

Ammonium recovery from biocatalytic calcification reactor effluent by struvite precipitation

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Abstract

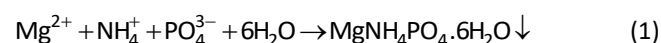
Chemical precipitation is a suitable method for the recovery and removal of ammonium in water and a fertilizer known as MAP (magnesium ammonium phosphate; $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$; struvite) is obtained. Additionally, the advantage of this method is that environmental conditions do not have any effect compared to biological methods. In this study, the recovery of ammonium ($C_{\text{mean}}=348 \text{ mg NH}_4^+/\text{L} \pm 38.1$; $n=25$) occurred after the hydrolysis of urea in the biocatalytic calcification reactor (BCR) effluent and it precipitated as struvite. The effects of operating parameters, such as different phosphate and magnesium sources, $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ molar ratio, pH value, mixing speed-time, and fertilizer effect, were examined. The precipitates were characterized by X-ray diffraction and scanning electron micrograph. The optimum molar ratio of $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ was determined as 1.25:1:1. Studies using different pH ranges (7–10) and this molar ratio showed that the ammonium recovery of approximately 96% was reached at a pH value of 9.36. It was seen that the rapid mixing (200 rpm) of 30-s period and the slow mixing (30 rpm) of 2-min period were sufficient for MAP precipitation. Struvite that was obtained after precipitation was used as a fertilizer and it was observed to have a positive effect on plant growth.

Keywords: Ammonium Recovery, Biocatalytic Calcification, Chemical Precipitation, Fertilizer, Struvite.

1. Introduction

Nitrogen compounds are nutrients essential to all forms of life and when present in considerable quantities in receiving waters such as lakes and rivers they can cause eutrophication, resulting in excessive growth of algae and other microorganisms, as well as increased dissolved oxygen depletion and fish toxicity (Huang *et al.*, 2010a). Therefore, the removal of ammonium from wastewater is of great importance in the control of nitrogen pollution (Thornton *et al.*, 2007; Wen *et al.*, 2006). High content of ammonia nitrogen has a toxic effect on microorganisms, which may lead to a decrease in the treatment efficiency

of the biological process (Huang *et al.*, 2011). Struvite precipitation is a valid alternative for the removal of high ammonia concentrations such as piggery wastes due to its high removal effectiveness, reaction rate, and solid–liquid separation capability (Huang *et al.*, 2011). In addition, struvite could be directly used for horticulture and agriculture, such as potato production, and even used for fish farming, like trout and salmon population conservation (Wang *et al.*, 2010). Reaction of ammonium ions with phosphate and magnesium ions to form struvite, which is a white orthorhombic mineral with a crystalline structure and a precipitate with a very low solubility product (2.5×10^{-13} , 25°C) (Huang *et al.*, 2014; Lee *et al.*, 2003; Macintyre, 1996; Zhang *et al.*, 2004), has attracted much attention because of the extremely high reaction rates and low residual ammonium concentrations. The reaction is shown in Equation 1 (Zhang *et al.*, 2004).



Struvite precipitation was commonly used in different processes such as raw swine wastewater (Lin *et al.*, 2015), anaerobic digestate effluent (Hidalgo *et al.*, 2016), sewage sludge ash (Xu *et al.*, 2012), urine (Antonini *et al.*, 2011; Kemacheevakul *et al.*, 2014; Latifian *et al.*, 2014; Zhigang *et al.*, 2008), washing wastewater (Huang *et al.*, 2010b), and reject water of sludge thickening and dewatering (Ren *et al.*, 2015).

