WATER QUALITY ASSESSMENT WITH AQUATIC NON-STRUCTURAL BLOCKS MADE OF COAL ASH AGGREGATES MORTARS

by

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ABSTRACT

A handful of biochemical processes occur in aquatic environments. One of the problems that are mostly encountered in such environments is caused by excess nutrient input and subsequent algal bloom. A series of studies were conducted to assess feasibility of aquatic structures to enhance water quality. In line with resource recovery efforts, the aquatic structures were made of coal combustion byproducts (CCBs) mixed with cement. Optimum portions of cement and CCBs were determined and tested in a lab-scale simulated aquatic environment for their potential role in enhancing water quality. Parameters of water quality were measured including pH, turbidity, conductivity, biological oxygen demand, suspended solids, alkalinity, nitrate, phosphate, ammonia and algal growth throughout a series of experiments. Experiments for nitrate, phosphate and nitrification effects were studied separately. Each experiment showed that the coal ash concrete structures enhanced the water quality by improving the aquatic environment for at least one of the parameter measured.

RESUMEN

Diversos procesos bioquímicos están propensos a ocurrir en ambientes acuáticos. Un problema que se enfrenta en estos ambientes es el exceso de nutrientes y el crecimiento de algas. Se realizaron experimentos para evaluar cuan factible era el uso de estructuras hechas con productos secundarios de carbón para mejorar la calidad de agua. Con la intención de maximizar su recuperación, las estructuras fueron hechas de subproductos de la quema de carbón mezclados con cemento. Se determinó una mezcla óptima y se hizo una serie de experimentos a escala para determinar su beneficio. Varios parámetros fueron monitoreados con esta intención incluyendo pH, turbidez, conductividad, demanda de oxígeno biológico, solidos suspendidos, alcalinidad, nitratos, fosfatos, amonio y el crecimiento de algas en los experimentos. Experimentos para nitratos, fosfatos y amonio fueron realizados para entender mejor el efecto de las estructuras. Cada experimento demostró que las estructuras mejoraron la calidad del agua en al menos uno de los parámetros monitoreados.

“Trust who you are
and be yourself
no matter what.”

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INTRODUCTION

Water quality is a major concern in our daily lives since water is one of the main components to conserve mankind existence. There are different factors that may affect water quality which includes but are not limited to: pH, high nutrients content, and dissolved oxygen depletion. Algal blooms are one of the phenomena that can disturb the quality of water as the result of an excess of nutrients in water systems, particularly phosphorus and nitrogen (Ahern et al., 2007). As a result of high concentrations of these nutrients in the water, a favorable environment is provided for significant increase of algal growth. Algae tend to grow quickly under high nutrient conditions, but algae life span is very short, resulting in a high concentration of biodegradable organic matter. The decay process of such biodegradable organic matter by aerobic bacteria may excessively consume or deplete dissolved oxygen in the water and with this depletion many water quality parameters are affected. There are many ways in which the nutrients can get into the water systems including fertilizers that are applied for agricultural purposes that finally reach water systems through runoff.

The purpose of this investigation is to use aquatic structures made of coal combustion byproducts (CCBs) to improve water quality problems with respect to algal blooms, or to at least, assess if such applications of waste utilization affect water quality parameters. Coal is the largest source of energy for the generation of electricity worldwide. World coal consumption was about 7.99 billion short tons (151 quadrillion Btu) in 2010 (USEIA Statistics, 2010) and is expected to increase to 11.06 billion short tons (209 quadrillions Btu) by 2035 (USEIA Outlook, 2011). CCBs are the solid residues generated by coal-burning during the production of electricity. The four major CCBs include fly ash, bottom ash, boiler slag and flue gas desulfurization which are distinctly and extremely different materials. Other types of materials obtained from coal combustion include fluidized bed combustion ash, cenospheres, and scrubber residues. Characteristics of each of these byproducts vary by coal source and its composition, and by the combustion technologies used, among other factors (Li et al., 2012; Elswick et al., 2007).

Fly ash and bottom ash are the two CCBs of interest in this project. Fly ash is the finest of coal ash particles. Fly ash is a fine powder formed from the mineral matter in coal, consisting of the noncombustible matter in coal plus a small amount of carbon that remains from incomplete combustion. It is most commonly used as a high-performance substitute for Portland cement or as clinker for Portland cement production (Asokan et al., 2002). Properties of fly ash vary significantly with coal composition and plant-operating conditions.

On the other hand, bottom ash is quite different from fly ash, both physically and chemically. Bottom ash is a coarse, granular, incombustible byproduct that is collected from the bottom of furnaces that burn coal for the generation of steam, the production of electric power, or both. Bottom ash is coarser than fly ash, with grain sizes spanning from fine sand to fine gravel. It is suitable as raw feed for manufacturing Portland cement, as well as road construction material (Hill et al., 2001; Kim and Lee, 2011; Qiao et al., 2008).

1.1 Justification

Coal is an important resource for the generation of electricity worldwide. In 2010, around 44.8% of the electricity produced in the United States was generated by burning coal (USEIA Electric Power Annual, 2011). For the same year, the United States produced more than 130 million short tons of CCBs. While 42.5% of this amount was used beneficially, nearly 70 million short tons were disposed (ACAA, 2010). Puerto Rico has a coal-burning power plant located in the municipality of Guayama. Fuel use for many activities in Puerto Rico is dominated by petroleum, but coal is the second important resource used. Figure 1 shows the distribution of electricity generation based on fuel source in Puerto Rico for 2006.

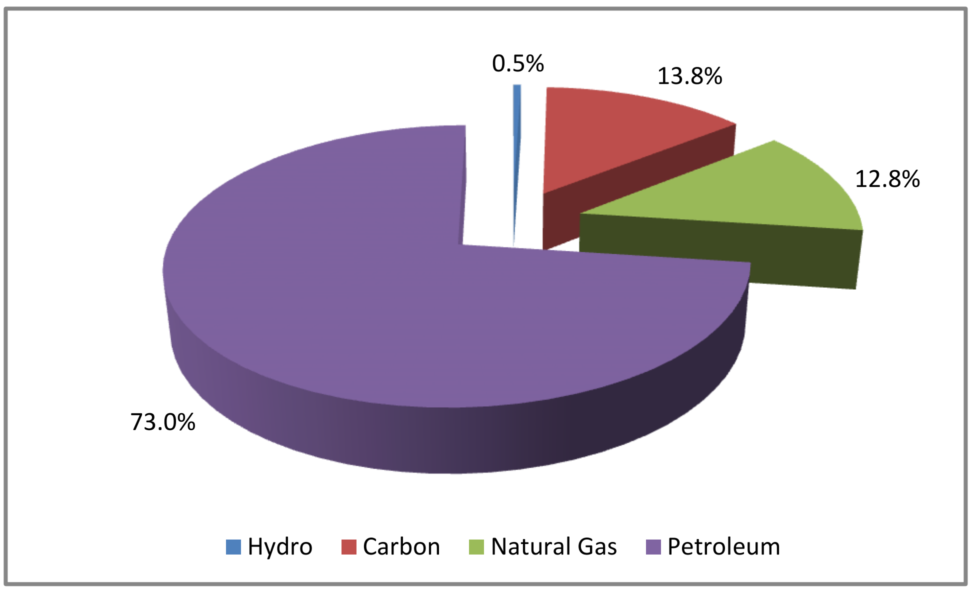

Figure 1. Distribution of Fuel Use in Puerto Rico During 2006. (www.aespuertorico.com)

The company AES (Applied Energy Systems) Puerto Rico produces around 454 megawatts yearly, representing 15% of the island's electricity consumption. The CCBs they produce are commercially available as the brand Agremax™. This product is a solidified composite of fly ash and bottom ash and is mainly utilized to fill commercial and private lands. The beneficial utilization of these materials varies a lot, but they are commonly used as a substitute for construction materials to minimize the disposal of them. Fly ash and bottom ash can be used as road base materials, manufactured aggregates, flowable fills, structural fills and embankments. Fly ash is also utilized to replace natural materials in the production of concrete. Some of the overall benefits of using CCBs are the reduction of landfill space used for disposal, and to eliminate the need to use primary raw materials (ACAA, 2010). In line with the aforementioned benefits or advantages of CCBs, this project focuses on the beneficial utilization of these materials for the development of aquatic structures which can enhance overall water quality.

1.2 Objectives

The overall goal of this study was to achieve potential water quality enhancement through beneficial utilization of industrial byproducts, specifically CCBs. To meet this goal, a laboratory-scale experiment was conducted to:

- Assess general water quality parameters after introduction of the aquatic coal ash aggregates mortars (CAAM) blocks made of CCBs,

- Evaluate possibility of the reduction of ammonia toxicity and abatement of algal bloom in the presence of CAAM, and
- Determine the optimum compositions and application rates of the CAAM resulting in water quality enhancement while achieving maximum recovery of the CCBs.

LITERATURE REVIEW

Information provided in this section will establish a background on the algal bloom problems in aquatic environments and the CCBs use in cement mixtures for the substitution of raw materials. At the same time, it describes the different areas in which these materials have been relevant to solve engineering problems by finding effective ways of recycling them. There is little information regarding the use of CCBs in aquatic structures, and only the use of fly ash has been well documented for this purpose.

2.1 Problems and Remediation related to Harmful Algal Blooms

Algal blooms have been a major problem in waterways due to the nuisance and maintenance required to keep them at a minimum level. The problem affects water systems indiscriminately and can occur in either freshwater or marine environment (Dionysiou, 2010). Freshwater ponds are affected by this phenomenon; basically the problem becomes a major concern since they are used for engineering and esthetic purposes. In the marine environment, they are a major problem in the coast for the toxicity that can come with it. Some problems that accompany algal bloom include toxic effects, economic losses and the resources degradation.

Anderson (2009) discussed some of its possible impacts and management of coastal algal bloom. There are several general consequences attributed to algal blooms including the cause of human illness through food chain ingestion and poisoning of aquatic fauna in aquaculture sites and marine environments through the production of toxins. On the other hand, non-toxic algae decay when the bloom ends provokes oxygen depletion leading to mortality of plants and animal in the affected area. Another major problem is the reduction in light penetration, which impacts negatively the ecosystem. Due to these negative impacts, an estimated $75 million were invested in the US over a 13 years period at the end of the 20th century (Hoagland and Scatasta, 2006). In the last few decades, the problem has increased becoming one of the causes of water pollution and by affecting human activities. Nitrogen and phosphorous are commonly found in agricultural, sewage, and industrial discharges being the major cause for algae bloom. Another factor is the dramatic increase in aquaculture activities in many countries. Management strategies include mitigation, prevention and control. Algae growth could be controlled by mechanical, biological, chemical, genetic or environmental strategies. Detection of this phenomenon has improved through the years and some of the emerging technologies include chromatography, simple test kits, remote sensing and probes for detection. Some of these tools help the fishermen perform tests for toxin presence in the areas where they perform their harvests.

Sevrin-Reyssac and Pletikosic (1990) made a discussion of cyanobacteria in a pond. Cyanobacteria, also known as blue-green algae, are present in pond mostly during summer due to warm and sunny weather. These organisms may impair the environment in various ways such as deoxygenation by decomposing in the water becoming potentially toxic to fish. Easy adaptation to pond conditions like reduced light penetration and nitrogen depletion are some of their main characteristics. Fertilizers are added to fish ponds to increase the production of fish which end up in the development of cyanobacteria. Reduction of cyanobacteria present in a pond was achieved in related studies by increasing the nitrogen to phosphorus ratio to 5 or more (Seymour, 1980). The use of aerators to break stratification and avoid low oxygen levels also made water conditions unfavorable to blue-green algae. More aggressive efforts have also been made to control the algal blooms and on the management schemes to reduce their magnitude. The most frequently used algaecides for this purpose are copper sulphate and simazine which block algal photosynthesis. The main problem with these chemical additions was that mortality of other species and microorganism occurred. These organisms still are the cause of the death of many fishes in ponds (Boyd, 1979).

O'Neil et al. (2012) presented a review to explain the influence of eutrophication and climate changes on the development of harmful cyanobacteria blooms in freshwater, estuarine and marine systems. There are many genera of cyanobacteria that cause harmful algal blooms and the toxins can be dangerous to both animals and humans. Nutrients are provided to the environment mainly by anthropogenic activities. Both nitrogen and phosphorous has been proven to be involved in the algal blooms proliferation (Kolowith et al., 2001). On the other hand, studies performed on the cyanobacteria showed that they will thrive under global climate changes (Paul, 2008). Parameters like temperature, carbon dioxide, pH and salinity affect the behavior of the cyanobacteria related to climate changes directly. This review presented information on freshwater species like Anabaena, Microcystis and Cylindrospermopsis, for the estuaries environments presented the species Nodularia, Aphanizomenon, and Anabaena found in the Baltic Sea, and for the marine environments presented the genera Lyngbya, Trichodesmium and the coccoid cyanobacteria Synechococcus. Overall, the review showed that cyanobacterial blooms where this species are present mainly occur under high temperatures and are related to high levels of anthropogenic nutrient loads, particularly phosphorus. Low nitrogen levels will favor the growth of cyanobacteria that are diazotrophic and show flexibility on nitrogen acquisition strategies. Low levels of CO_2 contribute to the blooms, so the increase of this compound due to climate changes may indicate suppression on their growth in the future.

The problem of algal blooms has been approached with remediation techniques recently developed among which can be mentioned the work performed by Wang et al. (2012). Their study presented an innovative procedure for the removal of cyanobacteria blooms from lakes using hydrogen peroxide followed by the addition of sediment clay plus polymeric ferric sulfate at specific concentrations. Microcystis colonies obtained from a lake reservoir in China were treated with hydrogen peroxide at different concentrations and the bacteria count in the colonies dropped as a higher peroxide concentration was applied (up to 60mg/L). Absorption spectroscopy tests showed that the dissociation of phycobilisomes, known as light- harvesting pigments, from core complexes is the most likely algaecidal mechanism.

2.2 Waste Materials in Concrete Mixtures

The incorporation of waste materials into other applications has been a recent approach for their reutilization and minimization in the cost of their disposal. Some of these materials include waste tires, plastics, glass and CCBs, among others. The overall discussion will turn toward the incorporation of waste material in concrete mixtures.

Waste tires have been incorporated to concrete structures and become very successful for these intentions. Evidence provided by Li et al. (2004) will be discussed briefly. In their study, two types of waste tire-modified concrete were investigated. One concrete was modified using waste tires in the form of chips while in the other concrete, the tire was in the form of fibers. For the chip-modified concrete, surface treatment with NaOH solution and physical anchorage were also investigated. For the fiber-modified concrete, fibers with various aspect ratios were utilized. Waste tires from trucks and cars were tested and incorporated in the batches. A total of 10 batches with different combinations were tested. The effect of waste tire resources was evaluated on strength and stiffness. Compressive strength, compressive modulus of elasticity, Poisson's ratio, and split tensile strength tests were performed on the samples prepared. The strength and stiffness of waste tire rubber-modified concrete were lower than those of normal concrete, regardless of the type of material used. Fiber mixture provided greater stiffness than other batches prepared. They concluded that fibers performed better than chips and the NaOH surface treatment didn't work on large-sized tire chips. They suggested that fiber length be restricted to less than 50 mm and that steel belt wires have a positive effect on increasing the strength of rubberized concrete. Overall, truck tires performed better than car tires.

Batayneh et al. (2007) studied the incorporation of various waste materials into concrete mixtures. Their approach mainly targeted the substitution of a percentage of the primary materials used in the ordinary Portland cement concrete. Materials used included demolished concrete, glass and plastic. The crushed concrete was used to replace up to 20% of coarse aggregates, and the plastic and glass were used as fine aggregates by replacing up to 20% of this material in the concrete mixes. Several tests were performed to characterize different properties of the mixes prepared. The series of tests performed included workability, unit weight, compressive strength, flexural strength, and indirect tensile strength. Overall results showed that the glass slump test did not depend on the amount added, for the plastic and demolition as more was added lesser slump was obtained. When using up to 20% of plastic and crushed concrete, as fine and coarse aggregate respectively, the strength of the concrete exhibited lower values for the compressive and splitting-tensile strength.

Another material that is considered a waste, but is used in concrete mixtures is CCBs. Fly ash is the most commonly used CCBs for this purpose. The primary use is as a substitute of cement usually at percentages lower than 35% to create fly ash concrete. Jahanian and Rostami (2001) showed the use of fly ash to produce alkali ash materials that created construction materials with desirable structural properties, and at the same time helped to recycles the material. For each type of ash, 10 mixes were produced, where the amount of fly ash and aggregate were kept constant while the ratio of alkali to solid were changed from 5% of total mix to 25% of total mix with increments of 2%. Cylindrical samples of 7.5 (I.D.) x 15 (L) cm and beams of 10 (H) x 10 (W) x 50 (L) cm were prepared. Three sources of Class-F (ASTM C618) fly ash were used and tested for strength. It gained its strength in two days making it very attractive for many construction applications.

