PHOSPHORUS AND ALGAE REMOVAL VIA ADSORPTION

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ABSTRACT

Algal bloom, commonly known as Red Tide in coastal areas, has become one of the major problems facing desalination plants due to the high biomass concentration of microalgae associated with it. It causes operational problems (i.e. membrane fouling) in addition to health risk associated with deadly species of algae. Phosphorus pollution is considered to be the primary cause of red tide since most of microalgae species grow rapidly in the presence of high phosphorus concentrations. Many recent studies showed the efficiency of using adsorption for phosphorus removal from wastewater; however, none addressed its removal from seawater or the removal of algae via adsorption. The objective of this dissertation was to investigate the efficiency of using adsorption as a treatment process to remove microalgae and phosphorus. A variety of phosphorus adsorbents were tested and compared with each other in order to determine the most efficient material for the treatment system. Batch and fixed bed column tests were conducted to assess the performance of the treatment system for algae and phosphorus removal. The effects of different parameters were investigated to maximize phosphorus and algae removal. Chlorophyll-a concentration was measured as an indicator for algae concentration. Preliminary results showed that activated alumina was the most suitable adsorbent (out of the ones tested in this research) for phosphorus removal from synthetic water. Further results obtained from batch experiments revealed that acidic conditions (pH = 5) and an adsorbent particle size of 0.6 mm were the most feasible experimental conditions for treating both phosphorus and microalgae from actual seawater. The removal percentages were more than 84% for phosphorus and more than 40% for chlorophyll-a using only 4 g/L of activated alumina. Column tests showed more than 50% phosphorus and chlorophyll-a removals even after processing 5000 pore volumes. The pattern of the results suggested that, most probably, adsorption was not the main mechanism of microalgae removal. Phosphorus recovery proved to be reasonably applicable under extreme alkaline conditions (pH = 13.1).

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1 INTRODUCTION

1.1 Background Information

As is well known, phosphorus is considered as the limiting nutrient responsible for eutrophication of water bodies, resulting in excessive growth of microalgae. This massive microalgae growth is due to the fact that these microorganisms reproduce by consuming phosphorus which can be increased due to human activities (i.e. disposal of wastes in water bodies) and natural processes (i.e. runoff from land and upwelling) [1]. The presence of even less than 1 mg/L phosphorus in water is sufficient to cause harmful algal bloom, or commonly named red tide in coastal areas [2].

The history of red tides goes back to even earlier than 1850 where people used to report them as abnormal phenomena. Red tide, irrespective of the color, is water color change due to the rapid growth of microalgae which causes mass mortalities of marine animals, operational problems in desalination plants, and high risks on human lives [3]. The water color associated with this phenomenon can be red, blue, brown, or green, which is why "Harmful Algal Bloom" (HAB) is a better description for this phenomenon. The microorganisms responsible for red tide are mainly phytoplankton (diatoms and flagellates); however, ciliates, bacteria, and zooplankton may sometimes be the cause of red tide [3]. Table 1.1 describes some species related to red tide and their possible impacts on the ecosystem [3] and [4]. One deadly species is the dinoflagellate taxon Alexandrium which is common in the northeastern and northwestern US. The so called saxitoxins produced by this taxon are known to cause paralytic shellfish poisoning in humans when ingested through contaminated seafood [4]. Another harmful species is the dinoflagellate taxon Lingulodinium polyedrum which is an armored genus responsible for high fish mortalities. This taxon also imposes severe impacts on the operation of desalination plants by increasing turbidity, suspended solids, & organic loading [3].

Even though it was mentioned above that phosphorus is the limiting factor for microalgae growth, nobody can deny the fact that there are many other physical and chemical factors that can stimulate microalgae growth (Table 1.2) [3]. Air temperature, precipitation, solar radiation, dissolved oxygen, inorganic nutrients, and trace metals among others can affect microalgae either negatively by inhibiting their growth or positively by providing the best environment for them. Studies showed that small differences in water temperature and air pressure during long periods of time are usually associated with red tide occurrences whereas large density stratifications prevent primary production of microalgae [3]. Strong winds can provide the perfect environment for microalgae by mixing the bottom cold nutrient rich water layer with the upper one [3]. Changes in these limiting factors can be owed either to natural processes as mentioned before or to anthropogenic activities coming from industrial wastes, wastewater treatment plants' effluents, and fertilizers used in farming [5].

