論 文

해수에 의한 영양염 제거에 있어서 영향인자의 평가

콜테스 아이자* ·김우항**

목포해양대학교 해양시스템공학부

Factors Influencing the Removal of Nutrient by Seawater

Cortes, Aiza·Kim Woo Hang

Department of Ocean Systems and Engineering, Mokpo National Maritime University,

Mokpo, 530-729, Korea

Abstract: *Nutrients in wastewater should be removed prior to release in the receiving waters to prevent the occurrence of eutrophication. In this study, seawater is used to remove ammonia and phosphate by the formation of struvite (MgNH₄PO₄·6H₂O). It aims to know the optimum conditions for the removal of nutrients using seawater as source of magnesium ions. Experiments were performed using jar tester and pH of ammonium-phosphate solutions were adjusted. Samples were drawn at different mixing times. It was shown that simultaneous removal of ammonia and phosphate is rapid, with no significant reduction beyond 10 min of mixing. Another important parameter is pH, where range 10-11 showed the optimum nutrient removal. Increase in the volume of seawater, which meant an increase in magnesium ions also lead to better removal.*

Key Words: ammonia and phosphorus removal, struvite, seawater

1. Introduction

Eutrophication in water occurs when there is an increase in the nutrients, containing ammonia and phosphate. Increase in nutrients would mean increase in primary production and could further decrease oxygen levels (when degradation occurs). It is therefore necessary to reduce, if not eliminate, nutrients before releasing them into the receiving waters.

Several methods are already available for the removal of ammonia and phosphate. These methods are physical, chemical or biological process. Physical methods such as zeolite and crystallization minimize disposal problems. Moreover, chemical methods such as precipitation and coagulation had been proven to be effective. However, physical and chemical removals usually have high operating cost. Biological removal of nutrient is also developing, taking advantage of the aerobic/anaerobic/oxic sequence. But, nitrogen and phosphate accumulating bacteria require optimum conditions for survival.

Seawater had also been proven to remove ammonium and

phosphate simultaneously (Kumashiro et al., 2001). The Mg^{2+} present in seawater allows formation of struvite crystal by the following reaction to occur (Bouropoulos and Koutsoukos, 2000).

$$Mg^{2+} + NH_4^+ + H_2PO_4^- + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O + 2H^+$$
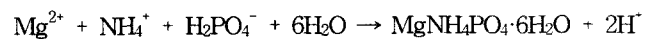
Doyle and Parsons (2002) noted that formation of struvite involves two steps. Ions first react to form crystals (nucleation) followed by growth.

Struvite crystal can allow for the recovery of nutrients (Booker et al., 1999). The characteristics of these recovered nutrients were suggested to be similar to typical fertilizer (Ghosh et al., 1993; Kumashiro et al., 2001). Moreover, Woods et al. (1999) had shown that recovery of the phosphorus may reduce the generation of sludge.

A major disadvantage of nutrient removal by magnesium would be the additional cost required to adjust the pH. Concentrations are also not low enough to be allowed to release to the receiving water, hence further treatment (such as biological treatment) is required (Schulze, 1991).

This is very beneficial especially in Korea where major seas surround the peninsula. The sea provides an

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* 비회원, sikuhay@yahoo.com

** 정회원, whkim@mmu.ac.kr, 061) 240-7293

inexhaustible source of magnesium, making removal of nutrients less costly and convenient.

The main aim of this study therefore is to know the optimum conditions for the removal of nutrients using seawater as source of magnesium ions.

2. Materials and Methods

Seawater was obtained from the coastal area of Daebandong in Mokpo City, South Korea. All seawater used was filtered to remove floating matter. It was found to contain a negligible amount of ammonia and phosphate, i.e., 0.01 mg/L and 0.00 mg/L respectively. Two volumes of seawater were used, 50 and 100ml.

Experiments were carried out in ambient laboratory temperature with a jar tester. The paddle of each stirrer shaft had a diameter of 5cm, while 500 ml beakers served as jars. Pure solutions of NH_4Cl and KH_2PO_4 were prepared. The standard ammonium solution was mixed with standard phosphate solution to obtain a concentration of 100 mg/L and 50 mg/L of nutrient respectively.

Several mixtures were made and adjusted to pH 6, 7, 8, 9, 10 and 11 respectively using NaOH or HCl. The mixing speed was 140 rev/min. While mixing, seawater was added. Samples were drawn using a syringe after mixing times of 1, 5, 10, 20 and 30 minutes. Samples were then filtered through 0.45 μm pore size membranes.