Andrade et al. (2009) studied the alternative of using bottom ash as a replacement for fine aggregates in concrete. The sand was replaced in different percentages by bottom ash aggregate. Two mixtures were prepared one with equivalent volume and another one with non-equivalent volume replacement. Several tests were performed including water loss through bleeding, setting time, heat evolution and plastic shrinkage. The results showed that in the concretes with bottom ash were susceptible to water loss by bleeding. Also, the highest content percentage of bottom ash showed a lower deformation through plastic shrinkage was obtained. The setting time was also affected by the presence of bottom ash. In conclusion, behavioral tendencies were maintained when bottom ash was employed as a replacement for natural aggregates.

2.3 Coal Combustion Byproducts in Aquatic Environments

There are a few reports discussing the behavior of these structures when incorporated to an aquatic environment. Alum et al. (2008) tested different kinds of materials to control algal growth development over cement structures in freshwater. Since commercially developed materials, like tributyltin, has caused environmental impacts and are not cost efficient, materials like copper slag, ammonium chloride, sodium bromide, and fly ash were tested to check their contribution to this matter. Two types of studies were conducted: one adding the algaecide material in the mortar and the other adding it as a surface coat. The data collected to determine the best candidate for the study purpose was measured based on the chlorophyll amount present. The treatment had different combinations of zinc oxide, ammonium chloride, sodium bromide and cetyl-methyl- ammonium chloride, either alone or combined. Only four of the treatments incorporated fly ash in the mixture. The fly ash was used both in binary and tertiary combinations. In the binary system of zinc oxide with fly ash, mortar coupons with 20% zinc oxide plus 10% fly ash yielded optimum levels of 99 mg/m^2 of total chlorophyll. On the other hand, the tertiary combinations that contained fly ash provided the best yields, even when the best results were obtained with the combination of zinc oxide and sodium bromide. The interactions among these materials were not fully understood; therefore further studies must be performed.

Guilbeau et al. (2003) evaluated the usefulness of different cements as substrates for artificial reefs and performed preliminary tests of conventional and pH-neutral molded cements for attachment of microalgae populations. Cements provide a surface that can be made suitable for the attachment and development of algae. Reefs made of Portland cement (PC), coal fly ash cement (FAC), blast-furnace slag (BFS), and various silicates were tested. The growth of algae on typical mixtures of these cements was measured under both fresh and brackish water conditions. Both carbonated and non-carbonated cements were examined. Carbonation was used to lower the initial pH of the cements at 8 to 9. Cement disks (25 g, 39 mm diameter, 13 mm thick) were molded using a cylinder and hydraulic piston device that allowed for carbonation of the cement while applying pressure to the piston. The amount of CO_2 added to the specimen was controlled by varying both the CO_2 pressure at the mold entrance and the amount of free space above the piston using spacers. Cement disks were made with the following products: PC, BFS, FAC, PC/slag mixtures, PC/fly ash mixtures and PC/reactive silica mixtures. Once samples were molded, three exposure treatments were used on the samples: (1) placement of molded disks directly in brackish water, (2) placement in a tank periodically refilled with brackish water, and (3) placement in a tank periodically refilled with freshwater. There were significant differences, depending on the materials combination used, in the initial rates of microalgae attachment to various cements. Lower pH/higher carbonation level increased attachment rates significantly. The most algae attachment was obtained with PC/amorphous silica mixtures (10 % wt. silica).

Alkali-activated, carbonated fly ash and blast-furnace slag cements were also significantly better than either plain PC or even PC/fly ash mixtures. Fly ash cement proved less reliable in freshwater than brackish water tests, while the opposite was true for BFS. Applying higher CO_2 feed pressures also increased extent of carbonation and decreased cure times for silica and BFS/PC mixtures to 1 h or less.

Chalee et al. (2010) tested FAC structures for 7 years at certain weather conditions specifically in marine conditions to verify its performance since fly ash was incorporated into the mixture. The objective of the study was to generate an empirical equation to help predict long term required cover depth of cement and FAC to protect against the initial corrosion of reinforcing steel in a marine environment. Concrete tubes were built with different percentages of fly ash as a replacement of PC, ranging from 0% to 50%. Two major changes were incorporated: (1) low water-binder ratios and (2) specific depth of the steel bars within the tubes. Casting was performed for 28 days and the concrete tubes were transferred to seashore. The samples were exposed to two wet-dry conditions daily. The study focused on the chloride penetration profile and content. On the other hand, steel bars were checked for corrosion signs. Chloride penetration was observed and measured as a lower content in blocks containing fly ash due to the lower permeability that it provided to the concrete structures. The difference in water-binder amount also showed a difference within fly ash containing samples where the higher FA content had higher resistance to chloride ingress. To perform the steel bars corrosion test, the concrete was broken and the embedded steel bars were removed from it. The corrosion on the embedded steel bars was measured in terms of the percentage of rusted area and image recording. After the data was analyzed, the steels bars with less signs of corrosion were the ones covered with the highest amount of fly ash replaced and the highest water-binder. This information agrees with the fact that there is a direct relationship between the steel corrosion and chloride penetration in concrete under a marine environment. An empirical model was generated to predict the required concrete cover depth to protect against the initial corrosion of reinforcing steel in cement and FAC for the exposure period longer than two years in a marine environment. It yielded good results for concretes with water to binder ratios ranging from 0.45 to 0.65 and fly ash replacement from 0 to 50% by weight of the binder. However, the study had a downfall because it was limited to a one-dimensional ingress of chloride into concrete structures.

Seabrook and Wilson (1988) studied the incorporation of lightweight concrete into offshore structures, considering its advantages with respect to buoyancy in shallow waters. The main objective was to identify this type of concrete to have a higher strength than normal concrete and to determine the feasible strength levels obtained with Canadian raw materials. A total of 162 trial mixtures were tested in this experiment. The variables included three levels of fly ash: 0, 12.5, and 25% by weight of cementitious material, silica fume: 0, 7.5, and 15% by weight of cementitious material and total cementitious content of 450, 500 and 550 kg/m^3. Fresh and hardened concrete sets were prepared and tested. The main difference among the sets was that the hardened concrete specimen was cured for 91 days in water. The curing time used for the hardened concrete led to slightly higher value in the strength test compared to the fresh mixture. In terms of design unit weight the results were the following: for the normal concrete a unit weight of 2,455kg/m^3 was achieved, for Type A 2,000 kg/m^3 and for Type B 1,975 kg/m^3 with a standard deviation in the order of 40 kg/m^3. The unit weight values for the two lightweight mixtures were about 5% higher than the target. In the compressive strength test, data for 28 and 91 days were analyzed. The test showed that there was not a consistent advantage of one mixture over another. Even though no consistent trends were produced, overall information was related to the data. It was evident that there were strength advantages in the use of silica fume and there was a general indication that fly ash content in the range of 12.5% would be desirable in this test.

2.4 Nitrification and Ammonia Toxicity in Aquatic Environments

As previously mentioned, nitrogen (N) and phosphorus (P) are key components for the algal bloom development. The nitrification process is the conversion of ammonia into nitrate through oxidation. The presence of N in water systems could become dangerous if it is dominated by ammonia and nitrite species due to their toxicity (Jensen, 2003; Randall and Tsui, 2002). The total ammonia nitrogen is obtained from the sum of ammonia (NH_3) and the ammonium ion (NH_4^+) present in a system. At high pH, the toxic form NH_3 is dominant, while at low pH values, the less toxic form (NH_4^+) predominates. Nitrogen is known to be an important nutrient for the metabolism of cyanobacteria; therefore it is necessary to have a better understanding of the factors that influence this process.

Hargreaves (1998) presented how N contributed to the fresh water system by analyzing possible paths where N was generated and removed from the water. The role of N in water is very important. However, it should be kept balanced to minimize water quality problems such as eutrophication. It is important to mention that fish can only assimilate a small amount of N, making the water responsible for assimilating their nitrogenous excretion having a great impact on both water quality and fish growth. Overall, the ammonia generated through fish excretion had toxic characteristics when present in elevated pH and temperature environments. Approximately 25% of N was retained by the fish and the other 75% was excreted. The paper also presented a discussion on the many processes related to nitrogen flux in ponds which includes: nitrogen fixation, ammonia volatilization and nitrification, among others. The addition of N through fixation depends upon phytoplankton composition. Even though phytoplankton is a minor contributor, occasionally it is important for the N budget of aquaculture ponds receiving formulated feeds. Ammonia volatilization is enhanced at elevated pH due to equilibrium relationship. Volatilization may be important as a mechanism of ammonia removal in poorly buffered ponds. In general, ammonia volatilization is enhanced by increasing ammonia concentration, pH, temperature, evaporation rate and wind speed.

On the other hand, nitrification is affected by dissolved oxygen concentration, temperature, substrate concentration, pH, numbers of nitrifying bacteria, and availability of surfaces. The nitrogen flux is a complicated process with too many variables influencing the outcome. Nitrification at the sediment–water interface is more important than nitrification in the water column since it is restricted by the availability of surfaces and possibly by light inhibition. Nitrification increases temporarily following phytoplankton death due to high ammonia concentration. Water column nitrification is an important mechanism of ammonia transformation in pond systems where particles are mainly suspended by mechanical aeration.

2.5 Nitrification Support by CCBs

The process of nitrification involves the conversion of ammonia into nitrate through autotrophic bacterial activities, which requires the two steps process shown in equations (1) and (2), where the first step involves ammonia oxidizers (Nitrosomas sp.) and the second involves nitrite oxidizers (Nitrobacter sp.) to complete the total oxidation reaction (3).

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 4H^+ + 2H_2O \qquad (1)$$

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \qquad (2)$$

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \qquad (3)$$

There are basic water parameters that are directly affected by the nitrification processes. One of these parameters is the alkalinity of the system where its destruction is often observed if nitrification happens. The alkalinity in a system is defined by the capability of water to neutralize an acid linked directly to the presence of carbonate, bicarbonate and hydroxide species being dominated by the following equation:

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO^{3-} \leftrightarrow 2H^+ + CO_3^{2-} \qquad (4)$$

The influence of these parameters is presented through different articles as evidence to support the CCBs influence in our experiments.

Li and Irvin (2007) studied the alkalinity and redox potential (ORP) as indicators for nitrogen concentration in a sequencing batch reactor, as alkalinity was directly related to nitrogen removal and was easy to be measured. The experimental reactor had a treatment capacity of 1.7 m^3 and treated synthetic wastewater with specific concentrations of chemical oxygen demand (COD), total kjehldahl nitrogen (TKN), ammonia (NH_4^+) and alkalinity. Three setups were tested where two parameters remained constant and one was varied to obtain the impact of each parameter on the nitrogen removal changing the COD concentration, dissolved oxygen (DO) and hydraulic retention time (HRT). The alkalinity was also measured after applying an inhibitor to the system at previously determined concentrations. The alkalinity difference of influent and effluent were also obtained for comparison. Results showed that the highest alkalinity drop in aerobic phase occurred at low COD concentrations. Under low DO conditions alkalinity decreased and as DO was increased gradually a more notable drop was observed. The HRT also had an influence in the alkalinity in the system during nitrification. An incomplete nitrification was observed under low DO and short HRT. The ORP results didn't show a clear behavior to become a direct indicator of nitrogen removal. In contrast, the alkalinity showed a reverse relationship with the effluent. The tests performed showed the alkalinity accuracy for indicating the nitrification/denitrification processes. When comparing alkalinity and pH in the systems they found that pH values decreased in the aerobic nitrification phase. Overall, alkalinity proved to be a better indicator for the nitrogen concentration on the system than ORP and the difference obtained for alkalinity reflected the efficiency of the combined nitrification/denitrification process.

Huesemann et al. (2002) showed the influence of carbon dioxide (CO_2) injections as a mean of CO_2 reduction in the atmosphere to seawater on nitrification. The study was performed with seawater obtained from two locations at different altitudes. Samples of 3.5L were taken from the two locations, added ammonium chloride at 50uM as the ammonium source and pH was adjusted to values of 6.0, 6.5, 7.0, 7.5 and 8.0 using either CO_2 to lower the pH or adding NaOH to increase it. The nitrification rate inhibitor, sodium chlorate, was added to three reactors and allythiourea was used in three control samples. Overall results showed that nitrification rates reduced as pH decreased for both samples, deep and superficial zones.

2.6 Phosphate Removal through CCBs

Phosphorus is used as an important nutrient by both plants and algae. It mainly comes from earth rocks and its release ends up in soluble phosphate ions. The amount of phosphate is a crucial factor in growth processes due to its role as a nutrient. The removal of phosphate, which is a major contributor to eutrophication, has been studied in conjunction with CCBs to check their effectiveness in this matter. Literature review showed that fly ash had a potential as an adsorption material of phosphate since it was cost effective and the raw material was readily available.

Chen et al. (2007) reported the results of a study performed with 15 fly ashes with different ratios of the fly ash to verify the P removal and sorption capability of the CCB. First of all, chemical composition tests were performed to find the amount of Si, Al, Fe, Ca, and Mg present in each batch. Sorption, fractionation of P and pH effects were the main tests performed. For the sorption experiment, P solutions with concentration ranging from 25 to 1000 mg P/L were prepared and pH was adjusted to 5. Samples of 40 mL of the solution with 0.4 g of fly ash were agitated for 24 hours and centrifuged before tested with UV spectrometer. To determine how the sorbed P was fractionated the solution of 1,000 mg P/L was tested and data for the weight of the centrifuge tube, fly ash added and residue after centrifuged were collected. The pH test was performed on samples with high, medium and low calcium content to verify for variations in calcium and iron concentrations. Sorption isotherms for high, medium and low calcium content were prepared using the Langmuir and Freundlich models. Based on the correlation values it was believed that calcium, especially the species CaO and $CaSO_4$ and iron contributed primarily to P immobilization. The fractional P analysis showed that the loosely bound P fraction and/or the calcium + magnesium-phosphate fraction were the dominant forms of P immobilized by fly ash. Low values of pH were related to high calcium concentration, while high pH values were measured at low calcium concentration. Depending on the calcium content, the process was determined to be favorable or unfavorable.

Agyeia et al. (2002) performed a study to determine the efficiency of phosphate removal of materials such as fly ash, slag, Portland cement and other blends. The composition of each material was obtained by X-rays fluorescence. The determination of phosphate removal was done using the yellow vanadomolybdo-phosphoric acid method. Samples of 2 g of absorbent were placed in 200 mL of water with different phosphate concentrations at a pH of 9 and 25 °C. The monitoring was performed at specific times until absorbance values leveled off. The effect of particle size and pH were also studied. The study concluded that the removal of phosphate for Portland cement was faster than for fly ash. Blends of Portland cement with fly ash or slag decreased the removal efficiency. Best results were obtained under high concentrations conditions, acidic pH and higher temperatures. A first order kinetic model, Frumkin isotherms, was appropriate to predict the phosphate removal based on the data obtained.

Xu et al. (2010) work showed how modifying fly ash with sulfuric acid enhanced the phosphate immobilization ability of the fly ash. A sample of 5 g ash in water was modified with sulfuric acid. After optimizing the sulfuric acid modification, phosphate immobilization studies were carried out. The effects of contact time, pH and dosage were then studied in detail. The selected modified ash was added to phosphate solutions with different concentrations, the pH adjusted to the desired value, shaken and measurements obtained from the supernatant. The results showed that contact time was not relevant, that for pH values between 5 and 9 results were almost constant and as the dosage increased the removal also increased. The sorption isotherms showed that the phosphate adsorption capability increased with the increase of phosphate concentration. The ashes were characterized after sorption and corroborated the presence of calcium, phosphate and oxygen. The possible reactions were established based on the results obtained, both adsorption and precipitation mechanisms contribute to the removal of phosphate by the modified fly ash.

MATERIALS AND METHODS

This section provides the overall information on the materials and methodology used for the intended purpose of a series of experiments. Analytical methods are also included in this chapter. It was divided in smaller sections since a series of experiments were performed throughout the project.

3.1 Materials

The materials used for the series of experiments performed during the current study are described in detail within this section. The information on CCBs characterization, tanks setup and CAAM blocks development are discussed.

3.1.1 CCBs Background

An important factor to understand the CAAM blocks behavior in the aquatic systems was to have available the information on the composition of the CCBs used for the mixtures preparation. Therefore, the chemical and physical information of both CCBs materials are necessary to understand their nature and composition.

Fly ash and bottom ash used in our experiments were characterized by AES Puerto Rico. The fly ash is generally classified as Class C or F, due to the calcium content based on the American Society for Testing and Materials (ASTM C618) Standards. Table 1 shows the chemical composition of fly ash as obtained from AES Puerto Rico. Based on the results provided, the compliance of most of the chemical requirements makes their fly ash fall in the Class C carbonate content description except for the sulfur trioxide percentage (Pando and Hwang, 2006).