In literature, there is a lack of knowledge about MAP precipitation in the biocatalytic calcification reactor (BCR) effluent, so in this study, physical and chemical parameters, which are effective in MAP precipitation, were investigated. The working principle of the recovery of ammonium ($C_{\text{mean}}=348 \text{ mg NH}_4^+/\text{L} \pm 38.1$; $n=25$) in the biocatalytic calcification reactor (BCR) effluent is to precipitate Ca as CaCO_3 by creating a high pH and alkalinity with the addition of urea. Effluent values of ammonium concentration clarified that urea was mostly transformed into ammonium in the process (Işık *et al.*, 2010). Magnesium and phosphate required for precipitation were provided from different chemical sources. Optimum molar ratio of $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ was determined. Studies using different pH ranges (7-10),

mixing rapid and period, used this molar ratio. Struvite obtained after precipitation was used as a fertilizer and it was observed that struvite has a positive effect on plant growth.

2. Materials and Methods

2.1. Wastewaters and chemicals

The wastewater of BCR effluent was used in the experiments. Some parameters of the wastewater sample are given in Table 1. In this study, pure $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, MgO , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, H_3PO_4 (%85), and $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ were used as the magnesium and phosphate sources. During the struvite reaction, the pH of the solution was adjusted to the desired value by the addition of 2 N NaOH.

2.2. Struvite precipitation experiments

All the experiments were carried out in triplicate at a wastewater temperature ranging from 20 to 25 °C. The experiments of MAP precipitation were carried out in 500 mL of wastewater in 600 mL beakers batchwise. The amounts of Mg^{2+} and PO_4^{3-} sources were added according to initial concentrations. The $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ molar ratio was initially adjusted by adding the appropriate quantity of chemicals, which is mentioned in the material section. Coagulation (200 rpm, 2 min) and flocculation (30 rpm, 5 min) were applied with jar test (Velp, FC6S). After 10 minutes of settling, the supernatant sample was taken and analyzed (Figure 1). According to results, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and H_3PO_4 (%85) were used as the magnesium and phosphate sources to determine optimum $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ molar ratio, pH, mixing speed, and time.

Table 1. Some parameters of wastewater

Parameters	pH	TOC (mg/L)	TN (mg/L)	$\text{NH}_4\text{-N}$ (mg/L)	$\text{PO}_4\text{-P}$ (mg/L)	Na (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)	Turbidity (NTU)
Mean	8.37	56.43	279.17	270.21	6.71	352.08	27.04	3.44	90.95	54.66
SD (\pm)	0.18	19.6	30.02	28.43	1.58	55.41	2.21	5.62	15.17	20.6

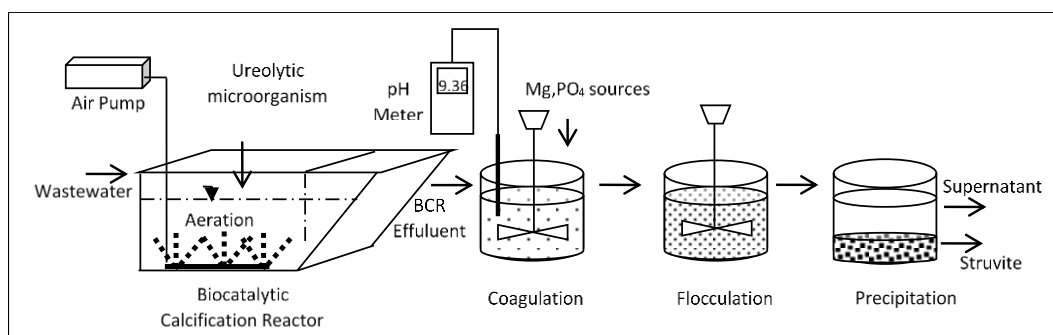


Figure 1. Schematic diagram

2.3. Evaluation of collected struvite as a fertilizer

To evaluate struvite, 200 gram of raw soil was taken from an upland area in Aksaray and sieved with a maximum aperture size of 3 mm prior to filling 8 pots. Two seeds of pepper (*capsicum*) plants were planted in the top 1.0 cm of soil, and different dry weights of struvite were added in each pot. The room temperature of laboratory was between 20 and 25 °C during the experimental period. 20 mL of distilled water was poured in each pot every 2 days. Plant growth has been observed in 75 days.

