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ACTIVATED SLUDGE ADSORPTION OF HEAVY METALS IN A MEMBRANE BIOLOGICAL REACTOR OPERATED FOR RECLAMATION AND REUSE OF RECIRCULATING AQUACULTURE SYSTEM WASTEWATER

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Introduction

Fish farming using recirculating aquaculture systems (RAS) can produce a wastewater containing high concentrations of total suspended solids (TSS), nitrogen, phosphorus, and biological oxygen demand ($cBOD_5$). Often, this wastewater flow is more highly concentrated in pollutants than that treated at municipal wastewater treatment plants. As a result, some form of solids removal and nutrient recovery is needed prior to discharge. And, if the intent is to reclaim and reuse this water resource, then advanced secondary wastewater treatment is required.

A membrane biological reactor (MBR) provides a highly-scalable, onsite wastewater treatment plant that utilizes an activated sludge system that removes nitrogen (nitrification and denitrification mechanisms), phosphorus (microbial assimilation), and $cBOD_{5.}$ Further, membranes submerged in the activated sludge are capable of filtering out a particulate-free permeate. Consequently, a MBR has the potential for nearly complete water recovery for reuse in a fish culture system.

Heavy metals introduced into an aquaculture wastewater stream can arise from fish feed vitamin / mineral supplements as well as from the corrosion of metal pipe fittings and other RAS equipment (Sharrer et al., 2010) Activated sludge processes have been shown to remove metals from wastewater as microbes in the sludge biomass adsorb metals ions (Hammaini et al., 2003; Iddou and Ouali, 2008; and Yuncu et al., 2006). The microbial adsorption mechanism typically described suggests a rapid, metabolically independent sorption to cell surfaces followed by a slower, active transport of metals across the membrane surface (Arican et al., 2002). Wastewater characteristics such as pH, temperature, and metals concentration in the wastewater have been shown to affect biosorption capacity (Hammaini et al., 2003).

Biological filters in RAS convert total ammonia nitrogen (TAN), which is excreted by the fish, into nitrate-nitrogen (NO_3-N). The net result is a backwash of biosolids that is low in TAN and high in NO_3-N. Thus, the biosolids discharge from RAS that use low water flushing rates could contain NO_3-N and orthophosphate (as P) concentrations as high as 100 mg/L and 3 mg/L, respectively. And, RAS utilizing biological filters operated at low flushing rates quickly consume alkalinity, which requires addition of sodium bicarbonate to maintain alkalinity concentrations above 100 mg/L (as $CaCO_3$).

The MBR located at the Conservation Fund Freshwater Institute (CFFI) was operated for the recovery of not only the water but the alkalinity, salts, phosphorus, and protein contained in a high-strength aquaculture wastewater. Further, an assessment of the capacity for an activated sludge to remove heavy metals from primary biosolids was performed. The objective of this research was to determine the capability of an activated sludge process to remove heavy metals from the wastewater flow as well as the capacity for an MBR to process RAS biosolids backwashed from a fish culture system with typical and elevated nitrogen and phosphorus.

Methods

In an experiment designed to determine the metals adsorption, nutrient removal, and resource reclamation capacity of a MBR, typical backwash wastewater collected from a RAS operated for rainbow trout (*Oncorhynchus mykiss*) culture was loaded to the MBR (control condition). And, in order to mimic waste produced from fish culture systems operated at low flushing rates, appropriate proportions of sodium nitrate and granular anhydrous monopotassium phosphate were added to the wastewater entering the MBR to achieve an additional 100 mg/L NO_3-N and 3 mg/L phosphorus (as PO_4). Each condition was maintained for 21 day and replicated four times.

Performance of the MBR was assessed by collecting water samples from MBR inlet and permeate sampling sites and analyzing for a series of water quality tests (Table 1). Samples of MBR permeate were also collected and analyzed at Cornell Nutrient Analysis Laboratory (Ithaca, NY) to determine dissolved metals concentration (EPA Method 3015) with units reported in mg/L. Gravity thickened sludge and activated sludge samples were collected and analyzed by Cornell Nutrient Analysis Laboratory for metals concentration (EPA Method 3052) with units reported in mg/kg. Activated sludge proximate analysis was performed by Barrow-Agee Labs (Memphis, TN) conditions to assess for protein content.