Table 1. Chemical Composition of Fly Ash from AES Puerto Rico*

Chemical Compounds	***Content Results (% by weight)***
Silica, SiO_2	39.41
Alumina, Al_2O_3	12.59
Ferric Oxide, Fe_2O_3	4.35
SiO_2+Al_2O_2+Fe_2O_3	56.35
Titania, TiO_2	0.51
Lime, CaO	27.02
Magnesia, MgO	1.27
Potassium Oxide, K_2O	1.17
Sodium Oxide, Na_2O	0.44
Sulfur Trioxide, SO_3	12.57
Phosphorus Pentoxide, P_2O_5	0.28
Strotium Oxide, SrO	0.14
Barium Oxide, BaO	0.23
Manganese Oxide, Mn_3O_4	0.02
Undetermined	0
Alkalis as Na_2O, Dry Coal Basis	1.12
Base to Acid Ratio	0.65

*Source: Pando and Hwang, 2006

Bottom ash characteristics are very important due to its intended use as sand substitute in our experiments. The chemical composition of bottom ash is somehow similar to fly ash. However, bottom ash is more inert and displays less pozzolanic properties than fly ash. The physical properties of bottom ash mimic better those of natural sand. The composition of the bottom ash is shown in Table 2. In our experiments the bottom ash was sieved to obtain a particle size of 0.42 mm which compares to a fine to medium sand size. The gradation results performed on the bottom ash obtained from AES, Puerto Rico is presented in Table 3.

Table 2. Chemical Composition of Bottom Ash from AES Puerto Rico*.

Chemical Compounds	*Content Results (% by weight)*
Silica, SiO_2	30.83
Alumina, Al_2O_3	12.2
Ferric Oxide, Fe_2O_3	3.95
SiO_2+Al_2O_2+Fe_2O_3	46.98
Titania, TiO_2	0.57
Lime, CaO	36.02
Magnesia, MgO	1.58
Potassium Oxide, K_2O	0.66
Sodium Oxide, Na_2O	0.55
Sulfur Trioxide, SO_3	12.82
Phosphorus Pentoxide, P_2O_5	0.37
Strotium Oxide, SrO	0.15
Barium Oxide, BaO	0.27
Manganese Oxide, Mn_3O_4	0.03
Undetermined	0
Alkalis as Na_2O, Dry Coal Basis	0.95
Base to Acid Ratio	0.98

* Source: Pando and Hwang, 2006

Table 3. Typical gradation for AES, Puerto Rico Bottom Ash.

Sieve Identification	*Sieve Size (mm)*	*Total % passing*
#4	4.750	98.08
#10	2.000	95.09
#20	0.850	91.62
#40	0.425	78.36
#60	0.250	51.97
#100	0.150	15.35
#200	0.075	1.69
P-200	0.000	0.00

3.1.2 Tanks Setup

The aquatic environment was simulated using glass fish tanks of 10 gallons. The components of each fish tank included: two artificial decorative plants (AQUA®Culture), 5.0 gram of decorative stones (AQUA®Culture), and a circulating filter (Tetra®) which was used for aeration. Light was provided to each tank with an aquarium light (Plants & Aquarium Fluorescent 20W, Phillips) that was mounted at approximately 3 inches above the tanks. Artificial light was provided for a period of twelve hours per day. Acrylic covers were put on the top of the tanks to minimize water evaporation. Figure 2 shows the typical setup used for the experiments.

Tanks were filled with 30 L of tap water and aerated for 24 hours for dechlorination before fish were added. Real pond water was sampled from the pond on campus and added in some of the experiments to introduce naturally-grown algae into the system. A total of 10 cichlid fish (Tilapia spp.) were used per tank for the experiments, unless otherwise stated. Tilapia is originally from the Middle East and Africa, and can be found in a diversity of water bodies either fresh or marine environments. These fish are herbivorous which help to control aquatic plant populations and common due to their use for aquaculture due to their ease to grow (MIT SGCR, 2012). Also, this species of fish are the dominantly populated species in the pond on campus. Wardley® Pond Food Flakes were used as fish gourmet and fed fish at specific amounts throughout the experiments.

Figure 2. Typical Tanks Setup Used for Experiments.

3.1.3 Aquatic Structures

Aquatic structures, CAAM, were prepared by mixing equal amounts (by weight) of cement (Ponce cement for General Use), fly ash and bottom ash. This combination was selected after performing a couple of preliminary trials with different mixtures. The CCBs used were obtained from AES Puerto Rico and their appearance is shown in Figure 3.

Figure 3. Fly Ash (left) and Bottom Ash (right) Acquired from AES.

Using identical plastic ice trays (Arrow Plastic Mfg. Co.) as the mold, CAAM blocks of approximately 2.54 cm x 3.81 cm x 3.18 cm were prepared. A residence period of 24 hours was provided in the mold. Then, the structures were taken out of the mold and were allowed an additional 7 days for curing under dry conditions by exposure to air at 22-24 ºC and a relative humidity percent of 70-80% (prior to use for the experiment). Figure 4 presents the shape and appearance of the prepared CAAM blocks.

Figure 4. Shape and Appearance of the CAAM Blocks.

3.2 Experimental Methods

Several methods were developed to achieve the objectives of the current study. The following chapter describes each method used in the subsections of fish gourmet amount selection, aquatic structure evaluation, effects of the numbers of CAAM blocks on water quality, and nitrification monitoring.

3.2.1 Fish Gourmet Amount Selection

Characterization of the fish gourmet was performed to obtain information of the concentrations of nutrients it would contribute to the systems. The gourmet was ground and weighted to obtain three different concentrations. Concentrations of 0.10, 0.05 and 1.0 mg/L of fish gourmet were obtained in duplicates. Contact was allowed overnight with agitation and filtration was performed before the analysis. The solutions prepared were tested for conductivity, total nitrogen (TN), total phosphate (TP) and chemical oxygen demand (COD) parameters.

The next step was to establish the amount of fish gourmet that was going to be provided to the systems. Since fish gourmet did not specify the amount that should be provided based on the volume of water and/or the numbers (or type) of fish. If too much fish gourmet is introduced to the system, the system will not allow accurate monitoring of water quality due to nuisance factors which would mask the effect of aquatic structures. On the other hand, if too little gourmet is used, aquatic structures would not make any differences in water quality regardless of their presence in the system or not. Therefore, it was intended to find the optimum amount of fish gourmet that would provide a nuisance environment, but still allow us to assess the effect of aquatic structures with respect to water quality enhancement.

Different amounts of fish gourmet (0.3, 0.5, 0.7 and 1.0 g per day) were tested considering the size of the tank and the numbers of fish (Figure 5). These amounts were introduced in a series of four tanks set with the conditions described in the Tank Setup (section 3.1.2). In this case, the aquatic structures were not part of the system since they were our instrument to verify any water quality enhancement occurring due to their presence. Water quality was monitored daily for a total period of 38 days to give enough time to the system to stabilize and observe any changes in water quality.

Each tank was analyzed for specific water quality parameters to check how the nutrients in the fish gourmet were affecting the system. Water parameters monitored at this point included pH, dissolved oxygen (DO), conductivity, turbidity, hardness, nitrate, temperature, color and alkalinity. At the end of the experiment other parameters like total nitrogen, total phosphate, suspended solids and biological oxygen demand (BOD_5) were also obtained.

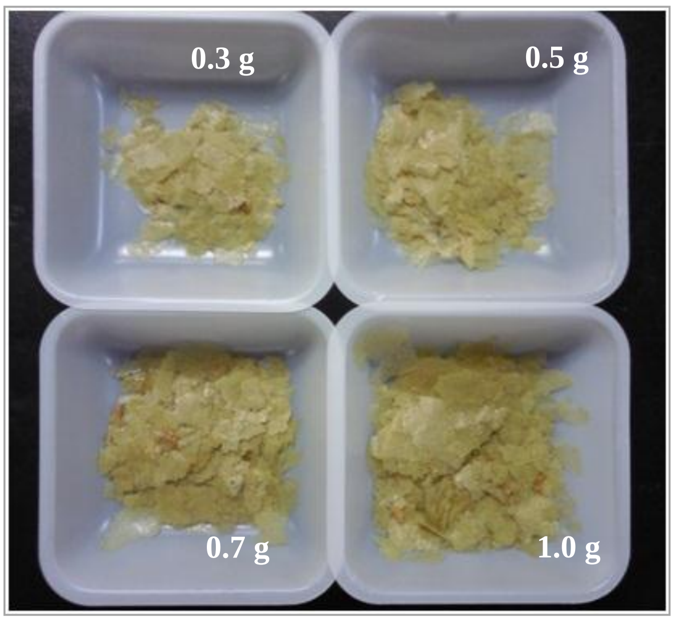

Figure 5. Fish Gourmet Amount Provided to Fishes.

3.2.2 CAAM Blocks Preparation, Selection and Structural Analysis

One of our objectives was to maximize the amount of CCBs utilization in the CAAM. Bottom ash has rarely been used for this intention, but it was part of our objectives to prove the successful incorporation of it into the CAAM blocks.

Several mixtures were prepared and tested for its resistance in water environment. Table 4 presents five different combinations tested. After the mixtures were prepared, blocks were cured as described in section 3.1.3. The different combinations were put in 100 mL of deionized water at room temperature, which covered the block completely. Both, pH measurements and visual inspections for any surface shrinkage were performed after three days under water. Three replicates were obtained for each batch from the same mixture. The best mixture combination was selected based on the measured changes in pH and surface shrinkage after water exposure (i.e., cracking).

Table 4. Mixtures Compositions

Mixture	*Cement (g)*	*Fly Ash (g)*	*Bottom Ash (g)*	*Water (g)*
A	-	200	200	155.6
B	200	200	50	178.6
C	200	200	75	218.2
D	200	200	100	197.7
E	200	200	200	225.0

Compressive strength test and curing procedures were performed using ASTM methods. Specifically, ASTM C109 was used for the preparation and compressive strength test of the specimens. Specimens were made using cubic molds of 5.08 cm x 5.08 cm x 5.08 cm. Curing methods were performed at both dry and wet conditions (ASTM C192). The compressive strength tests were done using a universal compression machine with a capacity of 300,000 kilograms (Forney, Model LT-1000-03).

The different mixtures were prepared and tested to assess the integrity and strength of the specimens in order to acquire information related to their structural strength and viability for the overall purpose of this study. The information obtained from the structural analysis was also used for the selection of the best CCB mixture satisfying our objectives.

3.2.3 Effect of the Numbers of CAAM Blocks on Basic Water Quality

The effect of the CAAM blocks on water quality was tested to see if this factor could bring a significant difference in water quality between the tanks having the different amount of blocks. The amount of CAAM blocks selected for a set of four tanks was 7, 14, 21 and 28, respectively, considering the size of the tank (30 L). All tanks received an equal amount of fish gourmet (1.0 g per day) during the experiment which was selected from the fish gourmet amount experiment.

The experiment was performed with the Tank Setup described in section 3.1.1, but with the addition of different amounts of CAAM blocks to the tanks. Each tank was tested for pH, DO, conductivity, turbidity, hardness, nitrate, temperature, apparent color and alkalinity. Other parameters such as total nitrogen and total phosphate were monitored on the last day of the experiment. Also suspended solids, surface biomass and BOD_5 were measured. Data was collected three times a week to obtain a pattern from the measurements obtained.

3.2.4 Effect of CAAM Blocks on Nitrate and Phosphate Abatement

An independent experiment was performed for nitrate and phosphate behavior in the systems with and without fish in the presence of the blocks. The system without fish served as the blank treatment. Tanks were setup as in section 3.1.1, only the 7 and 28 blocks systems were prepared. Water quality parameters monitored included: pH, DO, conductivity, turbidity, hardness, nitrate, phosphate, temperature, apparent color, and alkalinity. The last day of the experiment obtained measurements for total nitrogen, total phosphate, suspended solids and BOD_5 were obtained.

3.2.5 Effect of CAAM Blocks on Ammonia Nitrification

Ammonia nitrification tests were performed to assess the potential of the aquatic structures for reduction of ammonia toxicity by enhancing nitrification. Ammonia toxicity is known to detrimentally affect living organisms (e.g., fish) in water environments (Jensen, 2003; Randall et al., 2002).

Two experiments were developed during this stage of the investigation. One was done using the CAAM blocks in the presence of nitrifying bacteria but in the absence of fish, and the other one was done with the CAAM blocks in the presence of 10 fish with and without nitrifying bacteria.

In the first case, two tanks were setup: one was the blank without the CAAM blocks and the other was the treatment tank with 28 blocks. For each tank, glucose ($C_6H_{12}O_6$) was added to attain an initial concentration of 100 mg/L, ammonia nitrogen (NH_3-N) was added to obtain an initial concentration of 1 mg/L, 3 mL of mixed liquor were added, and 1mL of each of four different bacteria nutrients ($CaCl_2$, $FeCl_2$, $MgSO_4$ * 7 H_2O and a solution containing KH_2PO_4, K_2HPO_4, NH_4Cl) were added on day one. The mixed liquor was added to introduce nitrifying bacteria to the system and it was sampled from a local wastewater treatment plant in Mayagüez, PR. Each week glucose, ammonia nitrogen and bacteria nutrients were added to the systems. Basic parameters like pH, DO, conductivity, turbidity, temperature, apparent color, alkalinity, hardness, nitrate and total phosphorus were measured for a total of 70 days. Additional parameters such as ammonia concentration and COD were measured.

For the second experiment, three tanks were prepared with the variation of either blocks and/or nitrifying bacteria. The blank tank received the liquor with no blocks, for the other two tanks 28 blocks were added with the variation of the bacteria added. However, neither glucose nor nutrients were added to the systems. Instead, 1.0 gram of fish gourmet was provided once a week. This second test was conducted to verify if the microorganisms in the system could make a difference in nitrification in the presence of the aquatic structures. Only the concentrations of nitrate and ammonia were obtained.

The type of algae and bacteria was monitored at the end of the experiment. A bright field light microscope (up to 100X magnification) equipped with a digital camera was used for this task.

3.3 Water Quality Analysis

Several variables were monitored to evaluate water quality in the tanks during the experiments to obtain basic information on the systems behavior due to the presence of the fish gourmet, the CAAM blocks or a combination of both.

3.3.1 Parameters Measured in the Experiments

Basic water quality parameters included: pH, temperature, alkalinity, conductivity, DO, turbidity, apparent color, hardness, and nitrates. Other parameters were also obtained such as suspended solids (SS) and biomass. All parameters obtained are shown in Table 5 with the corresponding analytical methods used to obtain the measurements. Data acquisition was performed every day for the first experiment, but changed to data collection twice a week to establish a trend on the different water quality parameters. Most experiments were run for up to 38 days.

For some of the experiments other parameters were also tested on the last day of the experiments. Parameters such as total nitrogen, total phosphate, suspended solids, biomass attachment on the CAAM and BOD_5 were measured to compliment data obtained during the curse of the experiments.

Table 5. Methods to acquire Water Quality Data

Water Quality Parameters	*Instrument*	*Method/Brand*
pH	Portable meter	Orion Model 720A
Temperature	Portable meter	Extech Instruments
Alkalinity	Standard Methods (APHA, 1998)	2320B Titration
Conductivity	Portable meter	Oakton CON 6
DO	Portable meter	Extech Instruments
Turbidity	Portable meter	HACH 2100P Turbidimeter
Apparent Color	HACH DR/2010 Spectrophotometer	Method 8025
Hardness	HACH DR/2010 Spectrophotometer	Method 8030
BOD	Standard Methods (APHA, 1998)	5210B 5-Day BOD Test
Total Nitrogen	HACH DR/2010 Spectrophotometer	Method 10071
Ammonia	HACH DR/2010 Spectrophotometer	Method 10023
SS	Standard Methods (APHA, 1998)	2540D Total Suspended Solids
Biomass	Guilbeau et al (2003)	-
Nitrate	HACH DR/2010 Spectrophotometer	Method 8039
Total Phosphorus	HACH DR/2010 Spectrophotometer	Method 8190

3.3.2 Parameters Description and Importance

A brief description of the parameters measured in this study is relevant to a better understanding of the systems behavior. The most important parameters in this study included: pH, alkalinity, conductivity, nitrate, ammonia and total phosphate.

The pH measures the acidity or basicity of a solution based on the hydrogen and hydroxide ions in the system under study. In our case, unfavorable pH conditions, which might be caused by the addition of the CAAM blocks, would negatively impact the aquatic components such as bacteria and fish. In addition, many biochemical reactions are in a function of pH. On the other hand, alkalinity was measured, as it is the main water quality parameter determining the success of enhanced biological nitrification that the current study was intended for with the addition of the CAAM blocks. The changes in nitrate and ammonia concentrations can provide evidence of nitrification, which converts the toxic ammonia species into nitrate species. Phosphate analysis was done to assess the potential of the CAAM blocks on reduction of one of the key elements for algal bloom.

RESULTS AND DISCUSSION

4.1 Introduction

This chapter presents the discussion of the results obtained during this study. The results are compiled by the subset experiments including the selection of fish gourmet amount, CAAM blocks construction and their behavior in the aquatic environment, and effects of the CAAM blocks on water quality.

4.2 Selection of Fish Gourmet Amount

The results on the fish gourmet nutrients are presented to have an overall idea of how the fish gourmet contributed to some of the parameters tested in the systems. Table 6 shows the results on the effects of adding the fish gourmet into water based on the properties inherent to the gourmet. . Data were provided as an average value from the duplicates prepared from section 3.2.1. It is clear that as more fish gourmet is provided the contribution of N and P present in the system can increase, more ions are present which produce a more complex system. The systems considered in this study had an approximate fish gourmet concentration of 0.033 mg/L.