2.4. Analytical methods

The measurements of ammonium ($\text{NH}_4\text{-N}$) (SM: 4500-NH3 D), phosphate ($\text{PO}_4\text{-P}$) (Dionex ICS-1000 Ion Chromatography) (SM: 4110 B), turbidity (SM: 2130 B), total organic carbon (TOC) (EN: 1484), and total nitrogen (TN) (EN: 12260) (Shimadzu TOC- V_{CPN} /TNM-1) were implemented in wastewater. The pH of wastewater samples was measured by a pH meter (ORION) (SM: 4500- H^+ B). Na, Ca, Mg, and K were measured using an Inductively Coupled Plasma-Optical Emission

Spectrometer (SM 3120 B) (Perkin Elmer, Optima 2100 DV) (APHA, 2005). The collected precipitate was washed thrice with ultrapure water, dried in an oven at 35°C for 24 h, and then characterized by a scanning electron microscopy (SEM) (FEI Quanta 400 MK2) and X-ray diffraction (XRD) (Inel equinox 1000).

3. Results and Discussion

3.1. The usage of different phosphate and magnesium sources

Extra doses of different magnesium ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, MgO , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and phosphate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, H_3PO_4 , $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) sources were added to BCR effluent that contains sufficient ammonium concentrations in contrast to low magnesium and phosphate concentrations to satisfy the stoichiometric requirement of struvite formation.

As shown in Figure 2, the maximum ammonium recovery efficiency was provided by $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$. However, the recovery efficiencies of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ and H_3PO_4 were the same. For economic

reasons, in order to achieve the same concentration of PO₄ the H₃PO₄ (61€/kgPO₄) is used as it is cheaper than NaH₂PO₄·2H₂O (98€/kgPO₄). Therefore, H₃PO₄ and MgCl₂·6H₂O are chosen.

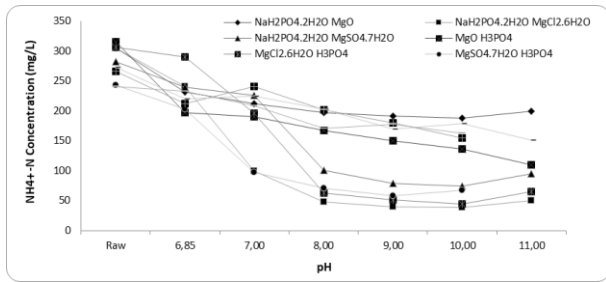


Figure 2. The usage of different phosphate and magnesium sources in precipitation.

3.2. The effect of Mg²⁺:NH₄⁺:PO₄³⁻ molar ratio to precipitation

In the first part, we investigate the effect of Mg²⁺:NH₄⁺ molar ratio on the precipitation (Figure 3); 2.25:1 ratio was obtained for the maximum efficiency of recovery. The recovery efficiency was very close for the ratios 2.25:1 and 1.25:1. Therefore, we took the molar ratio 1.25:1 and also reduced the magnesium concentration twice. Thus, the molar ratio 1.25:1 is opted.

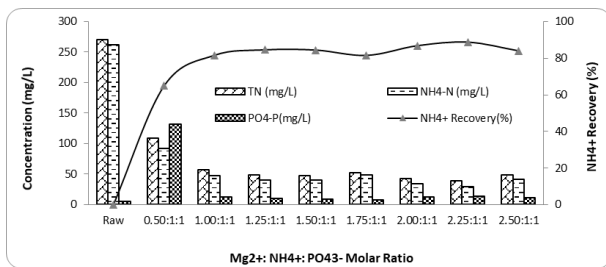


Figure 3. The effect of Mg²⁺: NH₄⁺ molar ratio to precipitation.

As shown in Figure 3, the ammonium recovery increased from 64.9% to 88.8% when the Mg²⁺:NH₄⁺ molar ratio increased from 0.5:1 to 2.25:1. However, any excess of Mg concentration over the 1.25:1 ratio did not result in the extreme increase in ammonium recovery. Figure 4 shows that PO₄³⁻ shortage in the solution is very important for the formation of MAP, and this was corroborated by Huang *et al.*, (2012).

