Lanthanum chloride or lanthanum carboxylate for orthophosphate removal in seawater aquarium - a feasibility study

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Abstract

High levels of orthophosphate (PO_4^{3-}, 2 to 5 mg/L) favor rapid growth of benthic algae in marine aquarium and mammal pools, which subsequently requires a team of divers for cleaning at Ocean Park Hong Kong. This study is to evaluate the efficiency of PO_4^{3-} removal with $La(Cl)_3$, the "Starver" by LoChlor and the laboratory prepared $La(gly)_3$ (Mills, 2005) and their impact on turbidity and pH.

Results of laboratory experiments with seawater indicated 4.8 ppm $La(Cl)_3$, 5.4 ppm $La(gly)_3$ and 5.4ppm Starver's $La(gly)_3$ increased turbidity to 0.76, 1.83 and 1.35 NTU, respectively. Filtration with 25µm mesh removed up to 15% turbidity only, whereas filtration with 0.45µm GF filter reduced 100% turbidity. Similarly, 1.8 to 3ppm PO_4^{3-} removed after the treated seawater filtered through 0.45µm GF filter only and no PO_4^{3-} reduction after filtered with 25µm mesh. $La(Cl)_3$ had no impact on pH, but both $La(gly)_3$ decreased 0.2 pH unit in the treated seawater.

In situ, addition of 5.49ppm $La(gly)_3$ to strainers before sand filters of a 51 m^3 sealion pool decreased PO_4^{3-} concentration to 3.0 ppm from 4.3 and lowered 0.2 pH unit within the first hour (2 circulations), and increased turbidity from 0.4 to 0.7 NTU immediately after the dosing.

Both results indicated the efficiency of $La(gly)_3$ or $La(Cl)_3$ for PO_4^{3-} removal depends on the efficiency of filtration. Lanthanum compound could pass through filters into poolaccording to turbidity increment after treatment. Therefore, application of lanthanum compound to an aquarium has to be managed very carefully and better to be conducted in a side loop equipped with high efficient filters to avoid any potential adverse impact on aquatic organisms due to leakage of lanthanum compound to the pool.

Introduction

High concentration of orthophosphates (PO_4^{3-}) in dolphin pool and aquariums (Fig. 1) favors rapid growth of benthic algae at Ocean Park Hong Kong. A team of divers is subsequently required to conduct regularly cleaning (Figure 2).

Figure 1

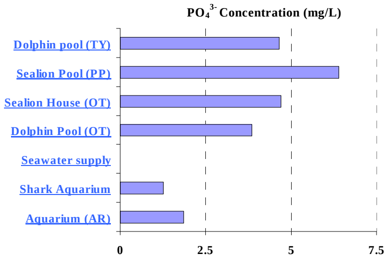


Figure 2

In order to reduce PO_4^{3-} concentration, some aquarium such as shark reef exhibit has applied lanthanum chloride ($La(Cl)_3$; Charanda, 2004). They found careful management of the dosing rate can reduce phosphate level to as low as 0.05ppm without leaking residual lanthanum in the water. Although PO_4^{3-} concentration was generally found reduced, some aquarist encounted fish mortality (Ennevor; 1994). Others (Mills, 2005) found the very fine suspended lanthanum phosphate and $La(Cl)_3$ particles could be carried through sand filters into the pool water and cause cloudiness in the pool. Those particles in the pool would continue to provide a source of phosphate for algal growth.

Mills (2005) claimed a new method to remove PO_4^{3-} from water through circulation without causing water cloudiness problem. The method is to load filter media with aqueous suspensions of lanthanum glycolate ($La(gly)_3$) and then remove lanthanum phosphate particles by backwashing sand filters. LoChlor also marketed similar product under the trademark "Starver", with active ingredient of 133g/L $La(gly)_3$ (hexahydrate). Both claimed their method/product can reduce PO_4^{3-} level, improve turbidity, and have no impact on pH and suitable for any type of marine animal exhibit.

To identify the feasibility of applying those methods to our pools and aquarium for phosphate removal, with laboratory experienements, we (1) compared the efficiency of PO_4^{3-} removal among Starver product, $La(gly)_3$ and the $La(Cl)_3$, and (2) evaluated their impact on pH and turbidity; with a marine mammal system, we (3) conducted a verification test with $La(gly)_3$.

