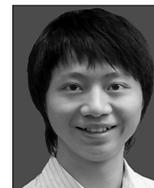


HANDLING OF RELEASED P FROM DIGESTERS LOADED WITH BIO-P SLUDGE

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Abstract

Phosphates are fixed in the enhanced biological phosphorus removal process and released from the Bio-P sludge in the digesters. The supernatant from digesters with large quantities of phosphate should be treated before it is recirculated to the treatment system to prevent phosphorus over-load in the system. Brackish seawater is concentrated to bittern for struvite precipitation; crystal pellets from drinking water treatment plant is generated to Grey and Yellow Powder for hydroxylapatite precipitation and adsorption. The laboratory results illustrate the bittern has an efficiency of over 90% for phosphate precipitation in the reject water without optimization at room temperature, pH 9.5, with the ratio of 1:1:1 between Mg, N and P. The Yellow Powder failed in the reject water as a phosphate precipitant. The Grey Powder as a phosphate adsorbent has been optimized in different ranges of pH from 4.4 to 9.5, powder amount from 5 to 10g, adsorption time from 0 to 7h, and temperatures from 20 to 60°C, which achieves 90% phosphate removal after 5h of adsorption with a capacity of 10mg/g, at room temperature and between pH 4.3–4.8. The bittern and Grey Powder are applicable to remove and recover phosphorus from the reject water, and potential to apply in wastewater treatment plants for practical purposes.

Key words – phosphate, EBPR, Bio-P sludge, digester, MAP, HAP, adsorption, bittern, Yellow Powder, Grey Powder

1. Introduction

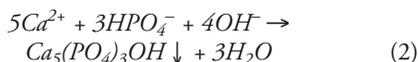
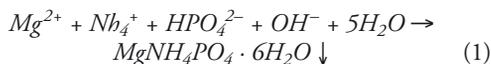
Phosphorus is not desirable to our water bodies which can be found in many wastewater streams and sewage sludge. However, it is also a non-renewable resource that is essential for all life forms on the earth and cannot be substituted (Esemen, et al., 2009; Petzet & Cornel, 2009).

Phosphorus removal and recovery is becoming an accepted practice for recycling in agriculture and industry. The enhanced biological phosphorus removal (EBPR) has been paid special attentions because of its high P-removal efficiency and no addition of chemical (Aspegren, 1995). The phosphorus within the biological treated sludge (Bio-P sludge) without any chemical induction is more recoverable for industrial processing into different application (De-Bashan & Bashan, 2004).

Some advanced treatment plants that use EBPR are facilitated with digesters for further sludge treatment. The phosphates is released from the sludge in the digester and removed with reject water in the centrifuge. It is desirable to recover this fraction from the supernatant instead of recirculating it to prevent large quantities of phosphorus recirculation. Parsons et al. (2001) suggested the digested sludge liquor as the best option for phosphorus recovery. Montag et al. (2009) also addressed that under anaerobic conditions especially in digesters, the polyphosphate accumulating organisms (PAOs) would release considerable phosphorus load into the supernatant liquor.

Magnesium ammonium phosphate (struvite or MAP) and Hydroxylapatite (HAP) are promising to perform phosphate precipitation (Eq.1 and 2) and another means for phosphate adsorption onto the calcite surface is also considered. Waste Mg or Ca products are investigated in

the laboratory on the general conditions as phosphate precipitant or adsorbent.



2. Materials and Methods

2.1. Materials

$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{SO}_4$ are adopted as pure sources of Mg, Ca, $\text{PO}_4\text{-P}$ and $\text{NH}_4\text{-N}$ for preparing synthetic solutions with distilled water. All these commercial chemicals are of analytical grade. Dr Lange cuvette test kits are applied for spot analysis of those elements.

Seawater from the Strait Öresund as Mg source is concentrated to bittern for phosphate precipitation as MAP. Crystal pellets from drinking water treatment plant as Ca source are generated into two kinds of powders (grey and yellow) to perform phosphate precipitation as HAP and adsorption. The Grey Powder is produced by annealing the original pellets over 550°C , and the Yellow Powder is made by further heating the Grey Powder over 800°C .

The adopted reject water comes from the dewatering section (centrifuge) after sludge digesters in Öresundverket, Helsingborg, a wastewater treatment plant (WWTP) operated with EBPR. The physico-chemical parameters of the fresh reject water are listed in Table 1.