Table 1.1: Some red tide species

Srl. No.	**Microorganism Group**	**Red Tide Species**	**Description**
1	Proteobacteria	Chromatium	Photosynthetic purple sulfur bacteria found in coastal saline deep lakes.
2	Cyanophyceae	Trichodesmium	Blooms extensively in tropical & subtropical areas & causes mass mortalities of marine organisms.
3	Cryptophyceae	Chroomonas	Unicellular flagellate found in polluted water.
4	Dinophyceae	Gymnodinium	Unarmored genus known to cause mass mortalities & neurotoxic shellfish poisoning by forming aerosols.
5	Dinophyceae	Alexandrium	Rare genus known to cause paralytic shellfish poisoning.
6	Dinophyceae	Lingulodinium polyedrum	Armored genus known to cause fish mortalities & significant impacts on desalination plants by increasing turbidity, suspended solids, & organic loading.
7	Bacillariophyceae	Skeletonema	Chains of cylindrical cells found in coastal waters known to cause oxygen depletion resulting in mass mortalities.
8	Bacillariophyceae	Pseudonitzschia	Long chains of cells known to produce domoic acid which causes amnesic shellfish poisoning resulting in mass mortalities of marine organisms.
9	Raphidophyceae	Chattonella	Blooms in coastal waters & causes mass mortalities of fish.
10	Pelagophyceae	Aureococcus anophagefferens	Non-motile genus known to form brown tides responsible for mass mortalities of filter-feeding mollusks.
11	Haptophyceae	Chrysochromulina	Motile with two flagella and a haptonema known to be harmful for coastal organisms.
12	Haptophyceae	Phaeocystis	Motile with two flagella and a haptonema known to produce substances that can lead to massive buildups of sea foam along coasts.
13	Euglenophyceae	Eutreptia	Algae with two long flagella found in brackish waters.
14	Chlorophyceae	Chlamydomonas	Egg-shaped algae with two equal flagella found in marine & brackish waters.

Table 1.2: Some red tide limiting factors

Srl. No.	**Limiting Factor**	**Effect on Microalgae Growth**
1	Tidal current speed	Higher horizontal diffusivity of water compared to the speed of microalgae growth restricts the appearance of red tides due to turbulence.
2	Water temperature & salinity	No specific relation between microalgae growth & water temperature and salinity. Different microalgae species reach optimal growth under different temperatures and salinities.
3	Major nutrients	Usually, an increase in total nitrogen, total phosphorus, & other nutrients results in the rapid growth of microalgae.
4	Chemical oxygen demand (COD)	An increase in COD would not necessarily increase the growth rate of microalgae since there are certain optimal COD concentrations for microalgae growth.
5	Vitamins	Studies showed that many microalgae species require a certain group of vitamins as a growth factor.
6	Iron	Studies showed that an increase in iron concentration increases the primary production of microalgae.

1.2 Problem Statement

The impacts of harmful algal blooms on the ecosystem and public health are very wide, ranging from aesthetic problems and bad odors to health risks and fish kills [5]. Sedimentation of organic matter during these phenomena can lead to the formation of sludge, organic acids, and anoxic water masses leading to fish death [6]. Water coloration leads to destruction of scenery and poor growth of seaweed due to blockage of sunlight. Additionally, nutrient absorption by microalgae may disrupt the growth of some other important marine organisms [6]. Production of toxins is considered the most vital effect of red tides on the ecosystem since these toxins lead, in most cases, to food web disruption, mass mortalities of marine organisms, and significant human health risks via consumption of contaminated seafood or direct exposure to water or aerosols containing these toxins. Consequently, many losses in revenue take place due to contamination of seafood products and effects on tourism [4].

One of the severe unmentioned impacts of HABs is the dramatic increase of biomass and organic load causing a significant hazard on desalination plants, especially, reverse osmosis desalination plants. Toxic compounds can also pose threat on desalination plants since it should be ensured that these products will be completely removed [4]. Recently in the UAE, HABs attacked Dubai (Figure 1.1) and Sharjah beaches resulting in many operational and productivity problems in desalination plants [7]. Eventually, the desalination plant in Sharjah was completely shut down causing water supply problems [8].