Method

1. Laboratory experiments to compare efficiency of PO_4^{3-} removal and impact on pH and turbidity with $La(Cl)_3$, $La(gly)_3$ or Starver product.

Reagent

Concentration of 24.2mg/ml $LaCl_3$ was prepared by dissolve 0.242g of Lanthanum chloride (Accuchem) into10 ml deionized water and mixed with a stir bar.

Lanthanum glycolate 538mg/ml was prepared by dissolving 102 g of lanthanum chloride hepta-hydrate granules (Accuchem) in 90 ml of commercial grade 70% weight/volume glycolic acid at 15°C for 8 hours with gentle stirring, which yielded 70g of $La(gly)_3$ in 130ml.

LoChlor under the trademark "Starver" has active ingredient of 133g/L lanthanum glycolate hexahydrate

Experiment set up

For each trial, each of the six 15L bottles (Figure 3, 3 for treatment and 3 as control) was filled with 10L of seawater of a marine mammal pool, respectively. Phosphate level in the seawater is close to 4 ppm. With 4.84mg/L $LaCl_3$ trial, 2 ml of 24.2mg/ml $LaCl_3$ concentration were dosed to 10L seawater. For 5.4mg/L $La(gly)_3$, 0.1ml of prepared 538mg/ml $La(gly)_3$\ was added to 10 L. With 5.32mg/L $La(gly)_3$ by "Starver", 0.4 mL of Starver (133g/L $La(gly)_3$) was added to 10 L.

Figure 3

Figure 4

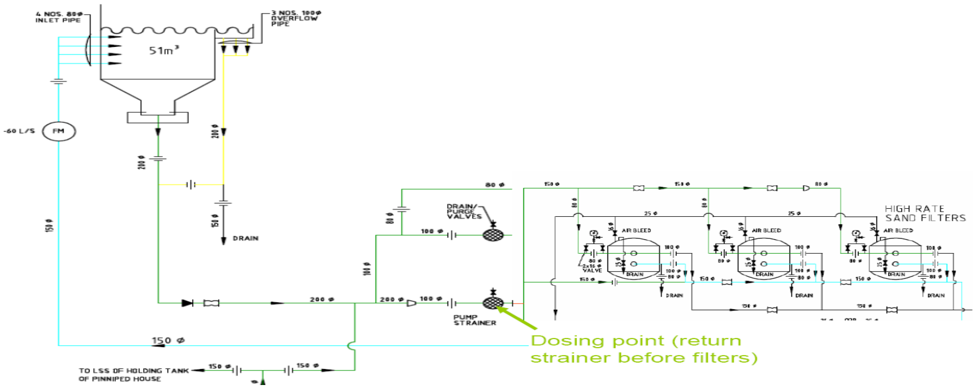
Both treated and untreated seawater were aerated for 24 hours at room temperature. Turbidity, pH and concentration of PO_4^{3-} in each bottle were measured both before and after filtration through a 25um filter or a 0.45um GF filter (Figure 4).

2. Verification with $La(gly)_3$ at a marine mammal facility

Two marine mammal pools of 51 m^3 each were used for this trial. One pool (#2) is the control and the quarantine pool is for treatment. Each pool has independent life support system(Figure 5), which includes ozone, protein fractionators and 3 rapid sand filters of $1m^2$ cross section area. Pool water turnover rate is 0.57 and 1.3hr, respectively, with filter pressure ranged between 8.5 and 9.9 Psi.

280 g of $La(gly)_3$ was poured into the strainer before the 3 filters evenly. Parallel water samples were collected from both treated and control pools at time 0, 0.5, 1, 2, 4, 6, 8 and 24 hours after treatment. Those samples were measured for pH, turbidity and PO_4^{3-} concentrations.

Figure 5



Results and discussion

1. Laboratory experiments to compare the efficiency of PO_4^{3-} removal from seawater among $La(Cl)_3$, $La(gly)_3$ and Starver.

24 hours after the three treatments, PO_4^{3-} concentrations in seawater without filtration are similar to the control. After filtered through 25 µm pore size filter, only 2-3% of PO_4^{3-} concentration was reduced. However, after the $La(gly)_3$ treated seawater filtered through 0.45 µm pore size filter, 80% of PO_4^{3-} was removed, and after the $La(Cl)_3$ and Starver treated seawater filtered through 0.45 µm filter, 42% of PO_4^{3-} was removed. (Figure 6, 7 and 8).