Parameter	Method	Units
Total suspended solids (TSS)	Standard Methods 2560	mg/L
Total volatile solids (TVS)	Standard Methods 2560	mg/L
Total phosphorus (TP)	Hach Method 8190[b]	mg/L (as P)
	Hach Method 10127[a,c]	mg/L (as P)
Dissolved reactive phosphorus (DRP)	Hach Method 8048[a]	mg/L (as P)
Total nitrogen (TN)	Hach Method 10071[d]	mg/L (as N)
	Hach Method 10072[e]	mg/L (as N)
Total ammonia nitrogen (TAN)	Hach Method 8038[a]	mg/L (as NH_3-N)
5-Day carbonaceous biological oxygen demand ($cBOD_5$)	Standard Methods 5210 5-day BOD	mg/L
Alkalinity	Standard Methods 2302	mg/L (as $CaCO_3$)

[a] Adapted from *Standard Methods For the Examination of Water and Wastewater*

[b] Low range (0.02-1.10 mg/L-P)

[c] High range (1-100 mg/L-P)

[d] Low range (0.5-25 mg/L-N)

[e] Low range (10-150 mg/L-N)

Results

Activated sludge must be removed from the MBR at regular intervals to maintain a consistent suspended solids concentration, which is termed ‘biosolids wasting’. As a result, a small amount of potentially reclaimable backwash is lost along with the wasted biosolids. The research performed for this study indicated that the MBR processed approximately 7100 liters / day (1875 gal / day) of RAS backwash and the activated sludge wasting rate was approximately 460 liters / day (122 gal / day). The resulting wastewater recovery rate was approximately 93.5% (Fig. 1), indicating little loss of reclaimable backwash due to activated sludge solids wasting and disposal, i.e., approximately 6.5% of flow.

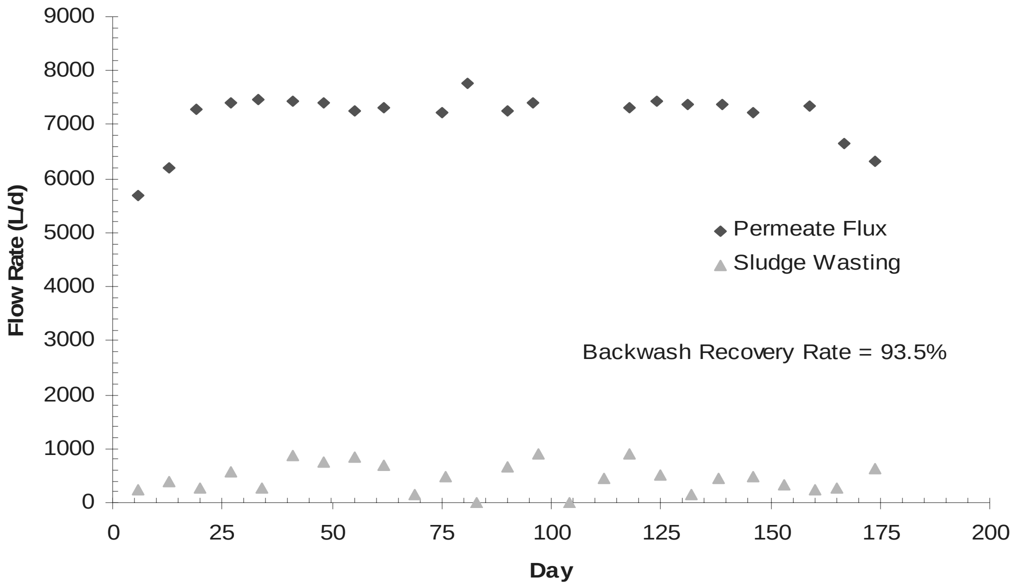

Figure 1 - Plot indicates MBR wastewater processing and activated sludge wasting rates.

The MBR performed extremely well, removing 99.97% and 99.98% of the total suspended solids (TSS) under control and test conditions, respectively (Table 1). Similarly, no difference in 5-day carbonaceous biological oxygen demand ($cBOD_5$) removal was apparent with 100% $cBOD_5$ removal under both test and control conditions (Table 1).