Figure 1.1: Red tide approaching the shores of Dubai in April 2009 [9]

Due to the aforementioned problems caused by red tides, many recent studies focused on either preventing red tide occurrence through reduction of phosphorus by removing it via adsorption [10], [11], and [12], or removing microalgae directly by microfiltration [13], UV irradiation [6] or other processes. The limitations of the existing knowledge base reside in the fact that no previous study investigated the removal of phosphorus from seawater. Also, no previous research studied the removal of microalgae via a low-cost treatment process such as adsorption.

1.3 Objectives

The overall objective of this dissertation was to investigate the efficiency of using adsorption as a treatment process to remove microalgae and phosphorus. The specific objectives of the study were:

- To identify a suitable adsorbent to remove microalgae and phosphorus from water.
- To determine the most suitable operating conditions to achieve high phosphorus and microalgae removal efficiencies.
- To investigate phosphorus recovery from the adsorbent.

2 LITERATURE REVIEW

As a result of the rapid increase of phosphorus pollution in industrialized areas all over the world, many recent studies have addressed this issue and proposed different solutions for phosphorus removal and recovery. Adsorption is one such effective technology. It does not require skilled labors or high energy consumption (only a pump) and can be easily employed using different readily available low-cost materials.

Ignoring seawater phosphorus pollution resulted in the rapid growth of microalgae causing harmful algal bloom, which imposed high risks on aquatic life, desalination plants, and in some cases human lives. Consequently, many people have proposed several solutions to eliminate microalgae, deactivate it, or prevent its severe damages. Among these solutions are microfiltration [13], flocculation [14], and UV irradiation [6].

2.1 Phosphorus Adsorption

It has been several decades since the beginning of phosphorus adsorption studies which are aimed to reduce phosphorus pollution. The challenge has been to find adsorbents that are inexpensive, readily available, renewable, and do not cause any operational problems (i.e. clogging and hardening). Several materials such as zeolite [15], diatomite [16], activated oyster shell [17], and red mud [18] have been investigated for application in phosphorus removal. Many studies showed that the phosphorus adsorption efficiency is primarily related to the oxide content of metallic elements [19] and that in addition to adsorption, precipitation can also help in phosphorus removal [20]. Also, it has been shown that many variables such as the solution’s pH, contact time, initial phosphorus concentration (PC), temperature, adsorbent particle size, and adsorbent dosage can significantly affect the adsorption capacity [21]. Table 2.1 & Table 2.2 summarize the objectives, methods, and achievements of some selected papers related to phosphorus removal from water bodies. These studies were carried out through conducting batch and fixed bed column experiments as a standard for the evaluation of adsorption.

For instance, it is observed from Table 2.1 that Liang and his colleagues were able to achieve maximum adsorption capacities and breakthrough timings reaching 1.598 mg P/g and 22 days, respectively, by using soils as adsorbents [10]. However, an adsorption capacity of 1.598 mg P/g for an initial PC of 500 mg/L is considered very low compared to the results obtained in this dissertation (see section 4.3.2). Also, a breakthrough occurrence after 22 days for a column size more than twice the one used in this dissertation and a flow rate of 0.6 mL/min is in fact too early compared to the results obtained in section 4.4.2. There are other studies such as the one conducted by Lan and his colleagues (Table 2.2) which shows more than 88% phosphorus removal using 20 g/L of 0.35 mm converter sludge as an adsorbent. This amount of removal with an initial PC of 50 mg/L is also relatively lower than the removal obtain in this dissertation which can be seen in sections 4.3.1 & 4.3.2.

Table 2.1: Previous studies on phosphorus adsorption (both batch & column experiments)