Figure 6

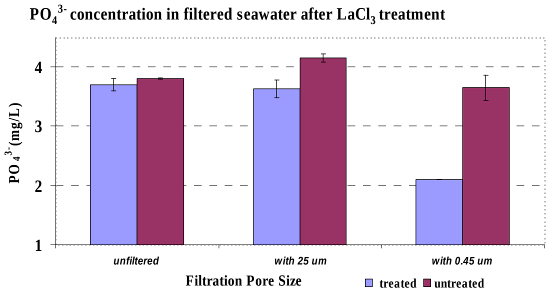


Figure 7

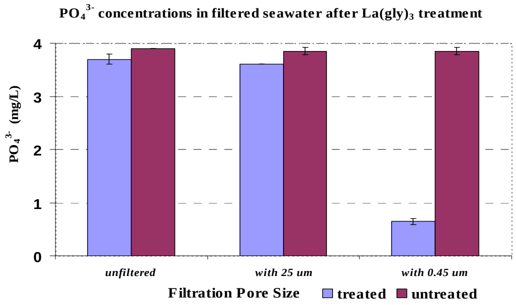
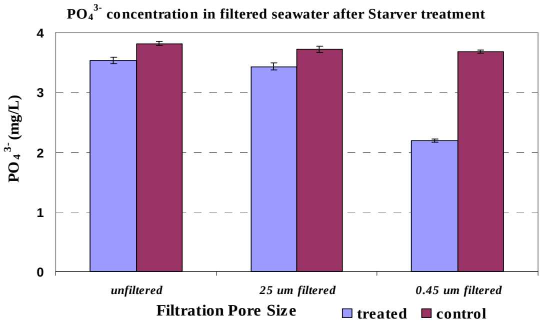


Figure 8



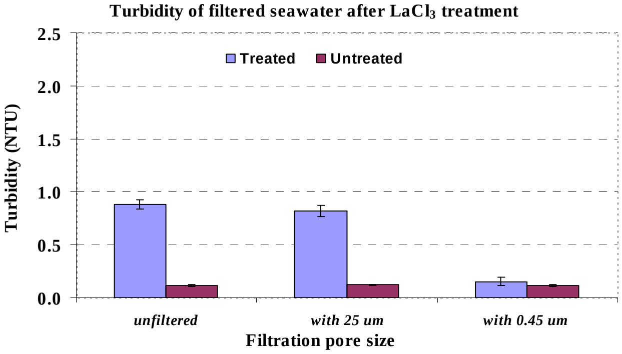
The results indicated that the efficiency of PO_4^{3-} removal mainly depends pore size of the filter, the smaller the pore size, the higher the efficiency. At the sametime, the lower efficiency of PO_4^{3-} removal by $La(Cl)_3$ and Starver after filtration with 0.45 µm filter implied $La(gly)_3$ could form larger lanthanum PO_4^{3-} compound and subsequently leak less lanthanum into water.

2. Laboratory experiments to evaluate the impact on pH and turbidity after $La(Cl)_3$, $La(gly)_3$ or Starver product treatment.

Impact on turbidity

Without filtration, $La(Cl)_3$ increased turbidity from 0.12 to 0.88 NTU in seawater (Figure 9). Turbidity was reduced (82%) after filtered with 0.45µm pore size only but not with 25 µm pore size.

Figure 9



Addition of $La(gly)_3$ to seawater increased its turbidity from 0.17 to 2.0 NTU (Figure 10), and addition of Staver to seawater increased turbidity from 0.19 to 1.54 NTU (Figure 11). Similar to the efficiency of PO_4^{3-} removal, turbidity was almost not reduced (< 20%) after filtered with 25 µm pore size, but greatly reduced (>90%) after filtered with 0.45µm pore size. Turbidity removal with 0.45µm pore size was less efficient (82%) in $La(Cl)_3$ treated water.