2.2. Experiments

The experimental structure is presented in Figure 1. Four processes are settled with different sub-works depending on the experimental requirements.

In the clean process, pure chemicals applied in the clean water to perform the basic mechanisms of MAP and HAP precipitation, basic pH, ratios of Mg/P and Ca/P, and temperature are investigated. In the semi-

Table 1. *Properties of reject water.*

Parameter	Value
pH	7.7
T	$\sim 30^\circ\text{C}$
$\text{PO}_4\text{-P}$	$260 \pm 24 \text{ mg/L}$
$\text{NH}_4\text{-N}$	$770 \pm 13 \text{ mg/L}$
Alkalinity	$53 \text{ mmol HCO}_3^-/\text{L}$
Ca	11 mg/L
Mg	25 mg/L

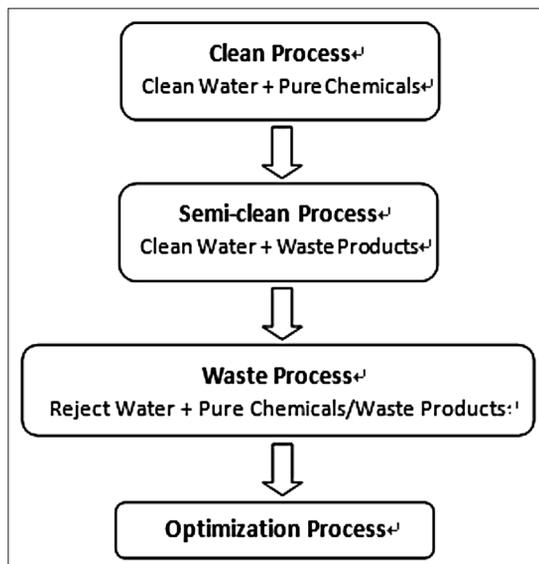


Figure 1. *Experimental design of lab work.*

clean process, waste products replace pure chemicals in the clean water to check the possibility of the wastes as precipitant or adsorbent, possible pH, ratios of Mg/P and Ca/P, waste amount and temperature are investigated. In the waste process, waste products are tested in the reject water to confirm the applicability. The pure chemicals are also investigated in the reject water to verify the basic mechanisms as comparison. In optimization process, the feasible means (precipitation or adsorption) from the waste process is estimated for the optimal conditions of waste products as precipitant or adsorbent.

Batch precipitation experiments (see Figure 2) are conducted in 1L beakers at room temperature ($20 \pm 5^\circ\text{C}$) where the pure chemicals or waste products are added into 800ml clean or reject water. Titration by pH trans-

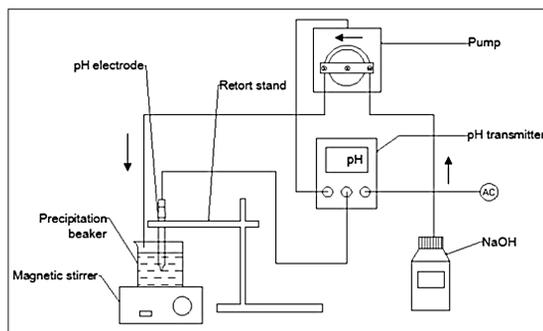


Figure 2. *The laboratory set-up for MAP and HAP precipitation.*

mitter and pump is performed with 1M NaOH addition. The samples are mixed on magnetic stirrers as that fast mixing (600 rpm) for 2 min, slow mixing (100 rpm) for 10 min, and settling for 10 min. After settling, filtration and dilution are performed in some cases. Dilution could be 10 times or 100 times depending on the performance of precipitation. The filtrates are analyzed for orthophosphate concentrations. The concentration of phosphorus in raw reject water was found as 200 mg/L by Destison (2006), which is used as a reference of making synthetic solution in clean and semi-clean process.

Batch adsorption experiments (see Figure 3) at room temperature ($20\pm 5^\circ\text{C}$) are run in covered conical flasks where the waste products are added into 250ml clean or reject water. The titration is performed with 3.5M HCl or 1M NaOH addition from the original pH down or up to different pH values, respectively. The pH was adjusted manually in the whole adsorption part. The samples are mixed at 300-400 rpm on magnetic stirrers for a period of 24 hours (Vamf, 2009). After settling, the samples are filtered and analyzed for phosphate concentrations. Phosphate concentration in the reject water is measured each time the new reject water is re-adopted prior to experiments.