Srl. No.	Adsorbent	Test	Studied Variables	Experimental Conditions	Results	Reference
1	Seven types of soils	Batch & column tests	Initial PC (0.1 to 500 mg/L).	Batch tests were conducted at 25^{o} C with 48 hr shaking period. Columns were 5 cm in diameter & 40 cm in height.	Maximum adsorption capacities ranged from 0.256 to 1.598 mg P/g. Breakthrough timings (at effluent phosphorus concentration (EPC) of 0.5 mg/L) ranged from 5 to 22 days under flows ranging from 0.3 to 0.6 mL/min.	[10]
2	Activated alum porcelain (AAP)	Batch & column tests	Initial PC & pH.	Initial PC in batch tests ranged from 0.08 to 0.16 mg/L. 2 hr shaking period, 300 g/L AAP dosage, & 1 mm particle size were used. Columns were 7.5 cm in diameter and 70 cm in height. The target EPC was 0.005 mg/L.	The optimum pH was found to be 6.5 which is suitable for drinking purposes. Column tests with 440 mL/min flow rate & 0.04-0.08 mg/L initial PC still removed 70% even after treating 5000 filter layer volume.	[11]
3	Activated aluminum oxide (AA) & granulated ferric hydroxide (GFH)	Batch & column tests	Contact time (column test only), pH, & adsorbent dosage.	Less than 0.065 mm particle size was used. The initial PC was set to 4 mg/L for batch tests and 0.3 mg/L for column tests. Batch tests were conducted at 20^{o} C with 96 hr shaking period. Columns were 2.5 cm in diameter & 20 cm in height.	Low pH values are favorable for both adsorbents. The optimal contact time for column tests was determined to be 30 min. Breakthrough timings (at EPC of 0.05 mg/L) were reached for GFH & AA after 8000 and 4000 bed volumes respectively with a flow rate of 2.7 mL/min.	[22]
4	Fly ash	Batch & column tests	Initial PC (20, 50, & 100 mg/L), adsorbent dosage, contact time, & temperature.	Particle sizes ranged from 0.063 to 0.125 mm. Columns were 5 cm in diameter & 65 cm in height.	The most effective temperature was found to be 40^{o} C with more than 99% removal. 10 min was found sufficient to achieve equilibrium. 10 g/L adsorbent dosage is more than enough to attain maximum removal. phosphorus removal remained more than 80% even after 3 days of column test operation with 44 mL/min.	[21]

Table 2.2: Previous studies on phosphorus adsorption (either batch or column experiments)

Srl. No.	**Adsorbent**	**Test**	**Studied Variables**	**Experimental Conditions**	**Results**	**Reference**
1	Steel slag, boiler slag, furnace ash, and quartz sand	Column test	Contact time and mixing ratios of steel slag with the other materials.	Columns were 8 cm in diameter & 100 cm in height with a flow rate & an initial PC of 33 mL/min & 1.42 mg/L respectively. The target EPC was 0.5 mg/L.	Mixing steel slag with other materials is more effective in removing phosphorus since it mitigates clogging & improves the removal capacity. The optimum contact time & mix ratio were found to be 2 hr & 20-30% respectively. Breakthrough timings ranged from 20 to 26 days.	[12]
2	Converter sludge	Batch test	Contact time, pH, & adsorbent dosage.	Less than 0.35 mm particle size was used. The initial PC was set to 50 mg/L.	Over 88% phosphorus removal was obtained under optimal conditions. The optimum adsorbent concentration, contact time, & pH value were found to be 20 g/L, 4 hr & 4 respectively. Maximum adsorption capacity was found to be 6.8 mg P/g.	[23]
3	Several natural materials & industrial by-products	Batch test	Adsorbent dosage (4 to 16 g/L).	Particle sizes ranged from less than 0.1 to 1.25 mm. Temperature was kept around 22^o C.	Oven dried alum sludge and bone char were found to be the most effective adsorbents. Blast furnace slag, cement kiln dust, & granular activated carbon did not perform well when municipal wastewater effluents were used.	[24]
4	Steel slag	Batch test	Contact time, pH, & adsorbent dosage.	Less than 0.35 mm particle size was used. The initial PC was set to 50 mg/L. The target EPC was 0.5 mg/L.	Over 99% phosphorus removal was obtained under optimal conditions. The optimum adsorbent concentration, contact time, & pH value were found to be 7.5 g/L, 5 hr & 6.7 respectively. Maximum adsorption capacity was found to be 18 mg P/g.	[19]
5	Gas concrete waste	Batch test	Contact time, pH, temperature, & mixing rate.	Particle sizes ranged from 0.063 to 2 mm. The initial PC was set to 100 mg/L.	Close to 99% phosphorus removal was obtained. 10-15 min is a sufficient time to attain equilibrium. No observable temperature or mixing rate effects were found. The higher the pH value the more effective the process is.	[2]

All recent studies were concerned with phosphorus removal from wastewater, tap water (to produce drinking water), and effluents of treatment systems; however, no one studied phosphorus removal from seawater which could be different due to the presence of other materials such as salt and nitrogen that may participate as adsorption competitors. For instance, some studies showed that phosphorus removal from wastewater and from artificially made water are different due to the presence of other contaminants in wastewater [24].

