). Although mainly amorphous broad peaks are present before phosphate removal test (Fig. 8 (b)), the peaks of phosphate minerals, brushite ($CaHPO_4{\cdot}2H_2O$) and hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), and tobermorite ($Ca_5Si_6O_{16}(OH)_2{\cdot}7H_2O$) appear in the samples after phosphate removal test (Fig. 8 (c), (d)). Amorphous CAS, which has high solubility, was thought to react with phosphate ion in aqueous solution to form calcium phosphate and thus cause the removal of phosphate ion from aqueous solution.

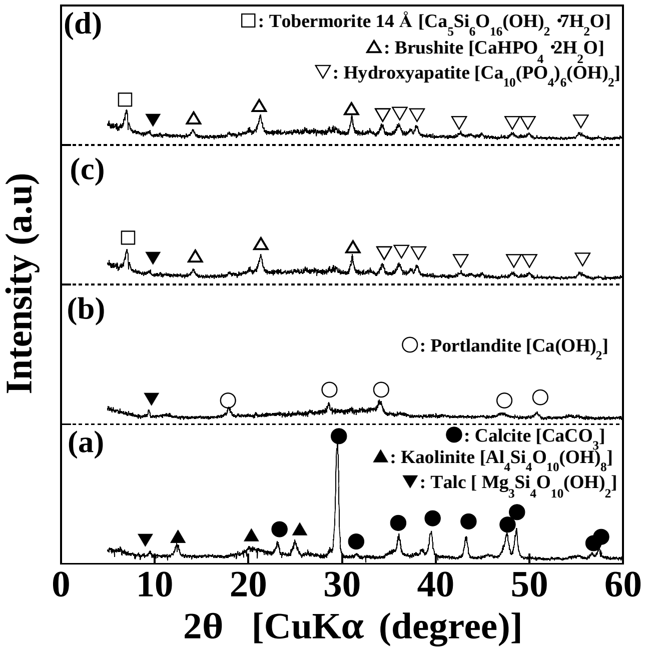

Figure 8. XRD patterns of (a) raw PS, (b) the granulated calcined PS particles and the granulated calcined PS after 10 days phosphate removal test in (c) 0.01 mM KH_2PO_4 solution and (d) 0.1 mM KH_2PO_4 solution.

IV. CONCLUSION

We attempted to prepare the phosphate sequestration agent from PS using granulation and calcination. The sludge can be granulated at 40 - 50 °C with the angle of 37.5 – 45 ° for less than 10 min. The particle shapes of granulated sludge can be kept after calcination at 800 °C, and the product, which was granulated at 50 °C with the angle of 45 °, indicates strong porous structure and high phosphate removal ability, depending on the formation of brushite and hydroxyapatite. Thus, PS is an inexpensive raw material for producing a phosphate sequestration agent, and this material is suitable for reducing environmental pollution caused by the presence of phosphate in water.

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