Serial experiments for different factors are conducted to perform the optimization. The pH is adjusted manually in the whole optimization process. Concentration of phosphate in raw reject water is measured each time the new reject water is re-adopted prior to experiments.

3. Results and Discussion

Phosphate removal has been performed as precipitation and adsorption respectively, both of which are tested in clean water and reject water to investigate the applicability. The optimization is conducted based on the adsorption means.

3.1. Phosphate Precipitation

Pure chemicals are utilized in clean water to perform the mechanisms of MAP and HAP precipitation. At two different values of pH 7.5 and 9.5, two ratios of Ca/P for HAP precipitation, and two ratios of Mg/N/P for MAP precipitation are investigated on the removal efficiency of phosphate, respectively. Two Ca waste products (Grey and Yellow Powder) replace pure chemicals for HAP precipitation, and two ratios of Mg waste product (seawater bittern) for MAP precipitation are investigated in the clean water. The bittern with the ratio of 1:1:1 between Mg, N and P for MAP precipitation and Yellow Powder with the ratio of 1.7 between Ca and P

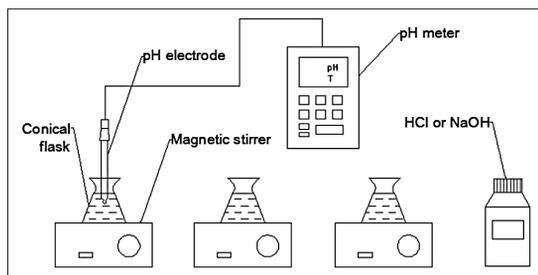


Figure 3. The laboratory set-up for P adsorption.

for HAP precipitation have been further investigated in the reject water. Pure Mg and Ca chemicals are applied in the reject water as well for comparing. The results of all the three processes are shown in Figure 4, No.1, 2 and 3, respectively.

It can be seen from the No.1 that precipitations of MAP and HAP are feasible at both levels of pH (9.5, 7.5) at room temperature. Generally, pH 9.5 has higher removal efficiencies than pH 7.5. HAP and MAP precipitation at pH 9.5 both reflect significant efficiencies

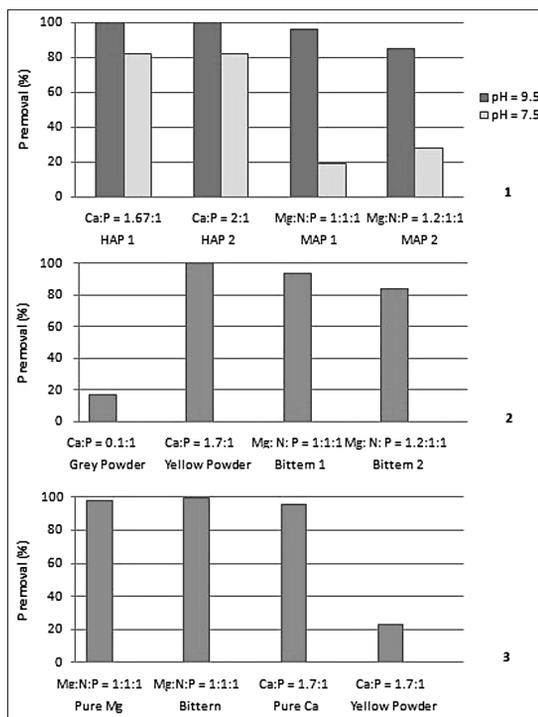


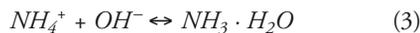
Figure 4. The results of precipitation in clean water with pure chemicals/waste products, and in reject water with pure chemicals/waste products respectively.

even though HAP is a bit higher than MAP. The removal efficiencies in HAP are high but in MAP are low at pH 7.5. Two ratios between Ca and P in HAP precipitation at pH 9.5 have similarly high efficiencies, while the ratio of 1:1:1 between Mg, N and P seems better than 1.2:1:1 in MAP. The experiments in the clean water reveal high pH (9.5) and room temperature are proper for their formation.