2.2 Algae Removal

The enrichment of water bodies with phosphorus and other dissolved nutrients resulted in eutrophication of these water bodies which in turn led to the growth of microalgae to the point where it reached algal bloom. Consequently, many studies focused on the removal of algae rather than phosphorus due to the high risks (i.e. difficulties in operation of desalination plants) that might be associated with algal blooms. The challenge has been to find treatment methods that are efficient in terms of cost, energy consumption, and applicability. Traditionally, sand filters have been used for pretreatment at reverse osmosis (RO) desalination plants; however, some studies showed that such filters cannot produce acceptable effluents from red tide-contaminated seawater for RO desalination plants' feeding [25]. As a result, sand filters are being replaced by low-pressure membrane systems such as microfiltration (MF) and ultrafiltration (UF), which proved to be very effective for microalgae removal [26]. Nevertheless, MF and UF systems may sometimes require heavy maintenance (i.e. chemical cleaning) which may result in shutting down the plant if the algae concentration is very high. Advanced oxidation processes (AOPs) such as the photocatalytic reactions of nano-semiconductors [27] and the micro-gap discharge method [28] have also proved to be powerful for microalgae elimination. Yet, AOPs might not be efficient from all aspects (i.e. cost, energy, and applicability) and are not necessarily suitable for all microalgae species.

Table 2.3 summarizes the objectives, methods, and achievements of some selected papers related to removal of different species of microalgae from water bodies. As the table shows, no investigations on the removal of microalgae via adsorption were conducted; however, if proved, such method would be very efficient. It can also be noted that none addressed the removal of the limiting factors of algal blooms (such as phosphorus) which means that regrowth of microalgae can easily occur after such treatments.

Table 2.3: Previous studies on red tide treatment

Srl. No.	Method of Treatment	Test	Measurements	Microalgae Species	Results	Reference
1	Plasma sprayed Pt-doped TiO_2 coatings on foamed waste-glass	Batch lab test	Change in residual algae, transmission, and pH value with respect to UV illumination time	Unknown	Red tide was completely removed within 3 hours. Some of the green tide was removed within 3 hours; however, it exhibited slight increase as time went on. Transmittance increased rapidly during the first hour but then a slow change was observed. pH value gradually increased from neutrality.	[27]
2	Microfiltration	Pilot test (1.5 years)	Chlorophyll-a content and turbidity for red tide measurements. Silt density index (SDI) for water quality measurements	Heterosigma akashiwo was dominant	Target flow rate (5 m^3/s) was always achieved except at red tide bloom. Target SDI (less than 3) was always achieved even at red tide bloom. Chlorophyll-a concentration was 136 mg/m^3 at red tide bloom. Red tide bloom caused membrane fouling, higher pressure, higher energy consumption, and lower flow rate. Chemical cleaning of membrane is required when flow rate decreases by 30%.	[13]
3	Addition of kaolin clay	Batch lab test	In vivo fluorescence (IVF) (an indicator of the plant pigment chlorophyll) for phytoplankton measurements	Prorocentrum minimum, Chattonella subsalsa, and Cyanobacteria	IVF reduction of 99% for Prorocentrum, 92% for Chattonella, 71% for normal concentration of Cyanobacteria, and 33% for high concentration of Cyanobacteria. Major IVF decrease occurred in the initial 2.5 hour incubation period. A relation between cell counts and IVF was obtained before the test. The effective clay concentration was not investigated.	[14]
4	Micro-gap discharge (AOT)	Pilot test	Cell counts of red tide species, chlorophyll-a content, and dissolved oxygen (DO)	29 different species	99.89% removal efficiency of all red tide species. A very high reduction in chlorophyll-a content and an increase in DO saturation to 100% was observed. 0.68 mg/L of hydroxyl radicals ($OH^{\bullet}$) was used in this test. The salinity, pH, and conductivity remained constants after addition of $OH^{\bullet}$. No regeneration was observed even after 64 hours.	[28]
5	UV irradiation	Batch lab and field tests and column field test	Number of moving organisms immediately after treatment and after incubation for certain time	Heterosigma akashiwo, Chattonella marina, and Gymnodinium mikimotoi	Lab: H. akashiwo was treated the most where C. marina was treated the least but overall treatment was efficient for all species. The following condition has to be met to achieve max. treatment: **(UV intensity)$^{1.9}$ x (exposure time) ≥ 5.4 x 10^{7}.** Field: Effective treatment of C. marina. Samples were incubated fort several days at $20^{o}C$ and 5000 lux after UV treatment. The relation between UV intensity and exposure time was expressed as $y=ax^{-b}$. No change in water quality was observed except for some reduction in ammonium nitrogen.	[6]