	TSS	**TVS**	**$cBOD_5$**	**Alkalinity**
Test Condition				
Influent (mg/L)	1827 ± 272	1488 ± 224	1073 ± 182	281 ± 8
Effluent (mg/L)	0.3 ± 0.1	0.2 ± 0.0	0 ± 0	560 ± 19
Removal Efficiency	99.98	99.99	100	-115
Control Condition				
Influent (mg/L)	2235 ± 346	1768 ± 266	658 ± 98	259 ± 5
Effluent (mg/L)	0.7 ± 0.3	0.2 ± 0.0	0 ± 0	312 ± 10
Removal Efficiency	99.97	99.99	100	-21

Table 1 - Mean (± se) total suspended solids, total volatile solids, 5-day carbonaceous biological oxygen demand, and alkalinity concentrations from the inlet and permeate sampling sites and removal efficiencies under control and test conditions.

Recovery of alkalinity was observed at both control and test conditions. Influent and effluent alkalinities were 259 ± 5 and 312 ± 10, respectively under control conditions and 281 ± 8 and 560 ± 19, respectively under test conditions (Table 1). According to the USEPA Nitrogen Control manual, for each gram of nitrate-nitrogen that undergoes denitrification, approximately 3.7 g of chemical oxygen demand is consumed, 0.45 g of new cell is produced, and 3.57 g of alkalinity is formed (EPA, 1993). As a result, complete recovery of alkalinity was accomplished under control conditions and enhanced recovery was observed under test conditions. The alkalinity recovered in the permeate could replace the requirement for inorganic carbon supplementation (as sodium bicarbonate or sodium hydroxide) in a fish culture system that operates at low make-up rates (approaching 100% recycle) and utilizes a nitrification reactor for ammonia removal.

The MBR also achieved impressive nitrogen removal at either typical or elevated nutrient loading rates. Total nitrogen (TN) entering the MBR was 86 ± 10 mg/L under control and 185 mg/L under test conditions with removal efficiencies of 98% under both conditions (Table 2). TAN and nitrate-nitrogen (NO_3-N) removal efficiencies were marginally reduced under test conditions, but permeate concentrations of TAN and NO_3-N were remarkably low at either nutrient loading condition (Table 2).

	Total Nitrogen	Total Ammonia Nitrogen	Nitrate-Nitrogen	Total Phosphorus	Dissolved Reactive Phosphorus
Test Condition					
Influent (mg/L)	185*	3.3 ± 0.9	105*	55*	5.6*
Effluent (mg/L)	2.1 ± 1.4	1.3 ± 0.6	0.6 ± 0.3	0.10 ± 0.03	0.10 ± 0.03
Removal Efficiency	98	60.6	88	99.8	96.1
Control Condition					
Influent (mg/L)	86 ± 10	2.1 ± 0.2	4.9 ± 1.4	50 ± 8	1.8 ± 0.2
Effluent (mg/L)	1.8 ± 0.5	0.4 ± 0.3	0.1 ± 0.0	0.05 ± 0.01	0.05 ± 0.01
Removal Efficiency	98	81	98	99.9	97.2

Table 2 - Mean (± se) total nitrogen, total ammonia nitrogen, nitrate–nitrogen, total phosphorus, and dissolved reactive phosphorus concentrations from the inlet and permeate sampling sites and removal efficiencies under control and test conditions.
* Estimated inlet concentration calculated as the sum of measured endogenous nitrogen / phosphorus and supplementary nitrogen / phosphorus.

Phosphorus recovery in the MBR occurs as bacteria in the activated sludge take in this nutrient in excess when subjected to alternating aerobic and anaerobic conditions. The MBR produced exceptional phosphorus removal efficiencies under both control and test conditions, producing permeate total phosphorus concentrations of 0.10 ± 0.03 under test and 0.05 ± 0.01 under test conditions (Table 2). The phosphorus captured in the activated sludge can be further used in terrestrial agriculture as a soil amendment, potentially displacing the need for phosphate rock derived fertilizers.

The activated sludge process showed a notable capacity to remove heavy metals from the wastewater flow. Treated MBR permeate samples collected for metals analysis indicated low concentrations of all metals of concern (Table 3). And, when compared to metals concentrations in RAS culture systems operated at either high or low exchange rates, MBR permeate samples indicated the lowest concentrations. Further, MBR permeate metals concentrations were well within recommended limits for fish culture (Table 3). As a result, reuse of MBR permeate back into a fish culture system would not likely be constrained by residual metals concentration. A further indication of heavy metals biosorption is evident in a comparison of metals in activated sludge and untreated gravity thickened sludge (Table 4). Specifically, metals concentrations (on a dry weight basis) in the activated sludge were either higher or approximately equal to concentrations in gravity thickened sludge. However, either the activated or gravity thickened sludge meets requirements for land application purposes under USEPA guidelines regarding residual metals concentrations in a biosolid (Table 3).