As the molar ratio of phosphate increases, ammonium recovery efficiency also increased in the second part of the study that affected the NH₄⁺:PO₄³⁻ molar ratio and hence the precipitation. In contrast, the amount of nutrient is also increased. So, Mg²⁺:NH₄⁺:PO₄³⁻ molar ratio 1.25:1:1 is preferred.

3.3. The effect of pH on precipitation of 1.25:1:1 Mg²⁺:NH₄⁺:PO₄³⁻ molar ratio

pH of wastewater is very important for MAP precipitation because the activities of both NH₄⁺ and PO₄³⁻ are pH dependent. Published values for the pH of minimum

struvite solubility range from 9 to 10.7 (Nelson *et al.*, 2003).

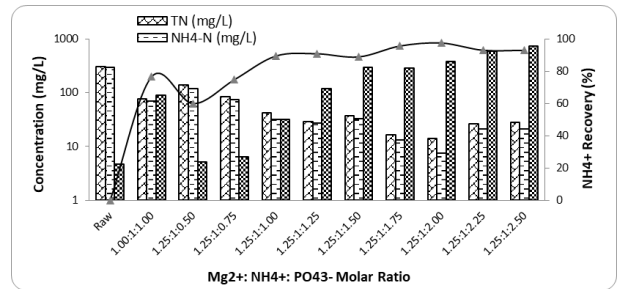


Figure 4. The effect of NH₄⁺: PO₄³⁻ molar ratio to precipitation

At the optimum molar ratio (1.25:1:1), to determine the maximum recovery efficiency, the different pH values are studied. When the pH was higher than the optimum point, Mg₃(PO₄)₂ was formed instead of MAP with pH increased, which led to the decrease of the ammonium removal ratio (Zhang *et al.*, 2009); moreover, ammonium ions convert to ammonia at a high pH.

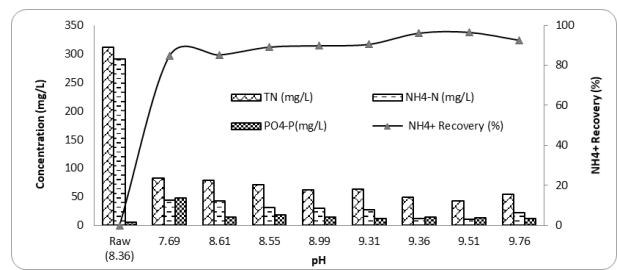


Figure 5. The effect of pH on precipitation of 1.25:1:1 Mg²⁺: NH₄⁺: PO₄³⁻ molar ratio

As shown in Figure 5, the maximum recovery occurs at pH 9.36 (96%). This may be due to the decomposition of struvite crystallization in the wastewater when the pH was decreased below the optimum point, thereby causing a decrease of the ammonium recovery ratio.

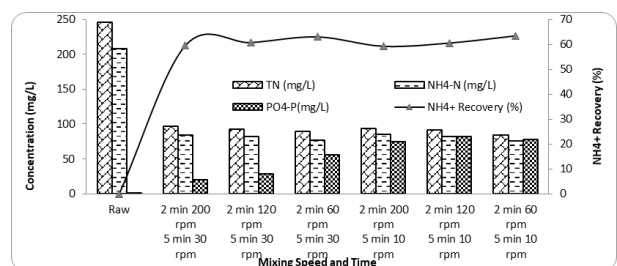


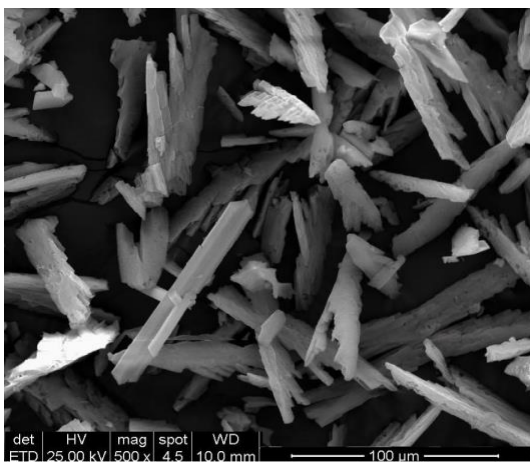
Figure 6(a). The effect of mixing speed and time to precipitation

As the molar ratio of phosphate increases, ammonium recovery efficiency also increased in the second part of the study that affected the NH₄⁺:PO₄³⁻ molar ratio and hence the precipitation. In contrast, the amount of nutrient is also increased. So, Mg²⁺:NH₄⁺:PO₄³⁻ molar ratio 1.25:1:1 is preferred.