Table 6. Fish Gourmet Properties.

Fish Gourmet Concentration (mg/L)	***TN[1] (mg/L as N)***	***TP[2] (mg/L as PO_4^{-3})***	***Conductivity (μS/cm)***
0.101	2	3.3	20.0
0.507	7	11.9	43.9
1.008	16	18.0	70.5

1 = Total Nitrogen, 2 = Total Phosphorus

On the other hand, the results obtained for the fish gourmet amount selection were critical to determine the amount of fish gourmet that was going to be used for the water quality monitoring experiments with the CAAM blocks. Many different parameters were monitored but only those ones relevant to the objectives of this study will be discussed in detail.

Dissolved oxygen concentrations, monitored on the 4 tanks with different concentrations of gourmet, decreased as the experiment progressed without a significant difference among the tanks. Temperature and hardness values were in the range of 21-25 ^{o}C and 40-60 mg/L as $CaCO_3$, respectively, throughout the experiment and did not show a significant difference between the different amounts of gourmet provided.

The turbidity and apparent color in the system can be used as an indicator of the detrimental conditions induced by the amount of fish gourmet present. As shown in Figure 6 and Figure 7, an increased trend was observed for both turbidity and apparent color as the experiment progressed. The tank that received the highest fish gourmet amount (Tank No.4, 1.0 g) produced the highest values for both parameters. For the tanks that received the least amount of fish gourmet, the two parameters were also increasing with no significant differences among the reactors.

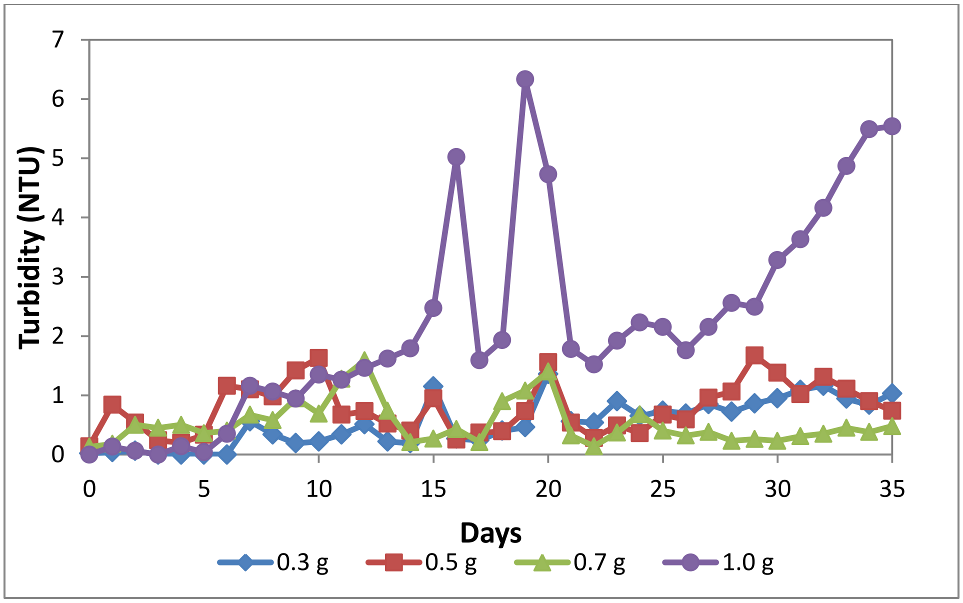

Figure 6. Turbidity Results for Fish Gourmet Experiment.

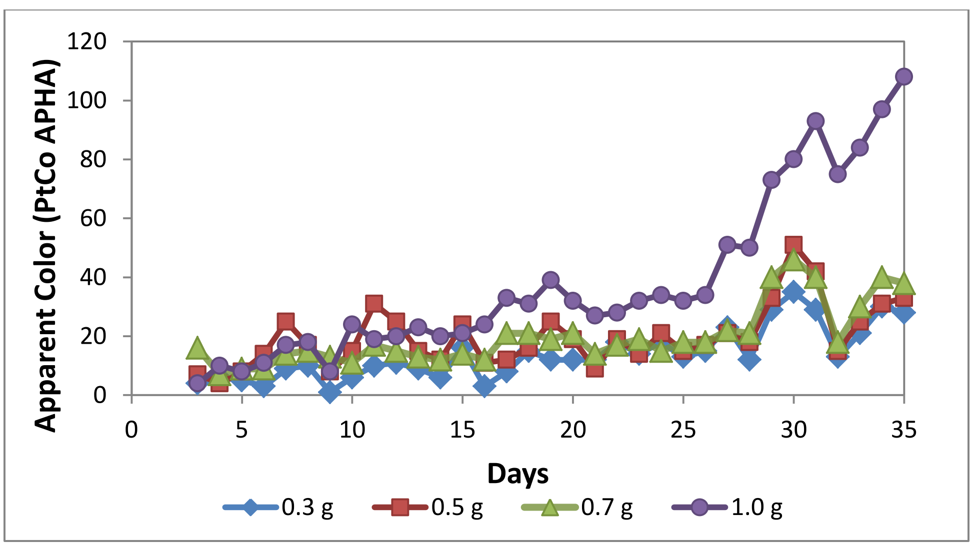

Figure 7. Apparent Color Results for Fish Gourmet Experiment.

Conductivity provides information on the amount of ionic species present in a system. In this experiment, a higher conductivity was observed as more fish gourmet was applied to the tanks as shown in Figure 8. This was attributed to the presence of diverse free ions in the system coming from the fish gourmet, fish excretions and other metabolic activities. Possible ions contributing to the increment in conductivity can be attributed to the nutrients present in the fish gourmet such as nitrogen and phosphorus content. From the fish gourmet analysis, results confirmed the presence of both species.

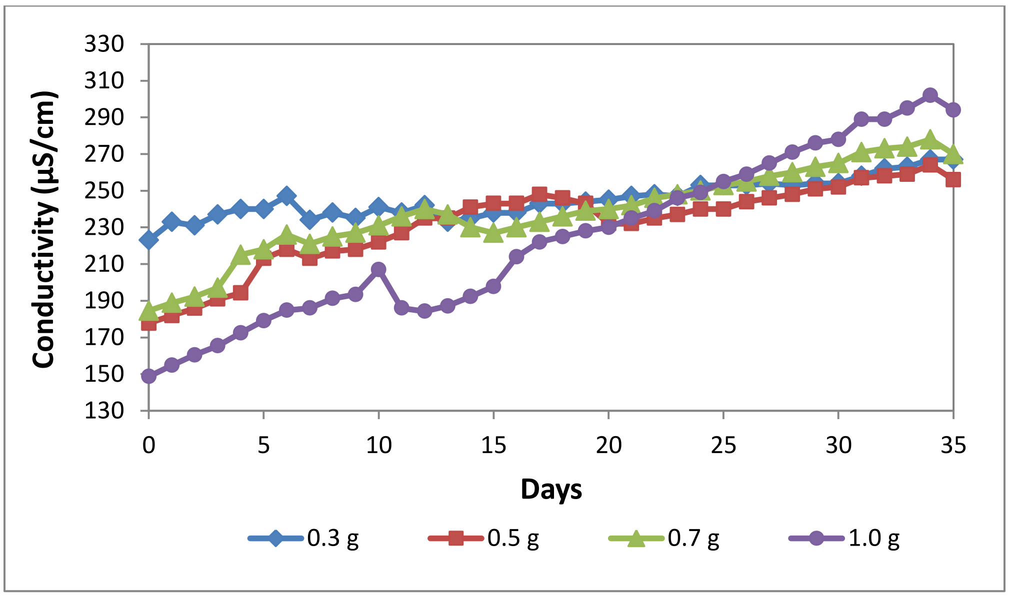

Figure 8. Conductivity Behavior Observed for Fish Gourmet Experiment.

The results obtained for pH and alkalinity are presented in Figure 9 and Figure 10. Similarly to the turbidity results, the change in pH in the tank No. 4 was the most dramatic. The pH value dropped to acidic conditions close to 6 for the system which received the highest amount of fish gourmet. The alkalinity trend also showed a drop in concentration for the tank No. 4. Again, it was observed that values were lower as more fish gourmet was added. These results imply that the system was not capable of buffering itself, since alkalinity is related to the carbonate and bicarbonate equilibrium with hydrogen and hydroxide. Basically, the hydrogen species dominated the system toward an acidic environment.

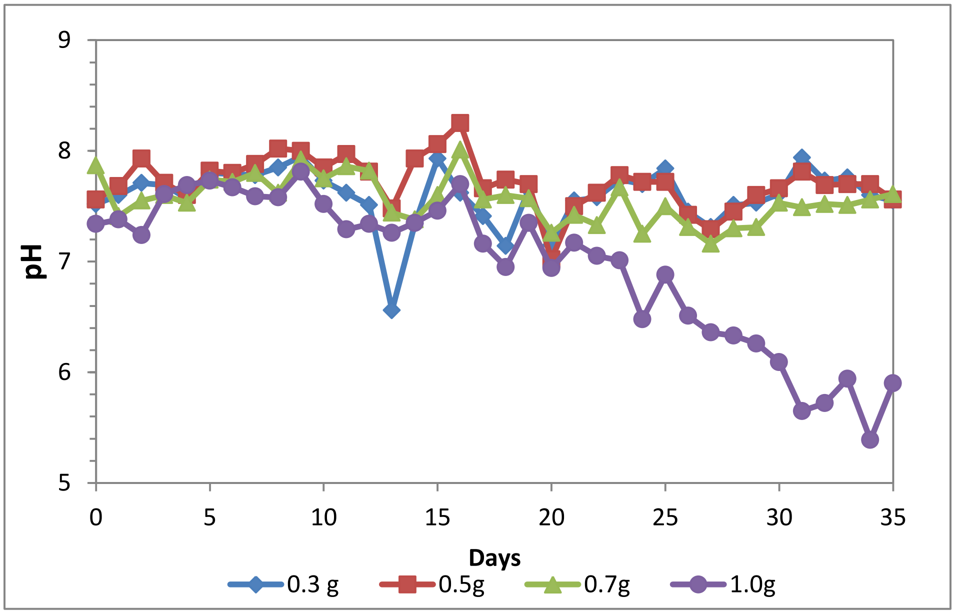

Figure 9. Results for pH as a Function of Fish Gourmet Amount.

Nitrate concentrations started to increase after approximately day 25 for all systems. However, it increased earlier and to greater extent in the tank No. 4, which received 1.0g of fish gourmet, as shown in Figure 11. A sudden increase of nitrate concentration can be attributed to ammonia nitrogen excreted by fish. It is likely that nitrification of ammonia nitrogen to nitrate nitrogen occurred in the later part of the experiment.

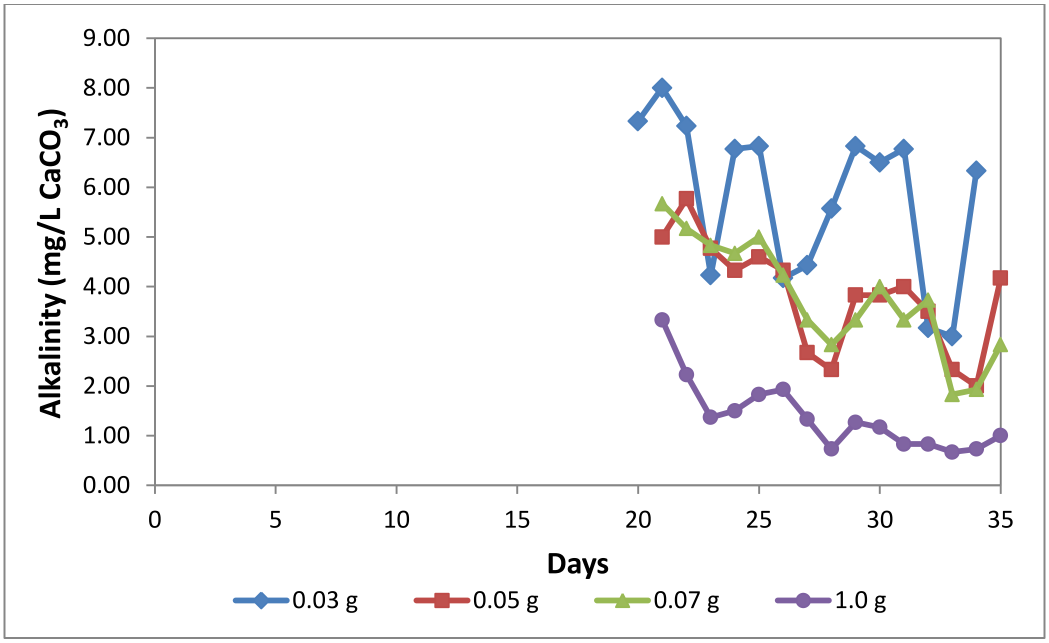

Figure 10. Results for Alkalinity as a Function of Fish Gourmet.

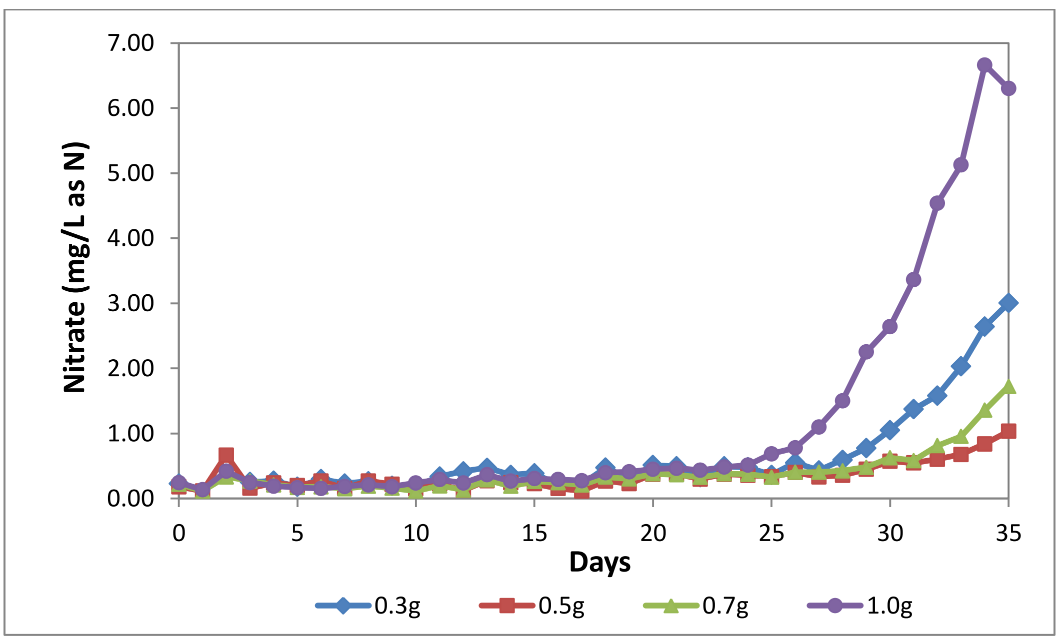

Figure 11. Nitrate Amount Increased as Time Passed for all Tanks.

Therefore, based on the water quality analysis results, the fish gourmet amount of 1.0 g was selected for the remaining experiments where the aquatic structures were used to verify water quality enhancement in the presence of the CAAM blocks. Some fish mortality was observed in tank No. 4 since day 17 of the experiment probably due to detriment conditions in the water provoked by the excess of fish gourmet in the system including high ammonia concentration. As more fish gourmet was added to the system more excretion was going to be happening. Visual comparison of the tanks at day 35 showed that more greenish water was produced in the tank No. 4, as shown in Figure 12.

Figure 12. Visual Appreciation of Tanks at the End of the Experiment.

4.3 CAAM Blocks Preparation

This experiment was conducted to decide how CAAM blocks were going to be made of the different compositions of cement, fly ash, and bottom ash. Since maximizing the amount of CCBs was important for this study, the combination of fly ash and bottom ash without cement was tested. However, the results were not desirable for further experiments as the block cohesion was not sustained when introduced in water. In this regard, focus was given to the mixtures of cement, fly and bottom ash combinations. In this case, cement and fly ash acted as the cementicious materials and bottom ash as the aggregate in the mixture.

Several mixtures, shown in Table 7, were prepared and tested for surface shrinkage and pH changes. The results were based on cracks formation on the blocks surface every 7 days, where the sign (+1) was assigned to the blocks with no cracks and (-1) to the ones with cracks when one or more were observed.

Table 7. Mixtures Results based on the Amount of Bottom Ash Added.

	Mixture Composition			***Results***		
	Cement (g)	***Fly Ash (g)***	***Bottom Ash (g)***	***Week 1***	***Week2***	***Week 3***
Batch #1	200	200	50	-1	-1	-1
Batch #2	200	200	75	+1	+1	-1
Batch #3	200	200	100	+1	+1	+1
Batch #4	200	200	200	+1	+1	+1

On the other hand, Figure 13 shows the pH results obtained during the surface shrinkage test performed for the mixtures above named Batch #1 through #4. The pH was measured three days after adding one block to 100 mL of water and replicates were obtained for 4 weeks. Results showed that pH changed dramatically from a neutral pH value to an alkaline value for each replicate. The difference in pH value was not evident between mixtures since all showed average values between 10.71 and 12.20.