2.3 Adsorption Isotherm Models

Freundlich and Langmuir equations were used to fit the experimental data of some of the batch tests. These equations were linearized in order to facilitate the fitting of the data since drawing and obtaining the equation of a best fit line is more practical than drawing and obtaining the equation of a best fit curve. The kinetic parameters obtained from these isotherms can help in understanding the adsorption capacity of the adsorbent under the various experimental conditions. They can also help in understanding the binding energy between the adsorbate and the adsorbent and the rate at which the adsorption density is increasing or decreasing as the effluent adsorbate concentration increases.

2.3.1 Freundlich isotherm

The equation for Freundlich isotherm can be described by:

$$Q = K_d C_e^{1/n} \tag{1}$$

Where Q is the adsorption density of the adsorbent [= $(C_o - C_e) / m$], C_e is the adsorbate concentration at equilibrium in the solution, K_d & n are material characteristics, C_o is the initial adsorbate concentration in the solution, and m is the mass of the adsorbent. K_d is considered as the adsorption density for a unit value of C_e which is often used to understand the adsorption capacity of various materials.

Equation (1) can be easily linearized and used to fit the experimental data through a linear regression by using the logarithmic function:

$$\log Q = \log K_d + \frac{1}{n} \log C_e \tag{2}$$

2.3.2 Langmuir isotherm

The equation for Langmuir isotherm can be described by:

$$Q = \frac{abC_e}{1+bC_e} \tag{3}$$

Where a & b are material characteristics. a is the maximum adsorption density where b is related to binding energy.

Equation (3) can be easily linearized and used to fit the experimental data through a linear regression by simple algebraic manipulation:

$$\frac{C_e}{Q} = \frac{1}{a} C_e + \frac{1}{ab} \tag{4}$$

3 MATERIALS AND METHODS

To achieve the objectives of this dissertation, bench scale experiments were used. The approach adopted was to remove microalgae and phosphorus from seawater. Batch tests were conducted to assess the performance of several adsorbents for phosphorus removal only. After choosing the most suitable adsorbent, further investigations on it were carried out using a combination of batch and fixed bed column tests. For these tests, several parameters were varied in order to obtain the most suitable operating conditions for both microalgae and phosphorus removal. Freundlich and Langmuir equations were used to fit the experimental data obtained from the batch tests so that kinetics of the adsorption process can be obtained.

3.1 Materials

Materials that were used as adsorbents were either collected from nature or purchased from chemical companies in Sharjah, UAE. These materials were subjected to preliminary batch tests for assessment as potential adsorbents. Table 3.1 describes the various materials that were used as adsorbents. Beach sand (0.075 mm particle size) and seashells (0.075 to 4 mm particle size) were collected from the beaches of Sharjah, UAE while aggregate (5 mm particle size), clay, and limestone powder (0.075 mm particle size) were acquired from the locally available materials in the laboratories of the American University of Sharjah (AUS). Granular activated carbon, limestone aggregate, activated alumina, and steel slag, which all had particle sizes of 4 to 5 mm, were obtained from local companies in UAE. Alum aggregate with a particle size of 5 mm was prepared in the laboratory by dissolving 20 g of alum in deionised water and then putting 1 kg of aggregate in the prepared water. This water was then evaporated in an oven under a temperature of 103^{o} C for 24 hours.

Table 3.1: Potential adsorbents tested in this research

Srl. No.	Adsorbent	Source and Method
1	Aggregate	Obtained from the construction lab at the American University of Sharjah (AUS), washed with distilled water, & then oven dried at 103^{o} C for 24 hr.
2	Alum Aggregate	The same aggregate mixed with alum at a ratio of 20 g alum per 1 kg aggregate.
3	Granular Activated Carbon	Purchased from Al Rama International Trading L.L.C in Sharjah, UAE.
4	Beach Sand	Collected from Sharjah beaches & then air dried for more than a month.
5	Clay	Obtained from the geotechnical lab at AUS.
6	Seashell & Seashell Powder	Collected from Sharjah beaches & then either used directly or smashed to very small pieces before usage.
7	Limestone Aggregate	Obtained from Sharjah Carbon Factory located in Sharjah, UAE.
8	Limestone Powder	Obtained from the construction lab at AUS.
9	Activated Alumina	Purchased from Oasis Chemical Materials Trading Company L.L.C located in Sharjah – UAE, & either used directly or smashed to small pieces before usage.
10	EAF Slag (Steel Slag)	Obtained for Emirates Steel Industries (ESI) located in Abu Dhabi, UAE.