Figure 10

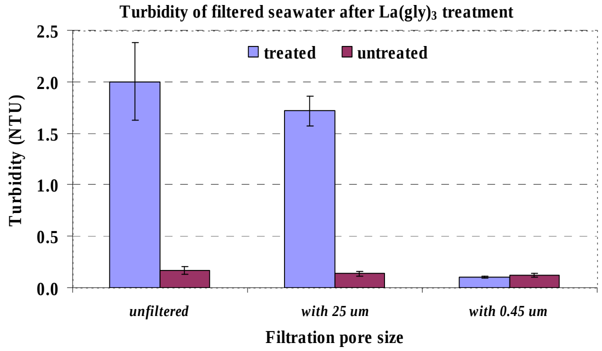
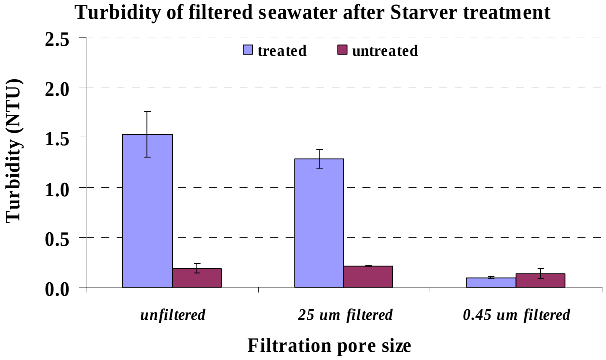


Figure 11

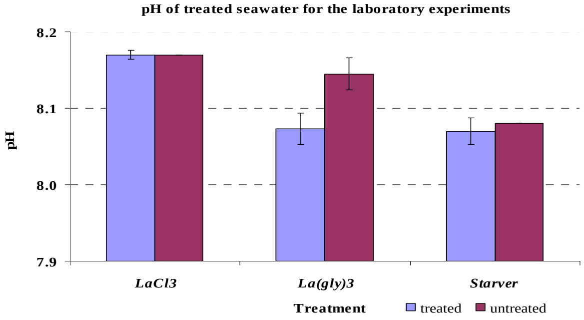


The results demonstrated any of the three chemicals could increase turbidity in seawater due to the formation of lanthanum compound particles, mainly of < 25 µm but > 0.45 µm in size. Without efficient circulation and filtration, PO_4^{3-} would not be efficiently removed from the system but the turbidity will increase. Therefore, it would be necessary to have efficient filtration system for any facility intended to apply either $La(Cl)_3$ or $La(gly)_3$ for the purpose of PO_4^{3-} removal.

Impact on pH

Although $La(gly)_3$ is more efficient in phosphate removal, it decreased pH from 8.15±0.02 to 8.07±0.02 in the seawater (Figure 12), compared without significant pH decrease after treatment with either $La(Cl)_3$ or Starver.

Figure 12

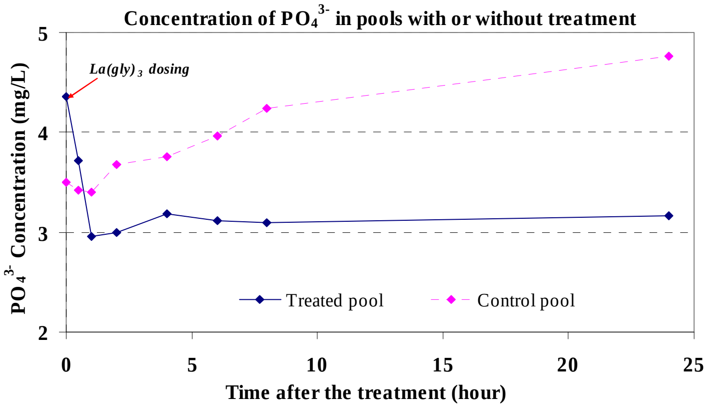


3. Verification with $La(gly)_3$ at a marine mammal facility

Efficiency of PO_4^{3-} removal

Figure 13 depicts the changes in PO_4^{3-} concentration within 24 hours inside the 51 m^3 sea lion pool after liquid $La(gly)_3$ addition (5.4 mg/L of the pool volume) to strainers before the three sand filters. After the completion of the first circulation (30 minutes), the PO_4^{3-} concentration decreased to 3.7 mg/L from the original 4.3 mg/L. After completion of the second circulation, the PO_4^{3-} further decreased to 3 mg/L. However, the rate of PO_4^{3-} removal fell away as the dose was exhausted after 2 circulations.