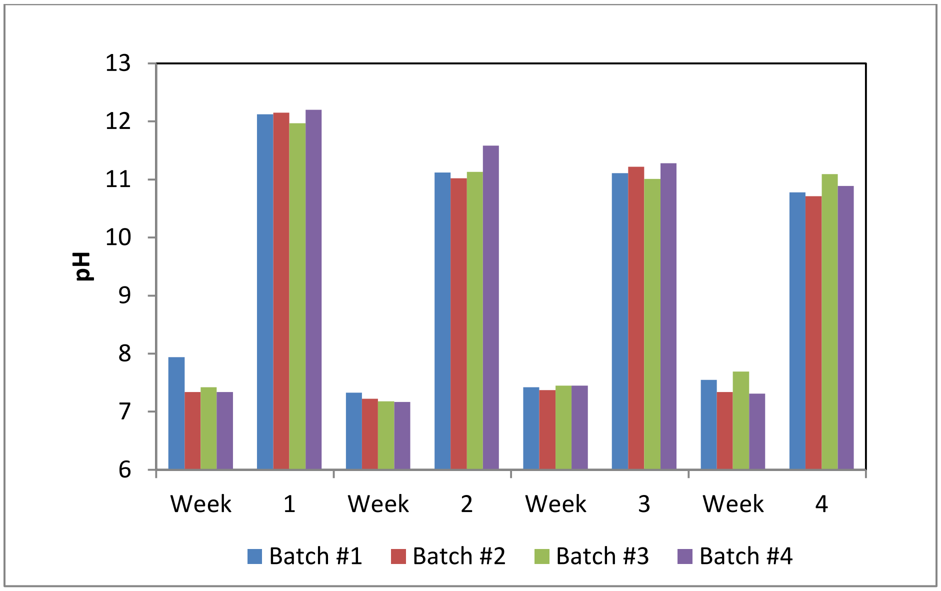

Figure 13. Results for pH Measurements Obtained for the Mixtures.

Based in both results, the pH changes (Figure 13) and surface shrinkage (Table 7), the mixing ratio of 1:1:1 (cement, fly ash, bottom ash) was chosen to make the CAAM blocks used for water quality enhancement experiments since Batch #4 provided the maximum amount of CCBs recovery. An additional test was performed to complement the information obtained from the above experiment. A standard test for compressive strength was performed to evaluate the physical strength of the CAAM blocks. Figure 14 shows the specimens prepared and tested in accordance with ASTM C109.

Figure 14. Compressive Test Specimens with 33% Bottom Ash.

The compressive strength test helped to choose the best mixing ratio for the CAAM blocks. The resistance test was performed by increasing the amount of bottom ash in the mixtures by approximately 16% to acquire a strength curve. Figure 15 shows the results for the different curing methods (dry and wet, using ASTM C192 for the later) versus the bottom ash content in the mixtures prepared for 7 and 28 days curing. Curing under wet conditions allowed the CAAM blocks to acquire a higher strength compared with dry conditions results. The addition of $CaCO_3$ prevented the carbonation of the mixture prepared, where carbon dioxide from the air can penetrate the structure and reacts with the calcium hydroxide, making the calcium ions to leach from the structure due to equilibrium processes and therefore loosing strength. In the curve for the wet curing, the optimum strength was obtained for the substitution of 33% of bottom ash as the fine aggregate. The goal of performing this test was to establish CAAM blocks intended use for non-structural purposes.

Curing of the species used in this study was performed under dry conditions with a relative humidity between 70 and 80% due to time constrains. The compressive strength values obtained for this technique were around 1200 psi. Despite the fact the samples were cured under dry conditions the strength obtained for this conditions allowed the use of the CAAM blocks toward a non-structural usage since normal concrete compressive test requirements vary from 2500 to 4000 psi for residential or commercial use, respectively. Even though, curing in wet conditions using ASTM C192 specifications demonstrated its capability of sustaining compressive strength of approximately 3000 psi based in a two replicates test. Based on the results, the mixture (1:1:1) made with more bottom ash addition (i.e., 200 g vs. 100 g) was selected so that the goals of the study could be met: maximum utilization of CCBs and accountable CAAM blocks to enhance water quality.

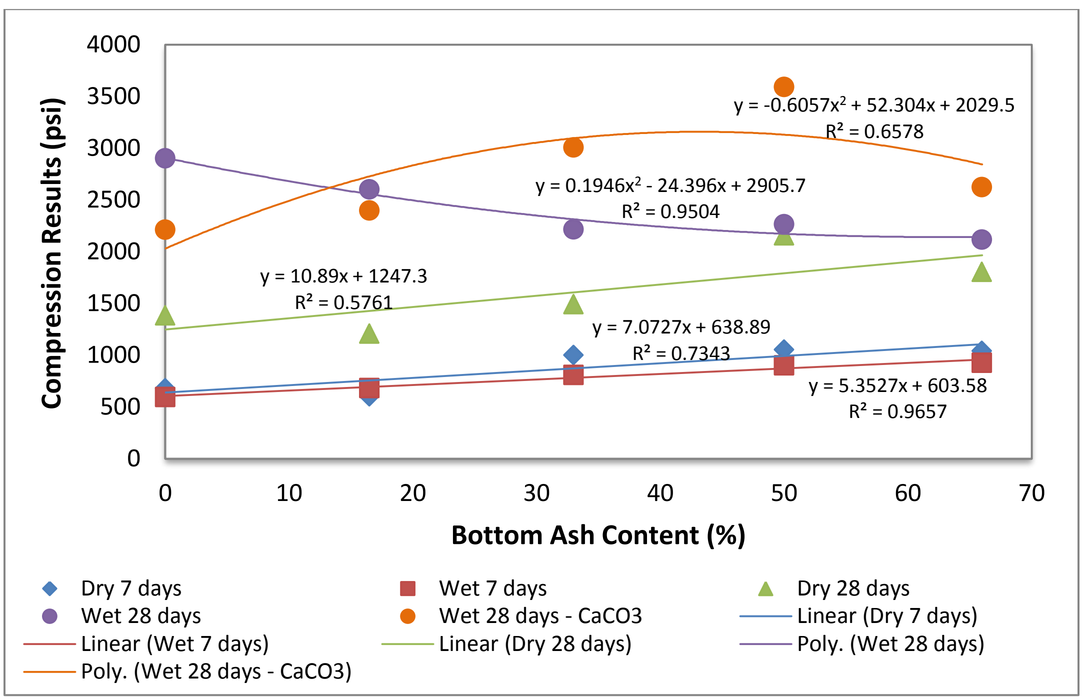

Figure 15. Compression Test Results based on the Addition of Bottom Ash.

4.4 Blocks Experiments

Different experiments were performed to test water quality enhancement due to the presence of the CAAM blocks. Results for the various parameters measured are presented to establish the blocks suitability on water quality enhancement capabilities.

4.4.1 CAAM Blocks for Water Quality Enhancement

The tanks were set up for the experiment of water quality enhancement in the same manner as described in the fish gourmet amount selection (section 3.2.1). The only difference in this set of experiments was the addition of the CAAM blocks. The fish gourmet was added at a rate of 1.0 gram per day, which had been decided from the previous experiment. Two tanks were prepared to acquire water quality data: one had 7 CAAM blocks and the other had 28.

In the experiment for the selection of the fish gourmet amount, some water quality parameters (temperature and hardness) did not change during the experiment, nor were different among the systems. In this regard, these parameters were not measured during this experiment. The result for the pH variation is presented in Figure 16. The pH did not decrease for the two systems where the CAAM blocks were present. Both systems had a very similar pattern, but the system with 28 CAAM blocks still showed a higher value of pH than the system with 7 CAAM blocks. We have seen that the blocks in water provided a higher pH value.

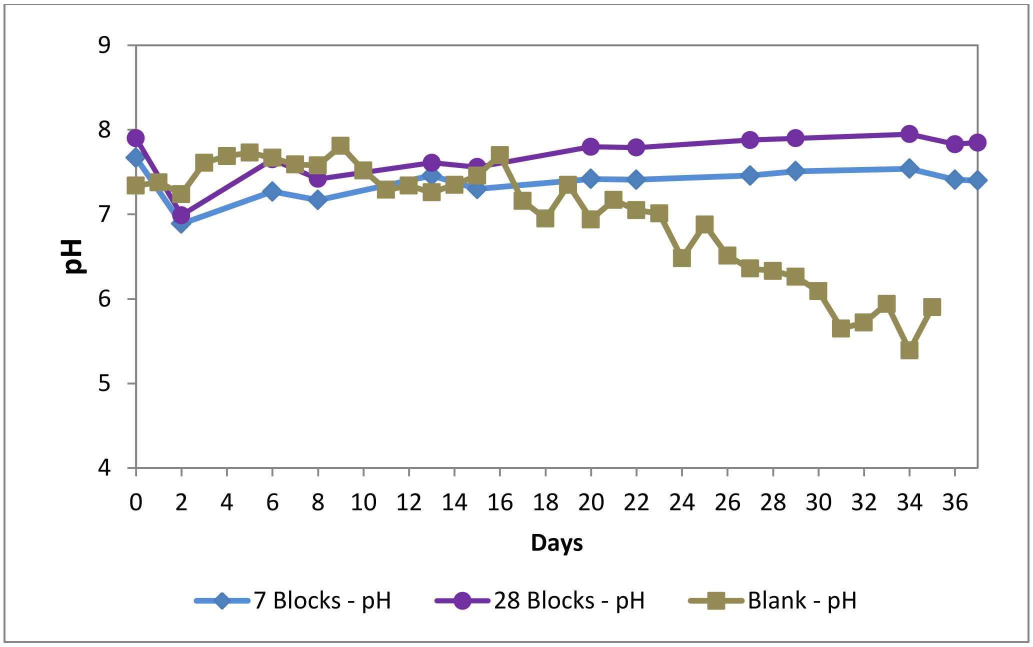

Figure 16. Results for pH with CAAM Blocks in the Systems.

Figure 17 shows the variation in alkalinity for the water quality enhancement experiment. In the case of alkalinity, there was a dramatic increase for the 7 and 28 CAAM blocks systems compared to the system without blocks. The tank with 7 CAAM blocks ended with similar values of alkalinity as for day 0. On the other hand, the tank with more blocks showed a significant difference after the fourth week of the experiment. The reason for this could be a buffering effect of the CAAM blocks combined with the amount of blocks in the system which would contribute with more ions to the system, especially carbonate species. This also helped keeping the systems with similar pH values.

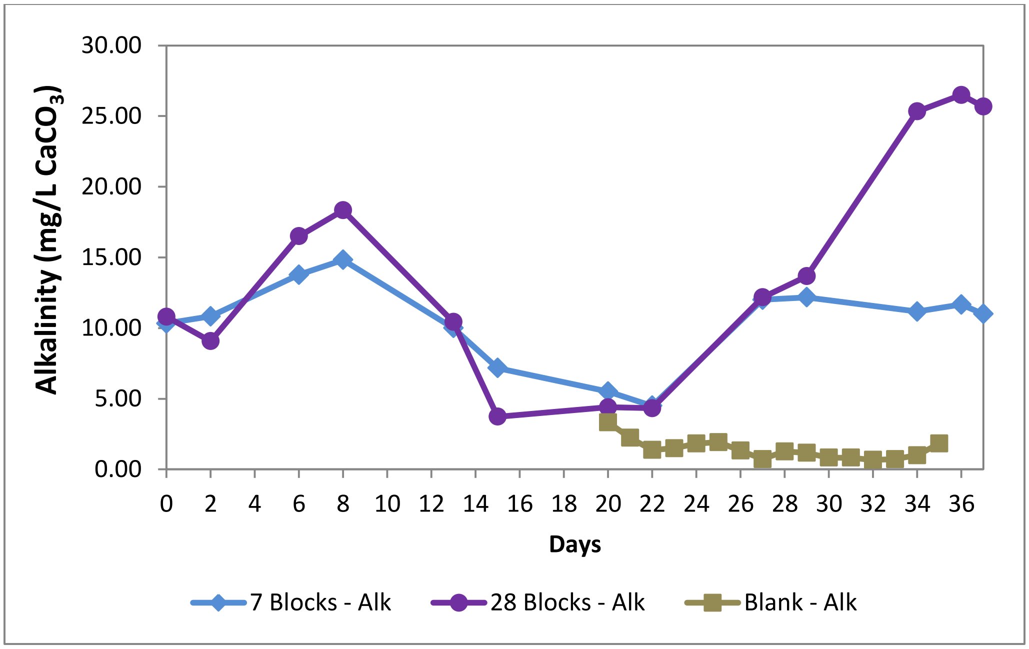

Figure 17. Results for Alkalinity with CAAM Blocks in the Systems.

Figure 18 shows the results for turbidity while Figure 19 shows the results for the apparent color measurements. Despite the higher values of turbidity and apparent color in the presence of the CAAM blocks in the early stage, the systems held the values low during the experiment. Overall, a better turbidity and apparent color measurements were found in the tank with more CAAM blocks. There were subtle changes but tank No.4 predominantly showed better results.

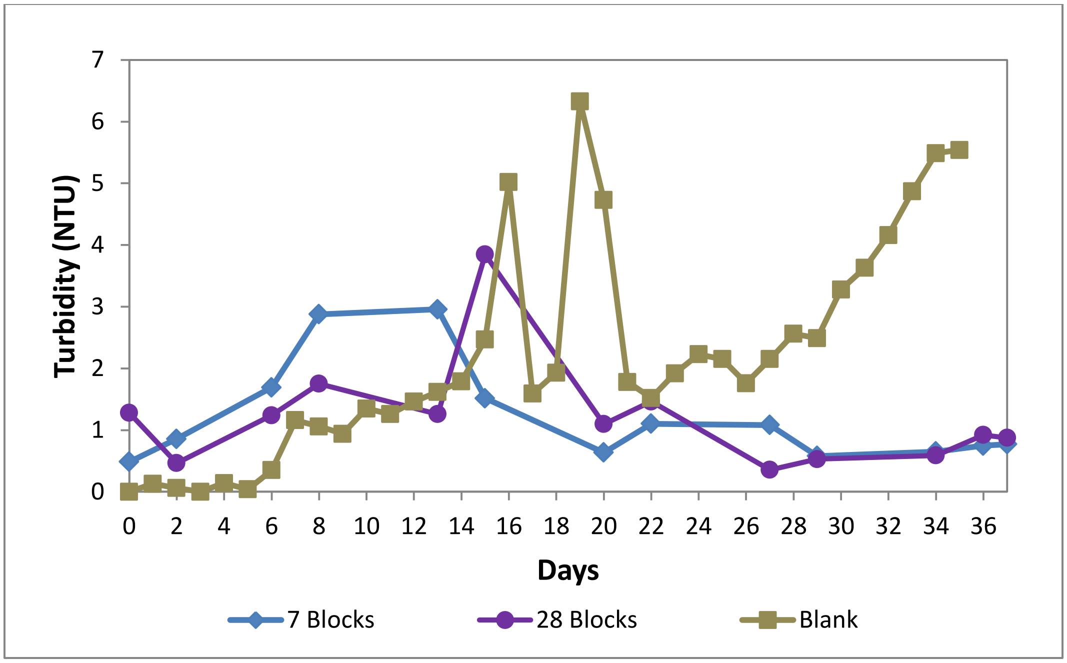

Figure 18. Turbidity Color Results in Tanks with Blocks.

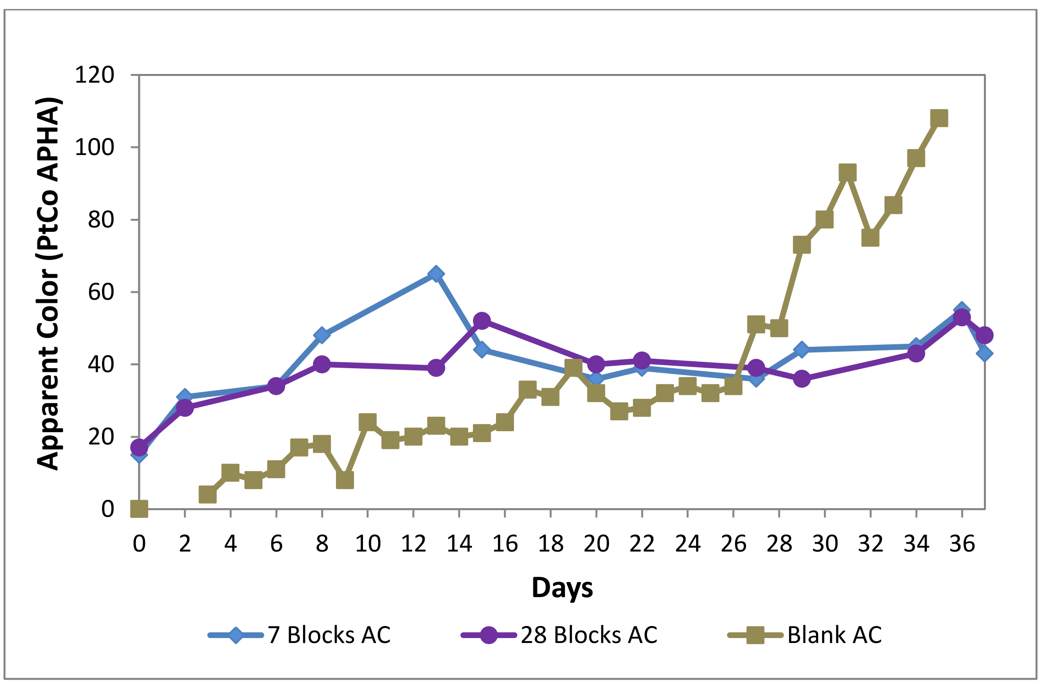

Figure 19. Apparent Color Results in Tanks with Blocks.