In No.2, the Grey Powder performs removal efficiency below 20% with an extremely low ratio between Ca and P, while the Yellow Powder has over 90% efficiency with the stoichiometric molar ratio between Ca and P. Comparing the results of two ratios in seawater bittern precipitation, the ratio of 1:1:1 between Mg, N and P is 10% higher than the ratio of 1.2:1:1. Generally, the Yellow Powder has higher removal efficiency than the bittern solutions. The bittern efficiently performs MAP precipitation at room temperature, pH 9.5, with the ratio of 1:1:1 between Mg, N and P. The Yellow Powder is very efficient for HAP precipitation at room temperature, its original pH (12.3), with the ratio of 1.7 between Ca and P. The Grey Powder fails to precipitate phosphate due to the low Ca^{2+} concentration in the solution, which is deemed out of the precipitation processes.

In No.3, pure Mg and Ca chemicals as comparisons have high efficiencies of phosphate precipitation. The bittern also keeps its high removal efficiency of phosphate under the waste conditions which suggests no necessity of improvement for bittern precipitation. However, the Yellow Powder which is expected to work efficiently however has a low efficiency around 20% of phosphate precipitation. The reason could be that the initial pH of reject water after the addition of Yellow Powder is affected by the two possible equilibriums in Eq.3 and 4, where the hydroxyl (OH^-) is involved lead-

ing to a pH drop. The low efficiency of Yellow Powder solution is because most of Ca^{2+} is consumed by Eq.5 during the pH adjustment prior to the formation of HAP. The phenomenon is addressed by Vanotti and Szogi (2009) that the formation of calcium carbonate in Eq.5 is complete at $pH \leq 9.5$; while and the precipitation of HAP (Eq.2) is very slow below pH 9.0.



3.2. Phosphate Adsorption

The Grey Powder is investigated in the clean water for the applicability of phosphate adsorption, and in the reject water to perform the adsorption of phosphate. Three synthetic samples with phosphate concentrations of 300, 400 and 500 mg/L, and three reject water samples with 260 mg PO_4 -P/L are added 5g powder in each. Phosphate and ammonium are measured before and after adsorption. The results in the clean water and reject water are shown in Figure 5 No.1 and 2, respectively. In waste process (No.2), three samples are tested on the possible pH region and the effect of ammonium. Reject 1 retains the original conditions without pH adjustment or ammonium removal; Reject 2 is only adjusted to pH 6; and Reject 3 is basified and boiled to remove ammonium and adjusted back to the initial pH (7.6) as in Reject 1.

In No.1, all of the three samples are efficient for phosphate adsorption with Grey Powder, amongst which the samples with 300 and 400 mg PO_4 -P/L achieve near 90% removal, and the sample with 500 mg PO_4 -P/L is approaching 80%. The Grey Powder has a certain load

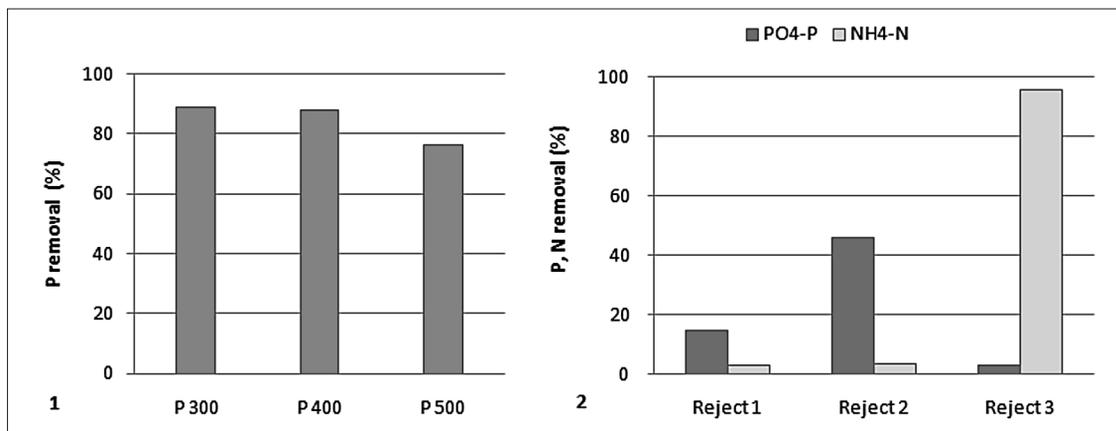


Figure 5. The results of adsorption in clean and reject water respectively.