Two types of water samples were used in this study. One of which was artificially made via the addition of potassium phosphate (KH_2PO_4) to deionized water (without cultivation for algal growth) and one of which was brought from the coasts of Sharjah, UAE and cultivated for algal growth. The first type of water samples were used immediately after preparation. The second type of water samples were collected at a distance of 4 to 5 meters into the coastal area of Al Khan open lagoon located in Sharjah, UAE. The time of collection was early morning (7:00 to 8:00 am) in the same day of the experiment. It took 15 to 30 minutes to transfer the water samples from the coast to the laboratory. The cultivation was done by adding the necessary amount of potassium phosphate to the water sample and then leaving it in the open air under the sun for 3 to 4 hours. The samples were used immediately after the end of the cultivation time. Different phosphorus concentrations ranging from 0.5 to 8 mg/L were used depending on the test. Chlorophyll-a concentrations ranged from 5 to 70 μg/L.

3.2 Methods

3.2.1 Batch test procedures

Three types of batch tests were used in this research. The first type of batch tests was conducted using several Erlenmeyer flasks filled with the same volume (200 mL) of water samples. A flask was filled with zero adsorbent concentration (blank) while the remaining flasks were filled with the same adsorbent dosage of different adsorbents in order to compare between the various adsorbents. The second type of batch tests was conducted using several Erlenmeyer flasks filled with the same volume (200 mL) of water samples and the same adsorbent but with different adsorbent dosages. The third type of batch tests was only different from the second type in that the particle size of the adsorbent was varied instead of the dosage. In all batch tests, the flasks were subjected to 3 hours of total shaking period followed by 3 days of total static period after which equilibrium was reached. These periods were previously determined by conducting batch tests with shaking and static time variations. Water samples were collected from the flasks at the appropriate time (refer to section 3.3 for more details) and tested for the required parameters. Freundlich and Langmuir equations were used to fit the experimental data of the second type of batch tests so that kinetic parameters of the process could be obtained.

3.2.2 Fixed bed column test procedures

Fixed bed column tests were conducted using 20 cm long cylindrical PVC columns with 2.25 cm diameter. As shown in Figure 3.1, water samples were pumped in an upward flow manner through columns filled with adsorbents using Heidolph pumpdrive 5001. Influents and effluents were tested for the required parameters and breakthrough curves were obtained from tests' results in order to assess the effectiveness of the treatment process.

Figure 3.1: Column test's assembly

3.2.3 Analytical methods

During batch and fixed bed column tests, water samples were tested for phosphorus concentration. Phosphorus occurs in water bodies as orthophosphates, condensed phosphates, and organically bound phosphates [29]. These forms occur in solution, in particles, or in the bodies of aquatic organisms [29]. For this research's purpose, only orthophosphate in solution was measured (i.e. no digestion was made). The colorimetric method used to measure orthophosphate is the standard method called "Ascorbic Acid Method" (section 4500-P E. in the standard methods book) which is suited for the range of 0.01 to 6 mg/L [29]. This method involves the reaction of orthophosphate with molybdate in an acid medium producing a mixed phosphate / molybdate complex that can be reduced by ascorbic acid giving an intense molybdenum blue color which is then measured at 880 nm.

Water samples were also tested for chlorophyll-a concentration as an indicator of microalgae biomass. The concentration of photosynthetic pigments is used extensively to estimate phytoplankton biomass [29]. Chlorophyll-a constitutes approximately 1 to 2% of the dry weight of planktonic algae. Therefore, an estimate of the algal biomass can be roughly obtained through multiplying the chlorophyll-a content by a factor of 67 [29]. Chlorophyll-a concentration was measured using the fluorometric method (section 10200 H. in the standard methods book) which is considered more sensitive than the other methods and thus smaller samples can be used [29].