In Figure 6 (a) and 6 (b), the different mixing speed and time are investigated. According to the results, the same maximum removal efficiency is obtained at (30 s 200 rpm, 2 min 30 rpm), (30 s 200 rpm, 1 min 30 rpm), and (3 min 60 rpm, 3 min 10 rpm). In consideration of the economic incomes and phosphate concentrations (8.35, 10.36, 13.46 mgPO₄-P/L, respectively) after precipitation in supernatant, the optimum mixing speed and time, 30 s 200 rpm, 2 min 30 rpm, is chosen. Stratful *et al.*, (2001) corroborated that the increase of mixing time from 1 to 180 min has a negligible effect on the production of struvite.

3.5. Evaluation of collected struvite as a fertilizer

SEM images of the struvite precipitates were taken that showed the presence of needle-shaped crystalline products of diameter 50–100 µm (Figure 7).



XRD analysis indicated that the precipitate peaks were suitable for those of the struvite standard pattern as you can see in Figure 8.

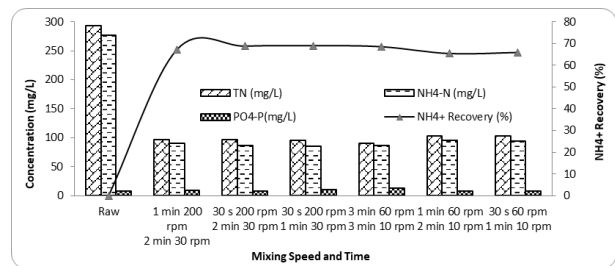


Figure 6(b). The effect of mixing speed and time to precipitation

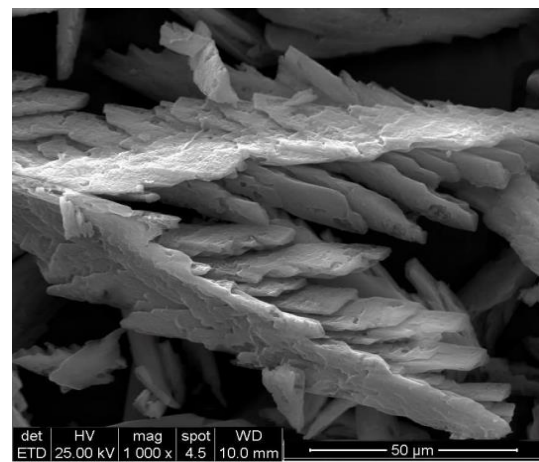


Figure 7. SEM photographs of the precipitates

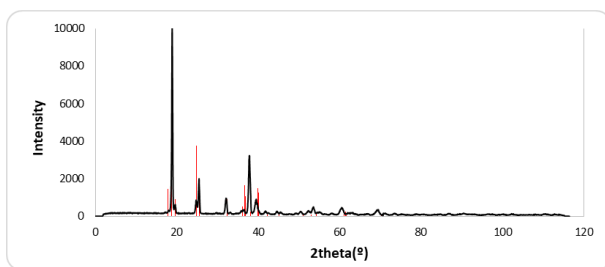


Figure 8. X-ray diffraction analysis of the precipitates

To evaluate struvite, 200 gram of raw soil was sieved to fill 8 pots. Two seeds of pepper (*capsicum*) plants were planted and different dry weights of struvite were added in each pot. No struvite is added in the first and second pots. 0.5–1–2.5–5–7.5–10 grams of struvite are added in the other pots, respectively.