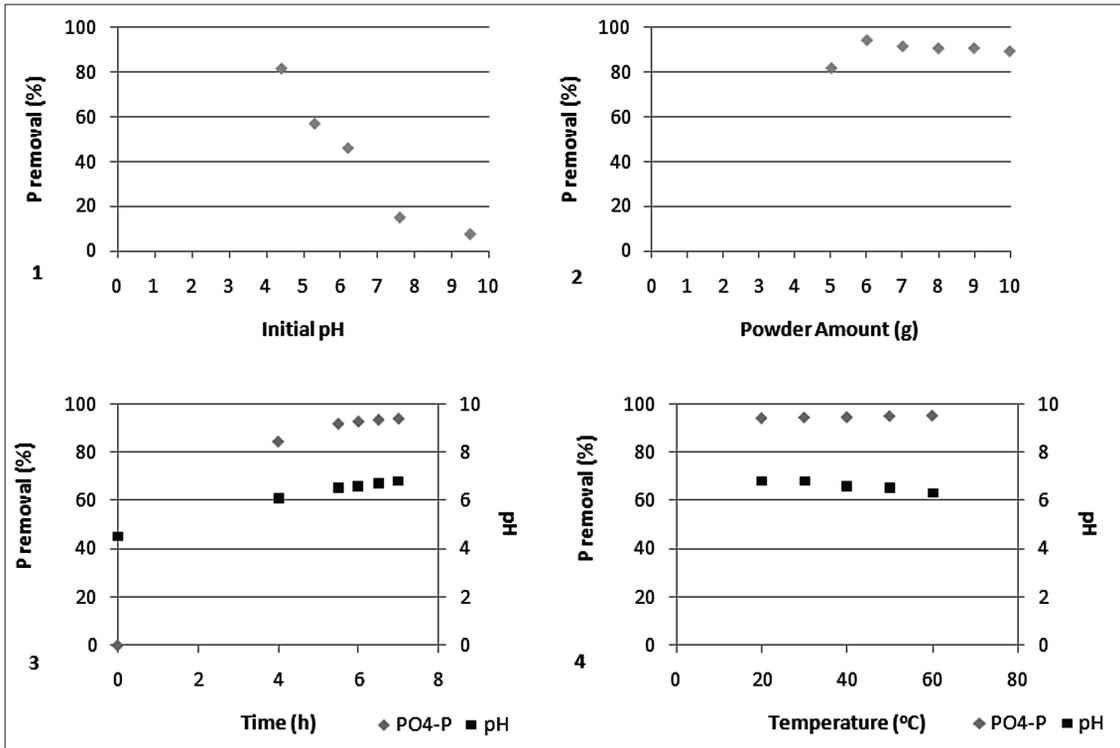


Figure 6. The results of adsorption by pH, powder amount, adsorption time, and temperature variations, phosphate removal efficiency changes as a function of initial pH between 4-10, powder amount between 5-10g, adsorption time from 0 to 7h, and temperature from 20 to 60°C, respectively. The primary axis on the left represents phosphate removal efficiency, and the secondary axis on the right represents pH values.

capacity of P adsorption. The concentration around 300 mg $\text{PO}_4\text{-P/L}$ seems more removable for the capacity of 5g Grey Powder and this amount of powder could be adopted in the reject water with a phosphate concentration of 260 mg/L.

In No.2, the significant reduction of ammonium indicates this content in Reject 3 has been almost removed before the adsorption, and the P removal efficiency after adsorption is however low. The ammonium contents in Reject 1 and 2 are both retained. It is assumed the presence of ammonium is positive for phosphate adsorption. The removal efficiency in Reject 2 with an acidic pH is higher than that in Reject 1, which reveals the pH below 7 is preferred by the adsorption. The Grey Powder is applicable in the reject water and the efficiency of phosphate removal is potential for optimization.

3.3. Optimization

Based on the possibility of the Grey Powder for phosphate adsorption above, it can be improved with a higher

efficiency by selecting optimal pH, powder amount, adsorption time and temperature. The results of the whole optimization are shown in Figure 6, No.1, 2, 3 and 4, respectively.

Five pH levels have been investigated in No.1 for the pH dependence of adsorption, all of which are measured at the beginning of experiments as initial pH because the pH may change during the adsorption.