Suspended solids and biomass experiments were performed at the end of the experiments to verify how the results agreed with the decreased values of turbidity and apparent color. The tests were made by filtration of the tank water for suspended solids and by cleaning the CAAM blocks using hydrogen peroxide solution for biomass deposited on the CAAM blocks (Guilbeau et al, 2003). Two replicates were performed for suspended solids and five blocks from each tank were cleaned for biomass measurements. The results were in agreement between each other with the presence of the CAAM blocks (Table 8). For the tank No. 4 which had more CAAM blocks (28), less suspended solids were measured in the water, but more biomass was found deposited on the blocks. These findings were in line with the results of turbidity and apparent color analysis. Although not studied in detail, the biomass grown on the blocks is assumed to be algae. The identification of the algae was performed during the nitrification experiment; the results are shown later in section 4.4.3.

Table 8. Suspended Solids and Biomass Results obtained in Blocks Experiment.

Parameter	***Tank 1***	***Tank 4***
Suspended Solid (mg/L)	4.3	2.3
Average Biomass (g/cm^2)	0.03	0.10

Nitrate results showed that the tank No. 4 had a tendency of getting higher results at a faster rate, as shown in Figure 20. Nitrification, which is the conversion of ammonia species into nitrate, occurred quicker in the tank with 28 CAAM blocks since higher nitrate concentration was obtained. On the other hand, the tank with 7 CAAM blocks did not make a difference in nitrification, compared to the blank system. This is indicated by the difference observed after day 20 when nitrate results started to be higher for the tank with more blocks (Tank No. 4).

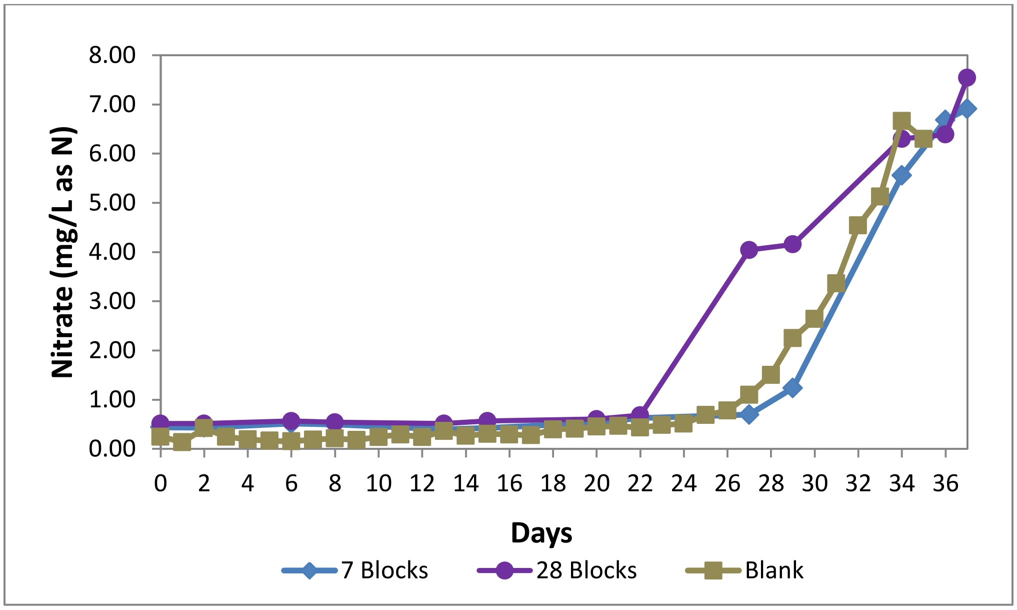

Figure 20. Nitrate Measurements in Tank 1 (7 blocks) and Tank 4 (28 blocks).

Total nitrogen in the systems was measured at the end of the experiment to complement the nitrate information obtained. Both tanks had a total nitrogen concentration of 15 mg/L as N. Even though at the end we observed a similar amount of nitrate in the systems, the tank with 28 CAAM blocks still showed a better ability to convert the ammonia species coming from fish excretions into nitrate.

The total phosphorus concentrations were very similar with 4.90 and 5.40 mg/L PO_4^{-3}, respectively for the 7 and 28 CAAM blocks tanks. The phosphate information obtained was measured during the last day of the experiment.

BOD_5 results were very different between the two systems: the 7 blocks resulted in 4.6 mg/L BOD_5 while the tank with 28 blocks had 21.7 mg/L. The higher value obtained for the tank No. 4 indicates that there was a high amount of organic matter, presumably nitrifying bacteria (not algae) in the system. Algae growth was not observed in the tank with 28 blocks from a visual perspective. BOD_5 data provided important information since it was used as an indicator to minimize organic loading to maintain desirable levels of DO in water. The presence of nitrifying bacteria is also an indicator of lower DO values since they use oxygen for their metabolic processes. DO concentrations in both tanks, with CAAM blocks, were lower than the concentrations measured in the blank system. However, the DO concentrations were above 6.0 mg/L so as to maintain the system in an aerobic environment.

4.4.2 Nitrate and Phosphate in CAAM Systems

A focused study was performed for nitrate and phosphate reduction in the presence of CAAM blocks since total phosphate results were only collected the last day of the analysis for water quality enhancement experiment. Two set of experiments were performed: one with the presence of blocks with no fish and another one with blocks and fish to see any background differences within more realistic aquatic environment.

Many parameters like pH, alkalinity, conductivity and hardness showed patterns similar to those obtained in section 4.4.1. The values for pH stayed between 6.5 and 8.5 and the alkalinity values increased to near 18 mg/L as $CaCO_3$. The conductivity increased as more structures were present in the systems and hardness values were higher for the system with more blocks when no fish were added.

The results on nitrate concentrations are shown in Figure 21. It can be observed that nitrate concentrations were very high when the fish were present in the blocks systems. Nitrate in the systems without fish showed no noticeable changes, which indicate that the amount of blocks was not an important variable if there was no remediation necessary; concentration values only got as high as 4-5 mg/L as N. On the other hand, when fish were added a difference can be noticed both in the amount of nitrate present in the system and the link this had to the amount of blocks present. Although the nitrate concentrations were higher in the presence of fish, which is expected due to their metabolic processes and the fish gourmet added to the systems, it is observed that the higher amount of block in the system allowed it to regulate the amount of nitrate to around 30-40 mg/L as N after day 16 of the experiment.

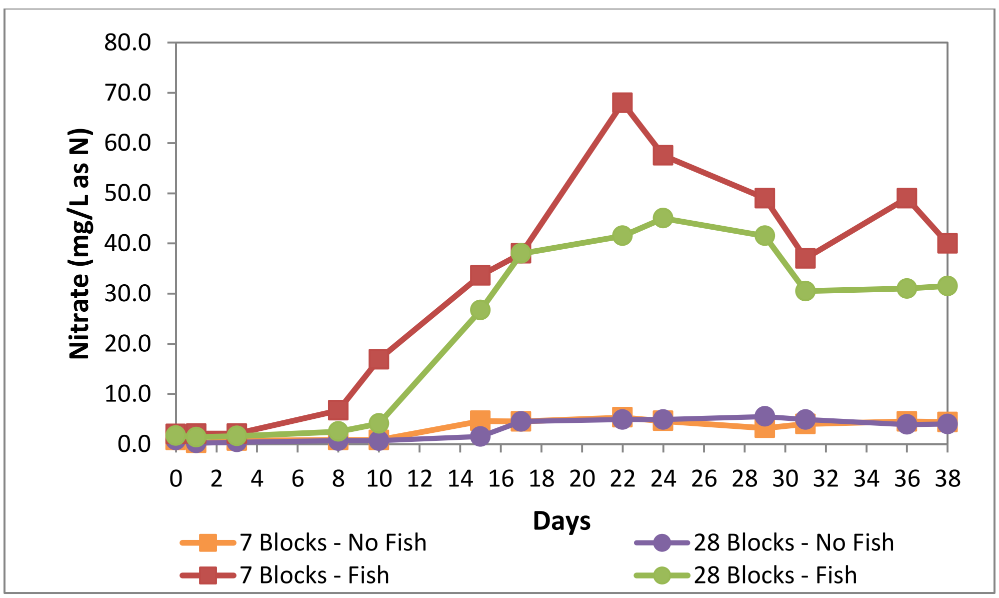

Figure 21. Nitrate Results in the Presence of Blocks with Fish Variation.

The data obtained for phosphate was very similar to the one obtained for nitrate in the sense of the observed increments in the system based on the fish presence. It can be seen in Figure 22 that when fish were not present in the system, phosphate concentrations were only about 40 mg/L as PO_4^{-3}. However, values went up to around 200 mg/L as PO_4^{-3} when fish were added to the system. In this case, there was no major difference in the results based on the amount of blocks present. The phosphate concentrations stayed very much alike until day 28 was reached. The increment could be attributed to the fish presence and their metabolic processes since this was the only parameter different in the systems.

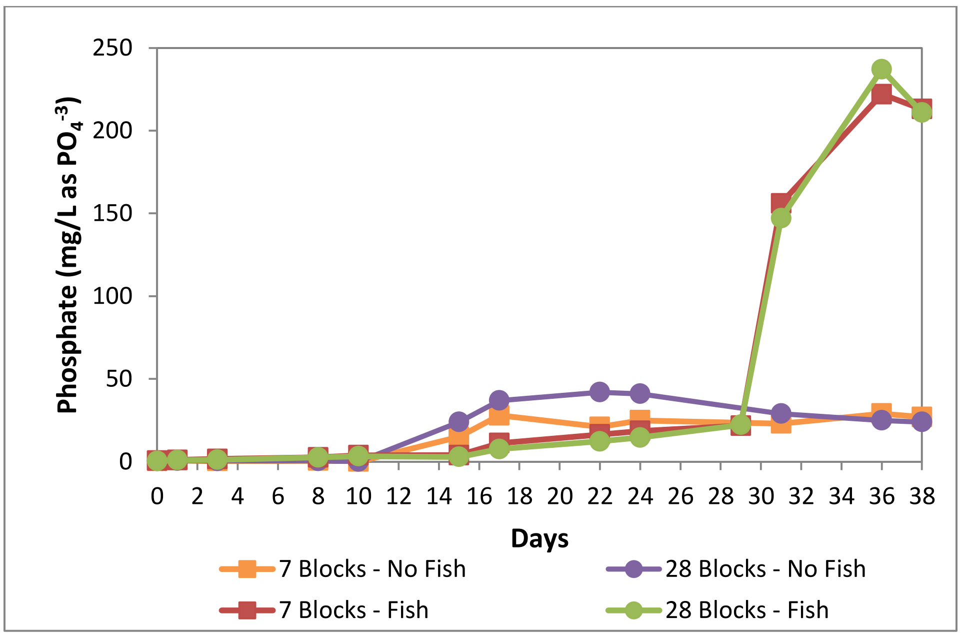

Figure 22. Phosphate Results using Blocks with Fish Variation.

Overall, the presence of CAAM blocks helped keeping the nitrate concentration leveled at approximately 35 mg/L as N for the tank with the highest amount of CAAM blocks. The phosphate results were not conclusive in this experiment. It seemed like the amount of CAAM blocks in the system did not affected the fate of the phosphate species under the established conditions.

4.4.3 Nitrification in a CAAM Blocks System

In section 4.4.1, where CAAM blocks were tested for water quality enhancement, an enhanced nitrification was observed with no algae growth. The nitrification experiments were performed in two separate trials as described in section 3.2.5. One experiment was performed without fish and the other one with fish in the presence of CAAM blocks.

For the experiment without fish, the tanks were set up as described in the Experimental Method (Section 3.2.4), in this case nitrifying bacteria were added to the systems under the same conditions, with 28 CAAM blocks and without the blocks. This set of experiments was performed to verify the nitrification enhancement in the system by the CAAM blocks for a total of 70 days. Water samples were analyzed once a week for the basic water quality parameters obtained for the water enhancement experiment. Additional parameters, COD and ammonia, were tested. Nitrifying bacteria was added to verify how ammonia nitrification could be improved in combination with the CAAM blocks minimizing the ammonia toxicity to fish and microorganisms in the system.

The results on the nitrification enhancement experiment with fish are presented in the following paragraphs. The presence of CAAM blocks in the system provided higher pH and alkalinity values due to the alkaline properties of the CAAM blocks as shown in Figure 23 and Figure 24. The system with no blocks had a significant drop in pH values, as observed in the previous experiment for the fish gourmet amount selection where no blocks were introduced in the systems. Figure 25 shows that the alkalinity of the system with 28 blocks increased significantly from approximately 8 mg/L as $CaCO_3$ up to 14 mg/L as $CaCO_3$. This represents a 43 % increment due to the addition of the blocks. On the other hand, the system with no blocks experienced a decrease in the alkalinity from 8 to 10 mg/L as $CaCO_3$.

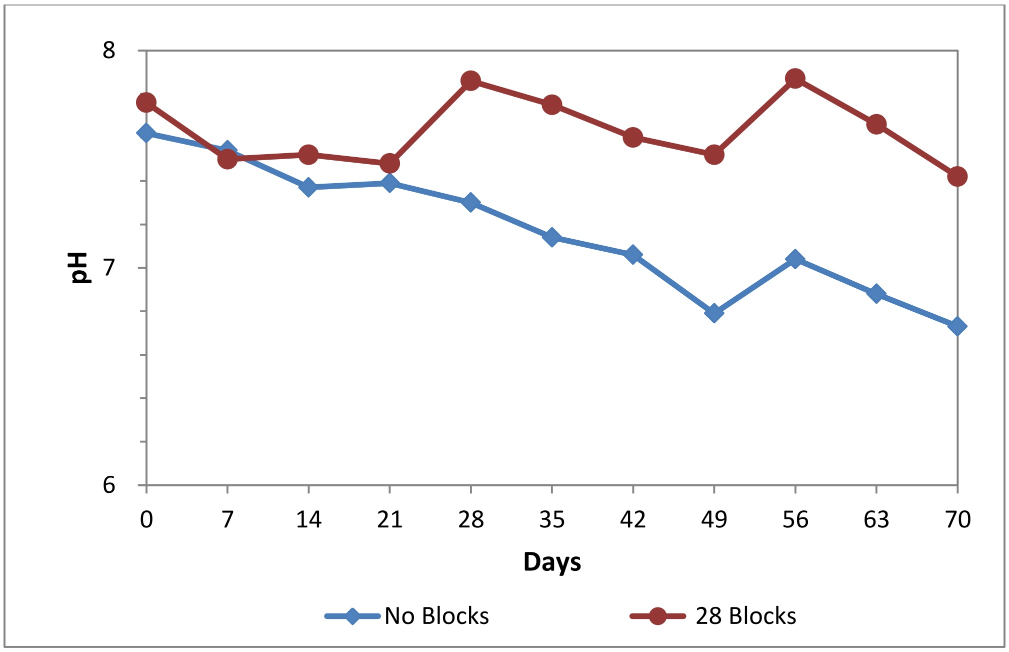

Figure 23. Results for pH in Nitrification Systems.

The tank with 28 CAAM blocks showed an increase in conductivity after 7 days (from 307 to 1018 µS/cm), however for the rest of the days the conductivity stayed more or less constant in the range of 1100~1200 µS/cm , as observed in Figure 25. In the experiment for the fish gourmet amount, the conductivity changes were attributed to the nitrogen and phosphorus ions in the system as well as metabolic activities. In this case, we attribute the increase in conductivity to the presence of CAAM blocks since the same fish gourmet was applied for both systems.