The filtrates were analyzed for ammonia and phosphate following the Standard Methods procedure. Ammonia was analyzed using the Phenate Method while phosphate was analyzed using Ascorbic Acid Method. Measurements were made using UV-Spectrophotometer.

3. Results and Discussion

3.1 Effect of reaction time

Removal of ammonia can occur as fast as 1 minute after addition of seawater (Fig. 1). For the next 10 minutes of mixing, there had been no significant reduction of ammonia. However, in terms of phosphate removal, this event is only true at pH 9, 10 and 11 (Fig. 2). Studies had already shown that increase in the reaction time have no further effect, suggesting that the nucleation step is fast (Stratful et al., 2001; Lee et al., 2002).
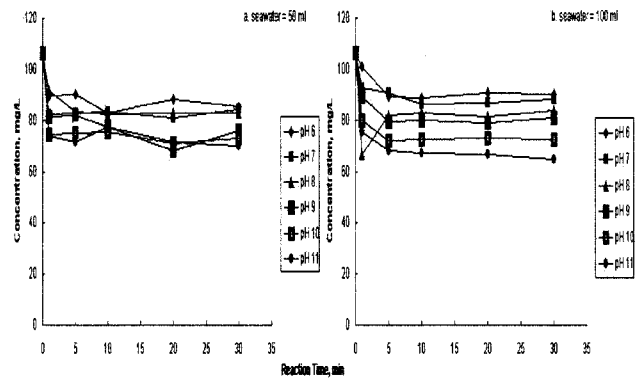

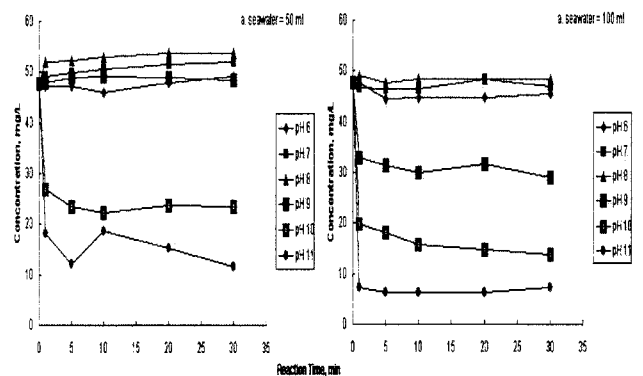Fig. 1 Effect of time, pH and seawater volume on nitrogen removal.

Fig. 2 Effect of time, pH and seawater volume on phosphate removal.

3.2 Effect of pH

For both ammonia and phosphate, greatest reduction occurred at pH 10-11 (Fig. 1 and Fig. 2). However, a more drastic difference can be observed in phosphate reduction (compared to ammonia reduction) between different pH. Lee et al. (2002) had shown that optimum removal is in pH 9-10 and eventually worsen at pH 11.8. This is primarily because as struvite formation increased, pH also decreases.

$$HPO_4^{3-} + Mg^{2+} + NH_4^+ + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \downarrow + H^+$$
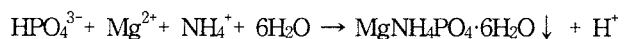
It was also found out that at small amount of crystals can only start forming at pH 7.5 (Stratful et al., 2001). Solubility of the struvite crystal increases with decreasing pH (Kumashiro et al., 2001).

3.3 Effect seawater volume

Doubling the amount of seawater can also increase the removal efficiency of both ammonia and phosphate (Fig. 1

and Fig. 2). This is due to the fact that the higher the level of magnesium, the more struvite will be formed (Doyle and Parsons, 2002; Strartful er al., 2001). The increase in sewater had little effect on ammonia compared to phosphate. Lee et al. (2002) had shown that seawater containing 120 mg/L of Mg2+ can remove 54% of ammonia and 81% of phosphate, given the pH is at the optimum (pH 10). Kumashiro et al. (2001) had also found out that when Mg/P ratio is maintained above 1.5, 70 % removal ratio of P was obtained.

4. Conclusion

Simultaneous removal of ammonia and phosphate is rapid, with no significant reduction beyond 10 min of mixing. Another important parameter is pH, where range 10-11 showed the optimum nutrient removal. Increase in the volume of seawater, which meant an increase in magnesium ions also lead to better removal.

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