Six different amounts of powder have been investigated in No.2 to check whether the phosphate removal efficiency varies with the powder amounts, and what is the adsorption capacity of the powder.

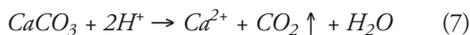
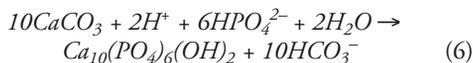
One experiment has been carried out in No.3, where the first sample is taken at the beginning of experiment, and the second is taken after 4h, the third one is then 1.5h later. The other samples are taken afterward every half an hour until the phosphate removal efficiency approaches the level after 24h. The changes of pH have been observed with hours.

Different temperatures have been investigated in No.4 to check the temperature dependence of phosphate

adsorption. The sample from No.3 after operation of 7h is heated from around 20°C to 30, 40, 50 and 60°C gradually. The changes of pH have been observed with temperatures.

There is a downhill trend for phosphate removal efficiencies with increased pH values in No.1. Generally, higher efficiencies show up at lower pH levels. The sample around pH 4 has removal efficiency over 80%, while the efficiencies between pH 7 and 10 are fewer than 20%.

The pH can affect the phosphate species. At the beginning of adsorption, the pH in the solution is around 7.5, where HPO_4^{2-} prevails (Yang, et al., 2007). The acidification stimulates the reaction in Eq.6 (Karageorgiou, et al., 2007). Meanwhile, another reaction expressed in Eq.7 exists in the solution during the acidification, which releases Ca^{2+} and consumes hydrogen as well. The HAP layer has been formed before acidic condition. When the pH is adjusted between 4-6, the phosphate is mainly in the form of H_2PO_4^- which is considered more easily adsorbed with Ca^{2+} onto the surface of calcium carbonate. The efficiency decreased with increasing pH under acidic condition implying H^+ is consumed during the adsorption. When the initial pH value is around 4, the consumption of H^+ will be satisfied. If the initial pH is only adjusted to around 6, the adsorption is not completed and this will influence the efficiency. This is why the lower pH is in demand and should be adjusted to around 4 not 6.



In No.2, the various amounts of Grey Powder from 5 to 10g give a series of high efficiencies of phosphate adsorption, most of which are over 90%. The powder amount of 6g has the highest efficiency with a short advantage.

Increase in powder amounts is supposed to provide larger surface of adsorption. However, the Grey Powder mainly consists of calcium carbonate. When acidifying the solution, part of calcium carbonate reacts with acid as in Eq.6, forming the surfaces of adsorption, while part of it as in Eq.7, releasing Ca^{2+} and carbon dioxide. The establishment of adsorption capacity of phosphate for the Grey Powder is the result of trade-off on the removal efficiencies of phosphate and the powder amounts. The adsorption capacity (qe , mg/g) of phosphate for the Grey Powder is calculated to be:

$$qe = \frac{(247 \text{ mg/L} - 14.6 \text{ mg/L}) \times 250 \text{ ml}}{6 \text{ g} \times 1000} \approx 10 \text{ mg/g}$$

No. 3 shows that the removal efficiency of phosphate increases with the operation time. The efficiency reaches over 80% after 4h of adsorption. It is rising up to 90% after 5.5h and getting steady over 90% in the following hours. The efficiency after 7h is similar to that after 24h, and the value of pH at 7h is very close to the value after 24h. The pH increases with time approaching the neutral level implying the hydrogen is consumed during adsorption.

The removal efficiencies of phosphate at different temperatures in No.4 join by a nearly horizontal line without observable slope. However, the pH decreases with increase of temperature from neutral level down to near pH 6.

Time and temperature are two factors influencing the energy and operation costs, the variations of which are only to evaluate the time and temperature dependence of phosphate adsorption with Grey Powder. The result above is sufficiently high and unnecessary to improve.

4. Conclusions

- The seawater bittern has sufficiently high efficiency (over 90%) of phosphate precipitation in the reject water at room temperature, pH 9.5, with the ratio of 1:1:1 between Mg, N and P.
- The Grey Powder as a phosphate adsorbent achieves 90% phosphate removal after 5h of adsorption with a capacity of 10mg/g, at room temperature and between pH 4.3-4.8.
- The seawater bittern and Grey Powder are both applicable to remove and recover phosphorus from the reject water, and potential to apply in the wastewater treatment plants for practical purposes.

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