As shown in Figure 9, plants numbered 4, 5, and 6 grow faster and bloom earlier than the others. Controlled struvite precipitation may not only reduce the load of phosphorus and ammonia returned to the mainstream treatment process but also produce a valuable and marketable fertilizer (Kruk *et al.*, 2014). The presence of magnesium makes struvite useful for crops that need this

ion, such as sugar beets (De-Bashan, Bashan, 2004; Pastor *et al.*, 2008).

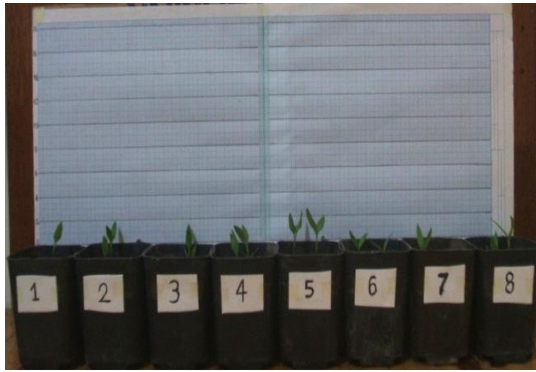
4. Conclusions

The recovery of ammonia from the wastewater with MAP precipitation is preferred because of economical and environmental conditions compared to biological nutrient removal methods. MAP precipitation was investigated for ammonia recovery from the BCR effluents. The results showed that a satisfactory ammonia recovery (96%, pH 9.36) could be achieved when a mixture of H₃PO₄ and MgCl₂·6H₂O was applied for chemical precipitation at a Mg²⁺:NH₄⁺:PO₄³⁻ molar ratio of 1.25:1:1 in 30 s 200 rpm, 2 min 30 rpm mixing time and speed. Although 96% recovery efficiency was achieved, a little increase of phosphate concentration due to the addition of phosphoric acid as a phosphate source was seen. Therefore, phosphate can be used as a nutrient in the receiving environment. This point should not be ignored.

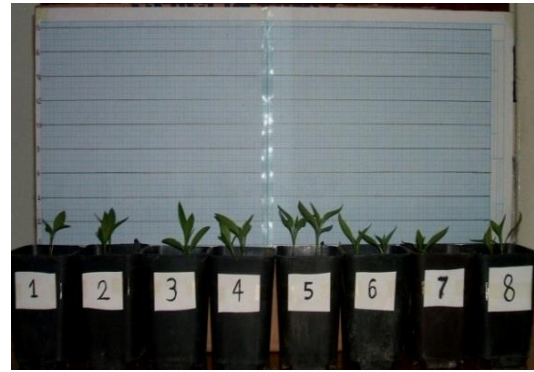
Although phosphate concentration was increased slightly as a result of MAP precipitation as supernatant, phosphate (1500–1600 mg/L PO₄³⁻) was added to achieve a molar ratio that recovered 99% of the struvite. MAP precipitation process can be accomplished in a high

ammonium as well as a high phosphate concentration, and this is a cost-effective method. Finally, struvite can be

used as a fertilizer for plant growth if it does not contain heavy metals and toxic substances.



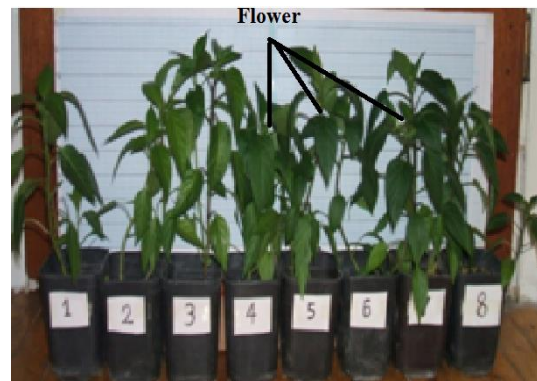
A. 15.Days



B. 25.Days



C. 45.Days



D. 75.Days

Figure 9. Photographs of pepper (*capsicum*) plants

Acknowledgements

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