Figure 13



For the purpose of comparison, the PO_4^{3-} concentration was monitored during the same period in an untreated 51 m^3 sealion pool without any water renewal or filter backwash (Figure 13). The PO_4^{3-} concentration remained at 3.5 mg/L after first circulation (1.5 hrs) but gradually increased to 7.9 mg/L overnight, due to accumulation of biological waste from sealions. Filter pressure remained at 9 Psi throughout the 24 hrs period for both treated and untreated pools. Interestingly, the treated pool has no further increment in PO_4^{3-} concentration over 24 hrs.

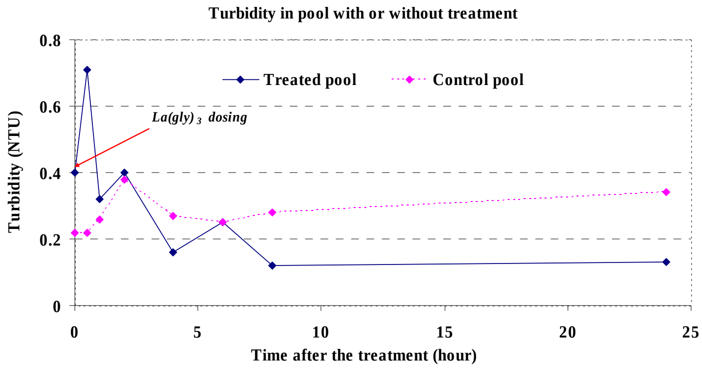
Application rate of lanthanum bonds to orthophosphate was denoted at a ratio of 1:1 (Mills.2005), i.e., it takes 1ppm lanthanum to remove 1ppm orthophosphate from freshwater. However, in our laboratory experiments with seawater, the ratio was 5:2 plus filtration with < 0.45 µm pore size. In the real-time trial at the sealion pool, only approximately 5:1 ratio was observed (1ppm orthophosphate removal with 5.4 ppm $La(gly)_3$). It is possible that the lower efficiency than 1:1 was due to the higher ions in seawater than in freshwater, as lanthanum can bond and flocculate other minerals (Tokunaga; 1999)

Impact on turbidity

In the treated pool, turbidity increased from 0.4 to 0.7 NTU immediately (<30 mins) after the dosing. The result, implied that, although lanthanum was expected to be loaded onto filters as flocculent to capture orthophosphate through mechanical filtration, some of the aqueous $La(gly)_3$ passed through the filters immediately after dosing

(Figure 14). Amount of La(gly)$_3$ loaded to the filters gradually increased through circulations and, therefore, the turbidity gradually decreased from 0.4 to < 0.15 NTU and maintained over the 24hrs, as compared to the stable turbidity in the control pool.

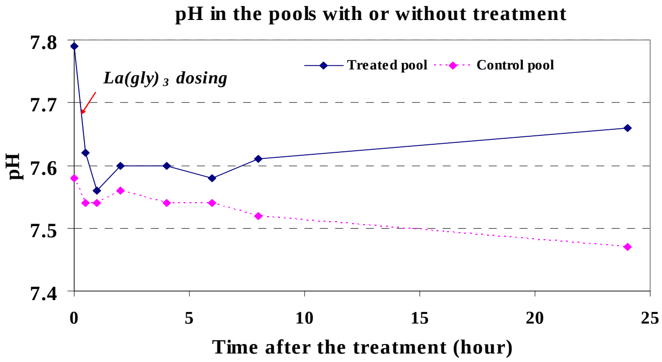
Figure 15



Impact on pH

Similar to the results of laboratory experiments, addition of La(gly)$_3$ decreased pH of the sealion pool from 7.8 to 7.6 within the first 2 circulations (Fig. 16). The pH decrement in the control pool was likely due to the accumulation of biowaste from the sealion after the suspension of filter backwash for 24 hrs.

Figure 16



Conclusion

Although all lanthanum compound tested can remove PO_4^{3-} from seawater, the efficiency of removal depends on the pore size of filters. Lanthanum compound could pass through filters and increase turbidity inside pool. Barry and Meehan (2000) have found lanthanum can cause significant mortality to Daphnia due to cloggin g filtration. Small lanthanum particles passed into pool could also potentially be trapped by gill lamellae of fish.

Therefore, application of lanthanum compound to an aquarium has to managed very carefully and better to be conducted in a side loop equipped with high efficient filters to avoid any potential adverse impact on aquatic organisms due to leakage of lanthanum compound to the pool.

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