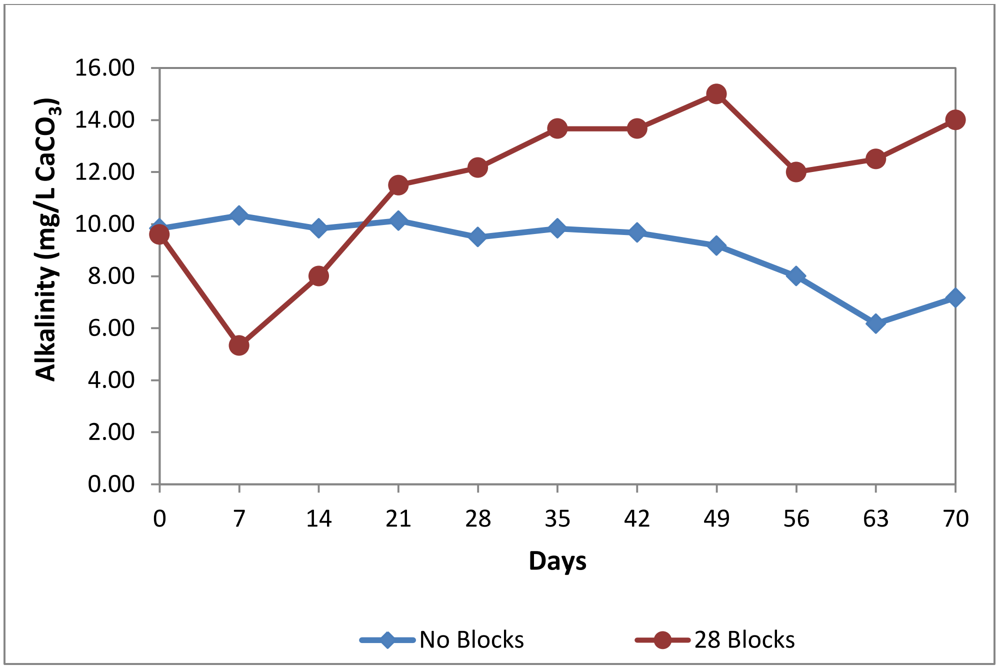

Figure 24. Results for Alkalinity in Nitrification Systems.

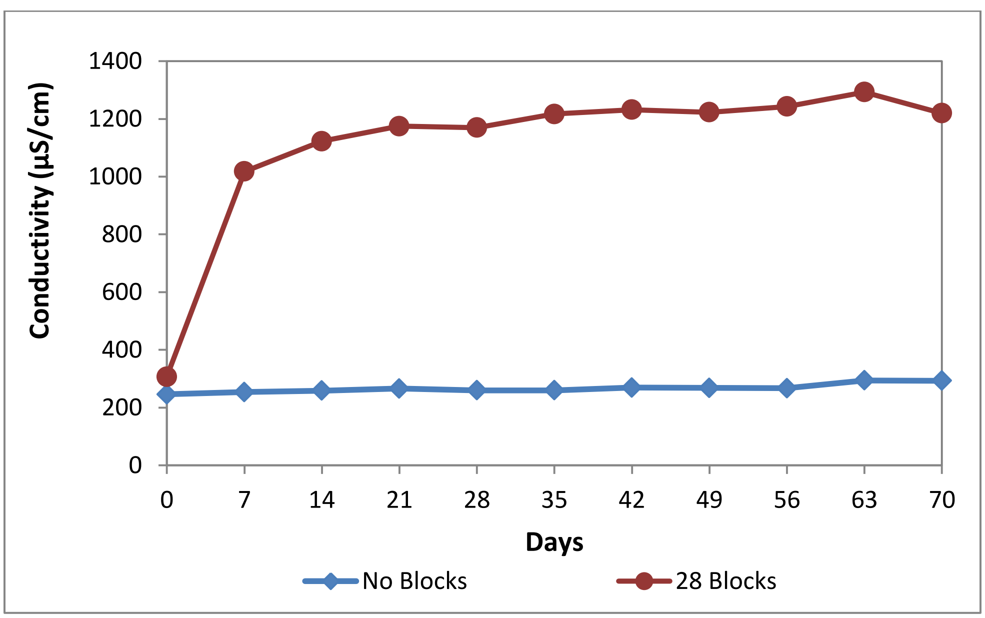

Figure 25. Conductivity Increased in Tank with CAAM Blocks.

Total phosphate results obtained are shown in Figure 26. The presence of blocks in this system, where bacteria were also added, showed that phosphate amount in the system decreased with the blocks. At the end of the 70 days total phosphate for the system with no blocks resulted in values between 5 and 6 mg/L as PO_4^{-3}, while adding 28 CAAM blocks generated a total amount of phosphate of approximately 1 mg/L as PO_4^{-3}. This represents an 80 % decrease when compared with the system with no blocks.

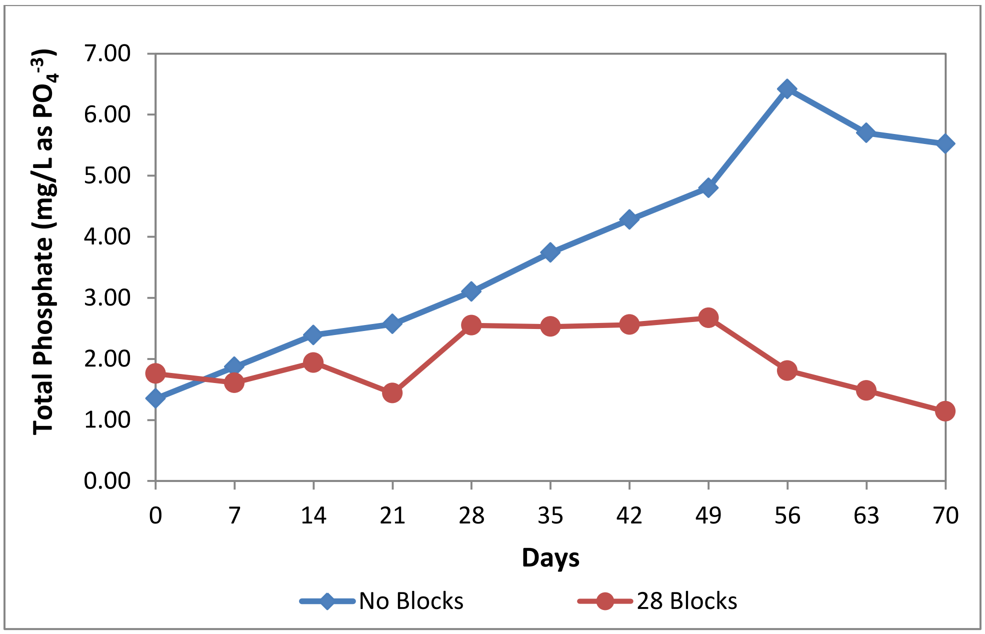

Figure 26. Phosphate Results for Blocks Presence with Bacteria.

For ammonia and nitrate values, the system with 28 CAAM blocks showed an enhanced ammonia nitrification leading to greater nitrate concentration but lower ammonia concentration in the system as shown in Figure 27 and Figure 28. The difference was more evident in the first half of the experiment approximately during the first 35 days.

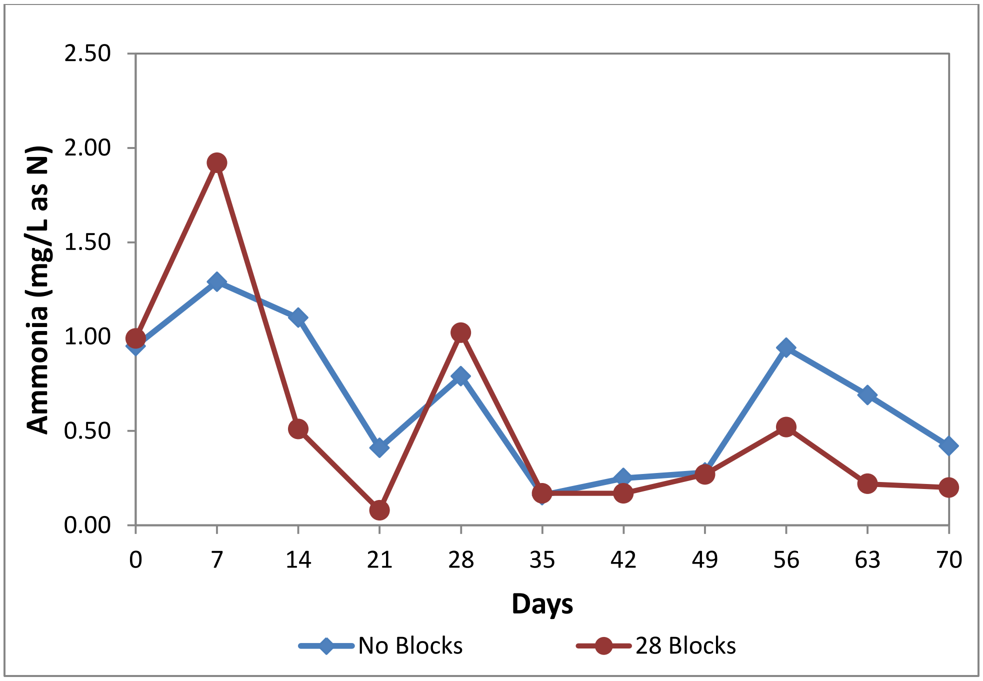

Figure 27. Ammonia Results for Nitrification Experiment.

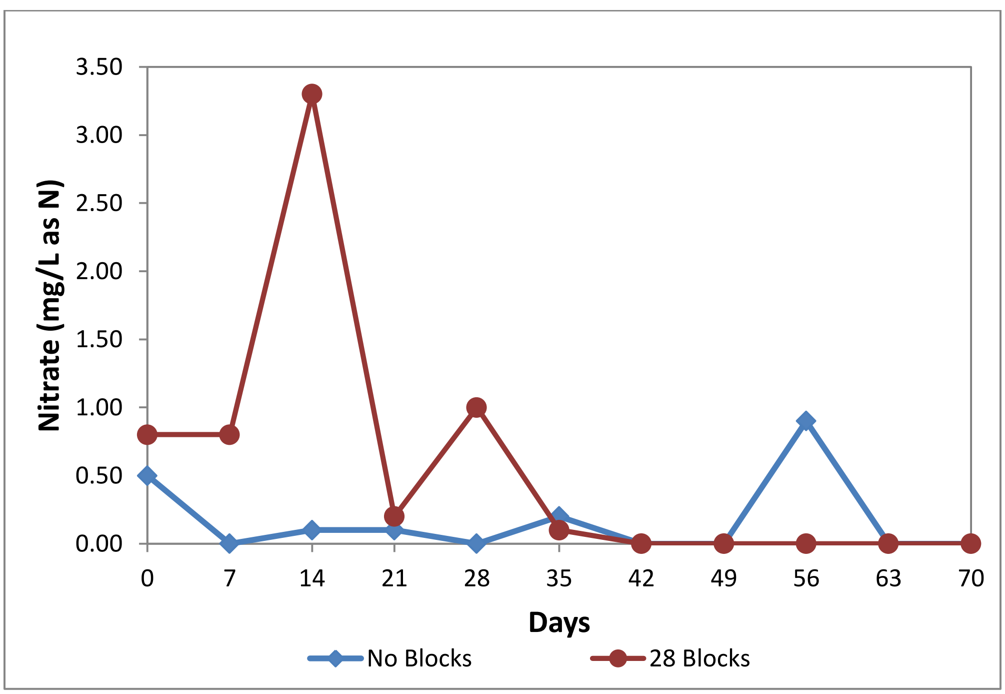

Figure 28. Nitrate Results for Nitrification Experiment.

On the other hand, hardness values dropped to nearly zero indicating that the calcium ions present were transformed and/or incorporated into other chemical species in the system. The nitrifying bacteria addition could also be responsible for this decrease since they produce CO_2 as byproduct for their metabolic activities and CO_2 stripping has been used for hardness removal (Kim et al., 2003). Phosphate concentrations showed a decreased trend in the tank with the CAAM blocks due to sorption capacity of CAAMs (Chen et al., 2007). As usual, turbidity and apparent color values were lower for the tank with the CAAM blocks due to the surface area provided for algae to attach. More biomass deposit on the bottom of the system was noticed in the presence of the CAAM blocks (Figure 29). Underlying biochemical mechanisms for this phenomenon is currently unknown.

Figure 29. Visual Appearance of Tanks in the Last Day of Experiment.

This experiment provided information on the CAAM behavior under bacterial presence, but the results were not clear enough to understand nitrification enhancement by the CAAM blocks. An additional experiment was performed where fish were added to see how the system behaved under their presence. Ammonia and nitrate measurements were obtained under the same experimental conditions but with the addition of nitrifying bacteria. One tank was set up with no blocks and the other one with 28 CAAM blocks. A total of 10 fish were added to each tank as shown in Figure 30. Fish gourmet was provided in a daily basis at a rate of 1.0 g per day. A blank with no nitrifiers was also analyzed in this experiment.

Figure 30. Nitrification Experiment with Added Fish.

The addition of nitrifying bacteria helped the conversion of ammonia to nitrate in the system (Figure 31.). Similar to the results previously presented, an enhanced nitrification was apparent at the beginning of the experiment (during the first 18 days), having earlier conversion of ammonia to nitrate by nitrifying bacteria in the presence of the CAAM blocks. The blank, where nitrifiers were added with no blocks, showed a similar pattern, however after day 28 of the experiment an increment in ammonia was observed. When the CAAM blocks were not added to the tank, the system was incapable of keeping the ammonia values down. Bacteria presence was not the key in diminishing the ammonia in the system even when an improvement in nitrification was noticeable when they were not added. Most likely, it seems that this effect could be attributed to the CAAM. Overall, the presence of the blocks helped keep the ammonia levels low throughout the experiment.

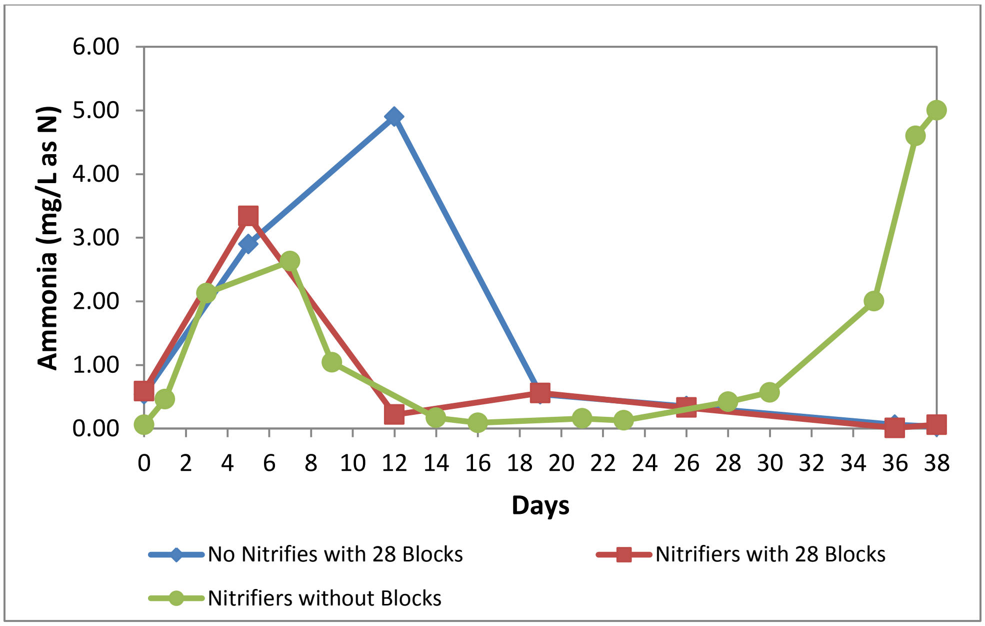

Figure 31. Ammonia Results for Bacterial Addition with CAAM Blocks.

Nitrate concentrations measured from the current study are shown in Figure 32. The data indicated that the presence of the blocks provided a similar amount of nitrate species in the system compared to the tank with no blocks. The presence of the bacteria helped increased the rate at which the ammonia conversion was obtained.

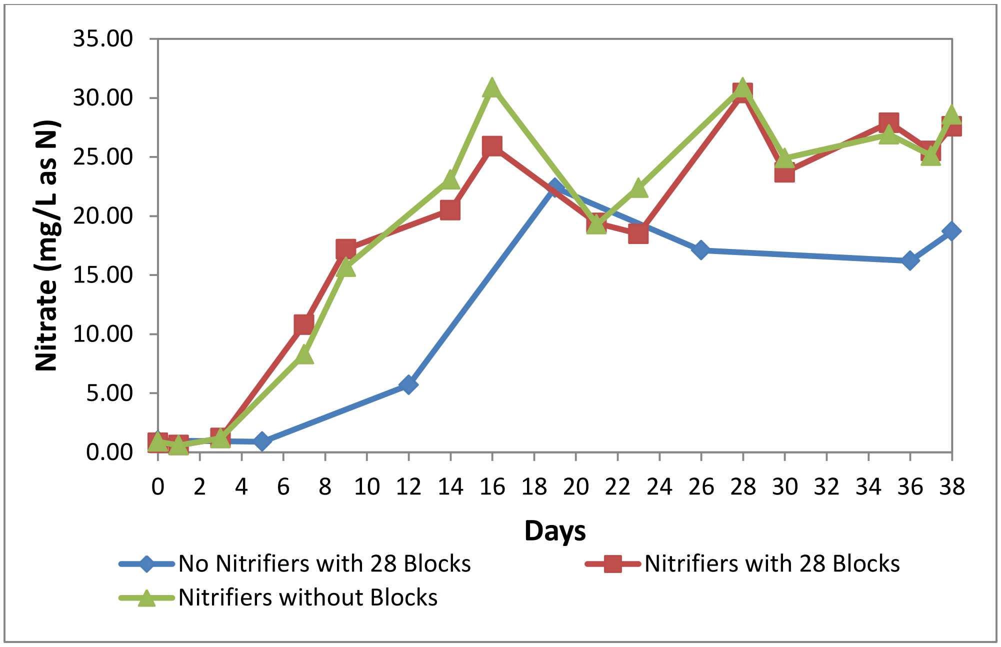

Figure 32. Nitrate results for bacterial addition with CAAM Blocks.