Parameter (mg/L)	High Exchange	Low Exchange	MBR Permeate	Recommended Limits [a] (mg/L)
Barium	0.06 ± 0.00	0.05 ± 0.00	0.02 ± 0.00	< 5
Boron	0.005 ± 0.003	0.045 ± 0.006	< 0.0015 [b]	< 5
Calcium	111 ± 0	104 ± 0	87 ± 4	4-160+
Copper	0.005 ± 0.003	0.045 ± 0.006	< 0.0008 [b]	<0.030
Lithium	0.003 ± 0.000	0.004 ± 0.000	NA	NA
Magnesium	11.0 ± 0.0	12.1 ± 0.1	15.7 ± 0.6	<28+
Potassium	3.6 ± 0.1	23.2 ± 0.6	8.9 ± 1.2	<10 +
Sodium	4 ± 0	62 ± 4	8.7 ± 0.2	<1500
Strontium	0.99 ± 0.01	0.91 ± 0.00	0.82 ± 0.04	NA
Sulfur	7.6 ± 0.1	12.6 ± 0.3	3.5 ± 0.0	<50
Zinc	0.012 ± 0.002	0.027 ± 0.001	0.011	<0.269

Table 3. Mean dissolved metal and nutrient concentrations in a recirculating aquaculture system operated at high and low water exchange compared to MBR permeate (Table adapted from Davidson et al., In Press).
[a] (Heinen et al., 1996; EPA, 1985; 1986) [b] Instrument detection limit

Parameter	Activated Sludge (mg/kg - dry)	Gravity Thickened Sludge (mg/kg - dry)	EPA Land Application Limit (mg/kg - dry)
Al	2434 ± 596	1101 ± 471	
Mn	369 ± 58	214 ± 56	
Fe	2148 ± 765	1753 ± 524	
Cu	170 ± 22	109 ± 30	4300
Ni	75 ± n/a	7 ± 6	420
Co	73 ± 67	20 ± 18	
Cd	37 ± n/a	5 ± 5	85
Mg	3423 ± 620	1565 ± 378	
Cr	65 ± n/a	11 ± 9	
Zn	429 ± 83	284 ± 78	7500
Sr	270 ± 46	117 ± 25	
Li	16 ± 5	4 ± 1	
Ba	101 ± 16	48 ± 12	
Ti	< 0.156*	< 0.156*	
Mo	< 0.123*	< 0.123*	75
Pb	<0.913*	<0.913*	840
As	< 0.582*	< 0.582*	75
B	< 0.141*	< 0.141*	
% Solids	1.5 ± 0.1	10.3 ± 2.0	

Table 4 – Mean metals and percent (%) solids concentration of gravity thickened sludge and activated sludge (* Minimum reporting limit).

Another potential resource recovery process could utilize the proteins captured by the microorganisms in the activated sludge as a feed additive. The protein content of the sludge generated in this experiment was 25.2 ± 2.9 % on a dry weight basis, which is a little less than the desired content needed for a feed additive. However, an MBR operated at a lower sludge age (a function of solids wasting rate) can produce a higher protein content activated sludge and further research on this aspect is now underway.

Conclusions

The activated sludge process associated with an MBR appears capable of effectively removing heavy metals contained in the primary wastewater flow. Concentrations of metals in the activated sludge were higher when compared to a gravity thickened sludge indicating evidence an adsorption mechanism in the sludge biomass. Metals concentrations in processed MBR permeate are quite low and is comparable to water in a RAS operated at a high exchange rate.

Installation of MBR technology includes significant capital and operating costs. However, reclamation and reuse of wastewater could be an option for land-based RAS culture system operating with limited water resources or utilizing a costly synthetic (or transported) saltwater. Further, the ability to perform on-site, biosecure wastewater treatment while reclaiming water, salts, alkalinity, phosphorus, and protein might make adoption of this technology even more appealing.

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