The identification of algae species present in the systems was performed at the end of this nitrification experiment with fish (Figure 30). Algae identification was performed the last day of this experiment through a bright field light microscope. Figure 33 shows two images obtained from the tanks: Figure 33 (a) shows algae formation for the tank without, while Figure 33 (b) shows the effect with 28 CAAM blocks. Algae formation on the top of the tank walls was prominent in both systems. Samples were collected and prepared in glass films for microscope inspection. The images show resemblance between the species found in the tanks and cyanobacteria.

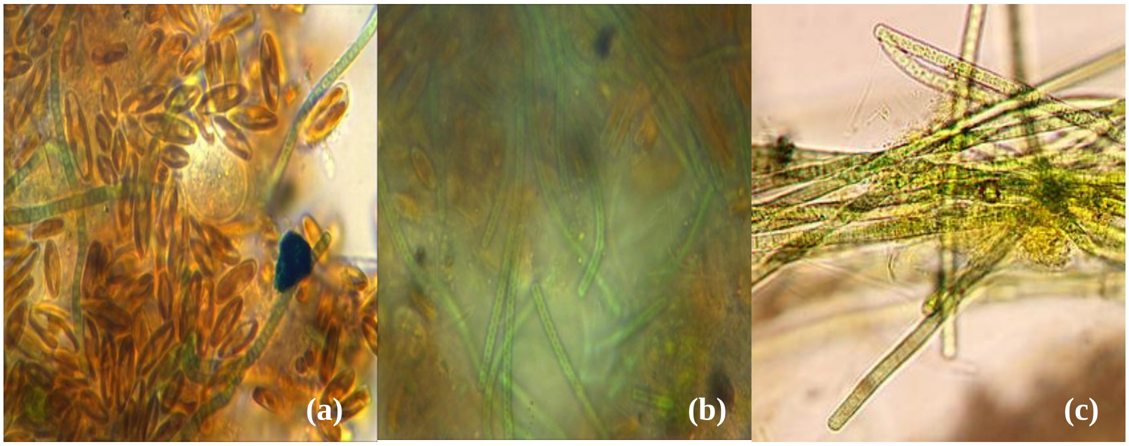

Figure 33. Algae Identification Images: (a) Tank with No CAAM Blocks, (b) Tank with 28 CAAM Blocks using Microscope and (c) Typical Image of Cyanobacteria
Source: http://www.sciencephoto.com

CONCLUSIONS AND RECOMMENDATIONS

In this project, resource recovery contribution was intended through the successful incorporation of coal combustion byproducts into cement structures with the goal of improving water quality parameters. The performance of a series of feasible experiments allowed concluding the following premises:

- The mixture of 1:1:1 ratio by weight of cement, fly ash and bottom ash proved to be resistant to surface shrinkage in water and had desirable compressive strength for their intended purpose.

- Parameters like pH, alkalinity and nitrate improved when the CAAM blocks were present in the system under the established conditions. Blocks contributed to a high conductivity environment which added ions for further reactions that helped with water quality enhancement.

- Apparent color and turbidity values were lower as more structures were present, the results were in accordance with suspended solids and biomass deposited over the blocks.

- A higher amount of CAAM blocks in the system helped in a bigger sense to maintain favorable water quality parameters. Approximately a ratio of 1 block per L of water was the best ratio to obtain better water quality in a system of 30 liters.

- Nitrification enhancement was observed when CAAM blocks were added to the system. The presence of nitrifying bacteria was an important key to the results obtained.

- The optimal composition (1:1:1) proved to be effective in the enhancement of water quality combined with a high recovery use rate of the CCBs.

Overall, the experimental results indicated that the CAAM blocks made from CCBs could be utilized as water quality enhancer under the conditions studied. No negative impacts were observed throughout the experiments performed. The only parameter with inconclusive results under certain conditions was the phosphate concentrations not dependent on the amount of blocks added to the system.

The findings obtained through the series of experiments performed provided additional ideas to compliment some of the findings and strengthen the data found in this project. The following recommendations are suggestions for further studies:

- Application of the blocks in a bigger scale environment with algal bloom problems such as a fish pond.

- Incorporate the optimized mixture into a more complex system like a marine environment to test the water quality enhancement behavior.

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APPENDIX

A. Algae Bloom and Ammonia Toxicity

In this experiment, we tried to verify the ammonia toxicity based on the amount of algae present in the system. Two reactors were setup with 2L of pond water collected from the Chancellor's house. A CAAM block was added on the reactor used as the treatment reactor based on space and pH values.

Results show that the presence of the CAAM block provided a higher value of pH and conductivity as observed in previous experiments. Nitrate and ammonia results showed very similar values implying no influence of the CAAM blocks presence. Phosphate results neither showed any differences between the blank tank and the tank with the CAAM blocks.

Table A.1. Data for No Blocks in the Ammonia Toxicity Experiment.

Day	pH	Conductivity (μS/cm)	Ammonia (mg/L as N)	Total Phosphorus	Nitrate (mg/L as N)
0	7.54	223	0	0.75	2.0
1	7.53	252	0.27	0.4	2.0
3	7.86	232	0.48	0.36	1.9
7	7.49	261	1.8	0.32	1.7
9	7.72	254	1.24	1.16	1.8
14	7.74	282	1.9	0.28	2
16	7.71	292	5.8	0.29	3.4
21	7.28	266	0.1	0.77	2

Table A.2. Data for 1 Block/L in the Ammonia Toxicity Experiment.

Day	pH	Conductivity (µS/cm)	Ammonia (mg/Las N)	Total Phosphorus	Nitrate (mg/L as N)
0	8.25	251	0.01	2.20	1.9
1	8.27	300	0.55	0.42	1.8
3	8.31	377	1.12	0.46	1.7
7	7.98	471	2.01	0.34	1.6
9	7.94	498	1.94	0.93	2.2
14	7.95	566	2.60	0.44	2.0
16	7.89	581	3.60	0.39	3.3
21	7.74	607	0.10	0.31	2.0

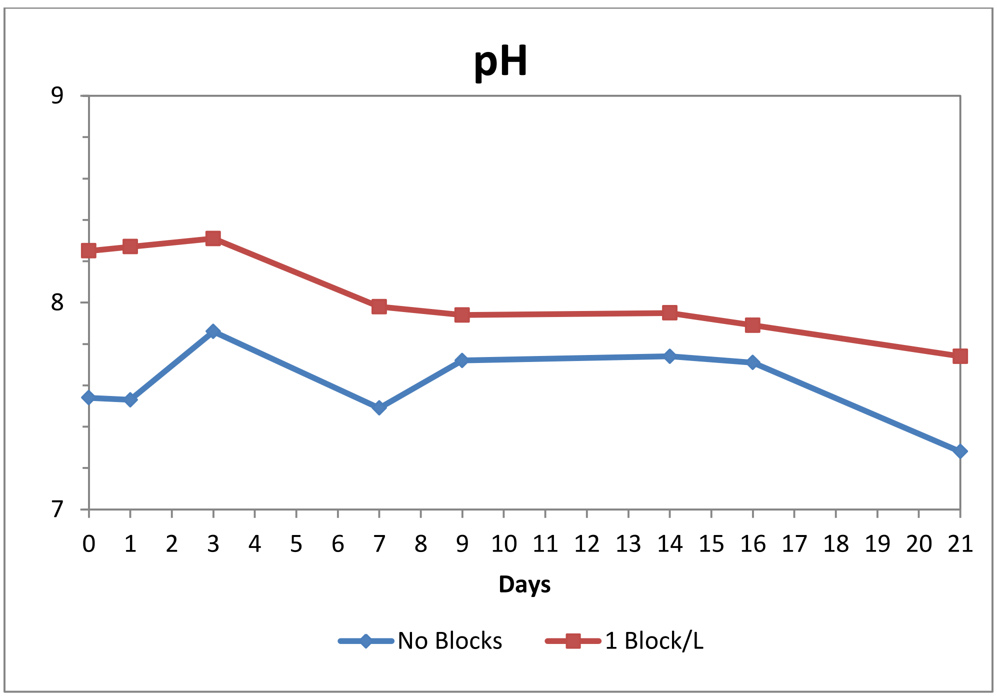

Figure A.1. Results for pH on Ammonia Toxicity Experiment.

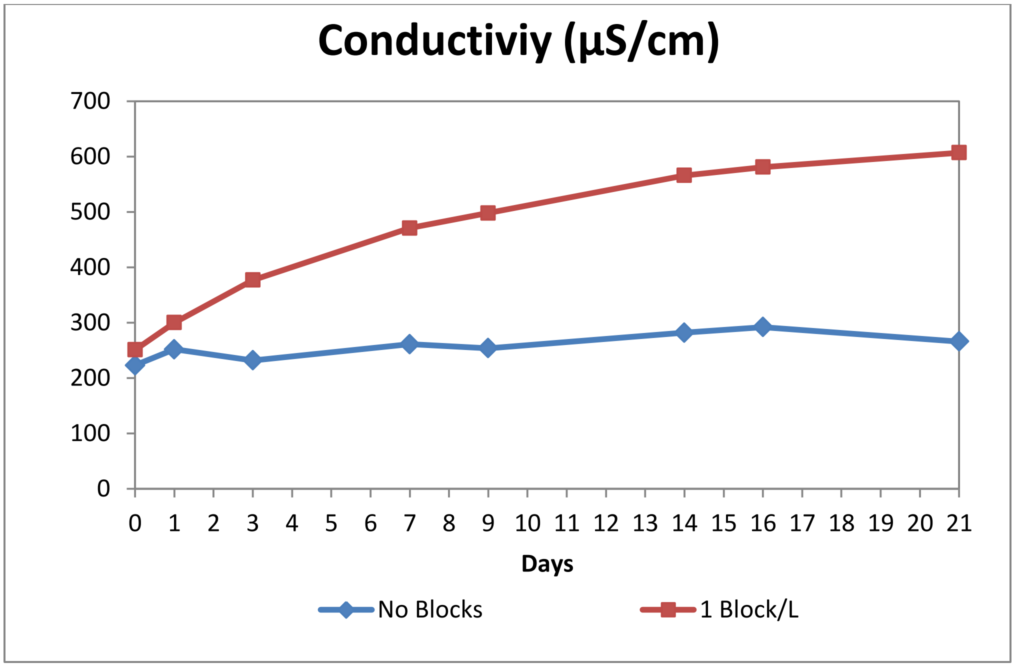

Figure A.2. Results for Conductivity on Ammonia Toxicity Experiment.

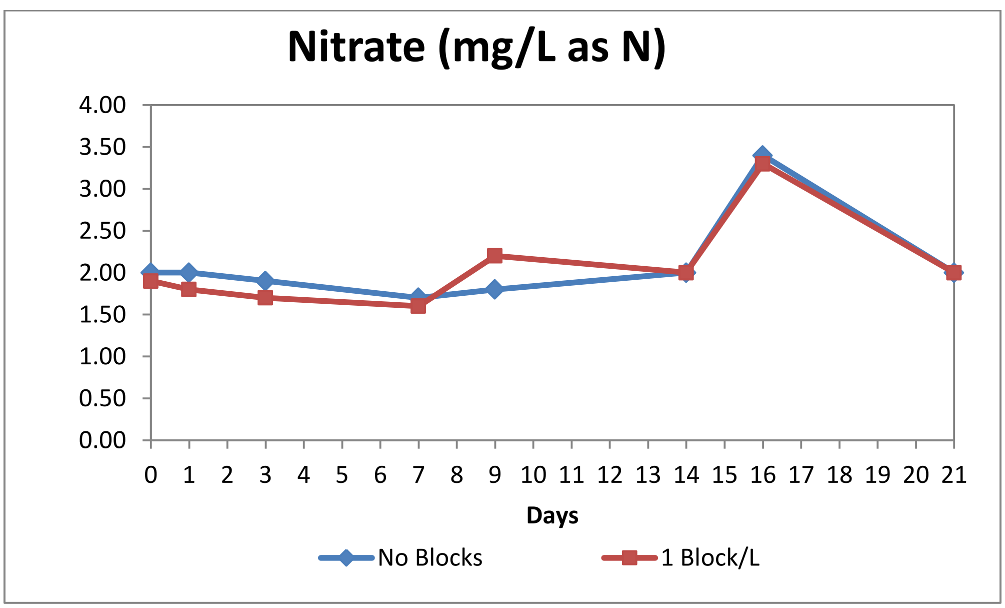

Figure A.3. Results for Nitrate on Ammonia Toxicity Experiment.

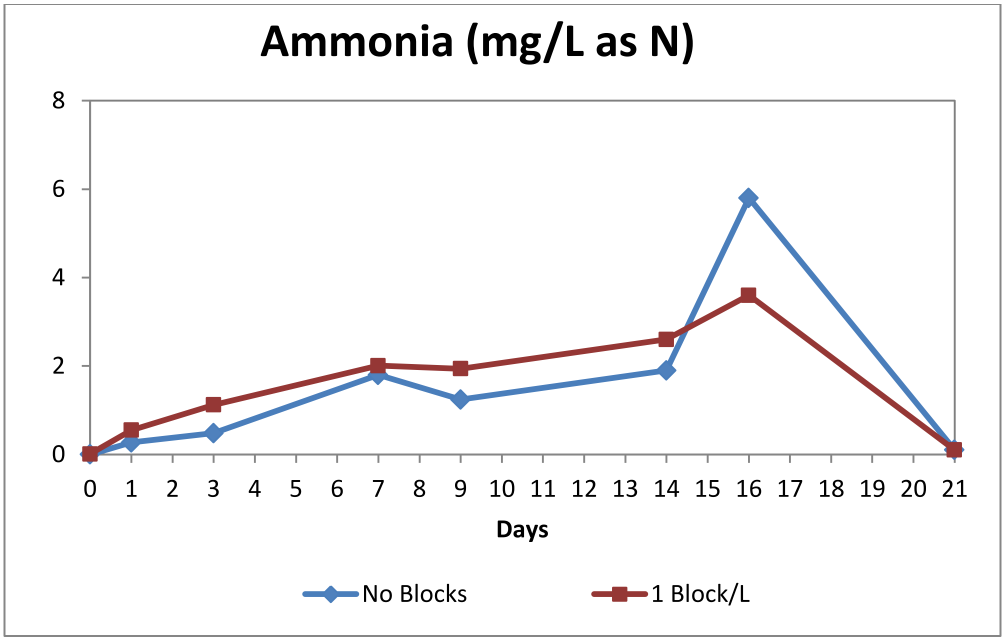

Figure A.4. Results for Phosphorus on Ammonia Toxicity Experiment.

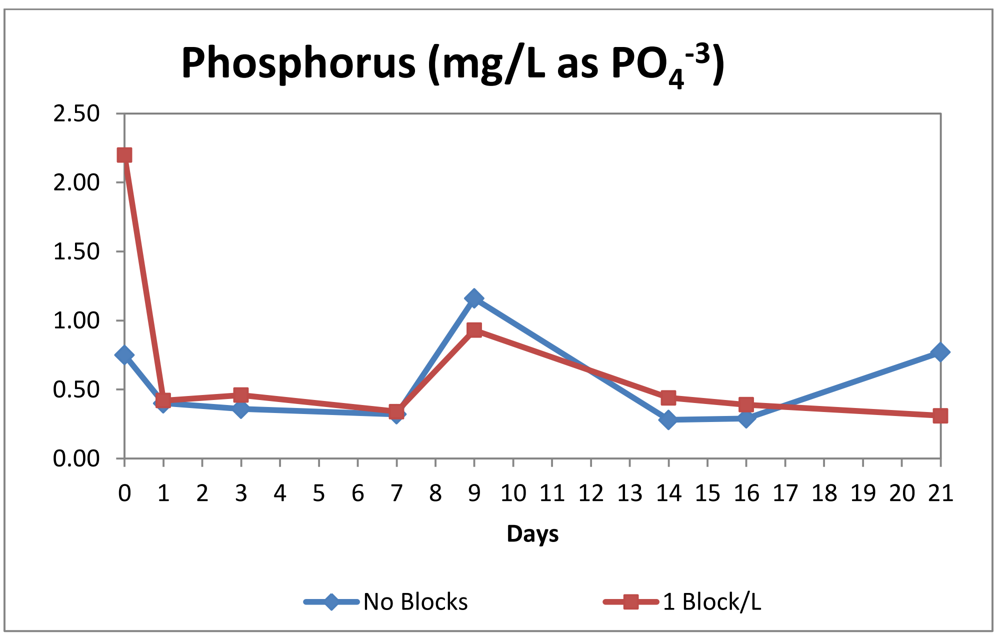

Figure A.5. Results for Phosphorus on Ammonia Toxicity Experiment.