Phosphorus was measured in duplicate using HACH DR5000 spectrophotometer. In-vivo chlorophyll-a concentration was measured in quadruplicate using fluorometer. Temperature and pH values of water samples were measured using pH100 probe provided by YSI Environmental.

3.3 Experimental Outline

3.3.1 Determination of the most suitable adsorbent

A set of batch tests was carried out for phosphorus removal only and with no pH, initial phosphorus, or particle size variations. An initial comprehensive preliminary batch test of the first type was first conducted on all 10 proposed adsorbents. This test was conducted for the purpose of getting an idea about the capability of a wide range of chemical and natural materials to adsorb phosphorus. Eleven flasks were used for this batch test with a constant adsorbent dosage of 10 g/L. Water samples were artificially prepared from deionised water via the addition of approximately 2.5 mg/L KH_2PO_4 (about 0.6 mg/L phosphorus).

Five additional batch tests of the second type were then conducted on the best four adsorbents in order to determine the most efficient one. Five flasks with an adsorbent dosage increment of 5 g/L were used for each of these five tests. Water samples were artificially prepared from deionised water via the addition of approximately 9.5 mg/L KH_2PO_4 (about 2 mg/L phosphorus). Phosphorus concentrations, pH values, and temperatures were measured after the expiration of the total shaking and static periods (refer to section 3.2.1 for more details about the duration of these periods).

3.3.2 Repeatability of experiments

Three identical batch tests of the second type were conducted for phosphorus removal only using the most suitable adsorbent in order to ensure that results are not varying too much for the same experimental conditions. Five flasks with an adsorbent dosage increment of 5 g/L were used for each of these three tests. Water samples were artificially prepared from deionised water via the addition of approximately 9.5 mg/L KH_2PO_4 (about 2 mg/L phosphorus). Phosphorus concentrations, pH values, and temperatures were measured after the expiration of the total shaking and static periods.

3.3.3 Batch tests

Sixteen batch tests of the third type were conducted with cultivated seawater samples using the most suitable adsorbent in order to investigate the effect of pH, initial PC, and particle size variations on the removal of both phosphorus and microalgae. Five flasks with a constant adsorbent dosage of 4 g/L were used for each of these tests. The adsorbent particle sizes used were 1.18, 0.6, 0.3, and 0.075 mm and the pH values used were 5, 7, 9, and the original pH of the seawater which is about 8. The initial PCs used were approximately 0.5, 2, 6, and 8 mg/L. pH control was carried out using HCl and NaOH solutions. Chlorophyll-a concentrations were measured after the first one hour of shaking while phosphorus concentrations, pH values, and temperatures were measured after the expiration of the total shaking and static periods.

3.3.4 Column tests

Two column tests were conducted with cultivated seawater samples using the most suitable adsorbent with a particle size of 0.6 mm and an influent phosphorus concentration (IPC) of 0.5 mg/L. The pH values used were 5 and the original pH of the seawater. pH control was carried out using HCl and NaOH solutions. Both phosphorus and microalgae removal were investigated. The column tests were carried out at approximately 11.2 and 20 mL/min flow rate with an adsorbent bulk density of about 770 kg/m^3 and a porosity of about 0.756. Influents and effluents were tested at different timings for phosphorus concentrations, chlorophyll-a concentrations, pH values, and temperatures in order to obtain breakthrough curves.

Two batch tests of the second type were conducted for each column test using the same water sample in order to determine the kinetics of each experimental set and see the effect of the adsorbent dosage. The first batch test was conducted for microalgae removal with five flasks and an adsorbent dosage increment of 4 g/L. Chlorophyll-a concentrations, pH values, and temperatures were measured after one hour of shaking. The second batch test was conducted for phosphorus removal with nine flasks and adsorbent dosages of 0, 0.25, 0.5, 0.75, 1, 2, 3, 4, and 8 g/L. Phosphorus concentrations, pH values, and temperatures were measured after the expiration of the total shaking and static periods.

3.3.5 Desorption batch test

A single batch test of the second type was conducted with deionised water using the most suitable adsorbent (in its consumed state after the column tests) in order to investigate phosphorus recovery. Seven flasks were used in this test with adsorbent dosages of 0, 1, 2, 3, 4, 8, and 16 g/L and a pH level of 13.1. The pH level stayed almost constant without the need to control it using HCL and NaOH solutions. Phosphorus concentrations, pH values, and temperatures were measured after the expiration of the total shaking and static periods.

4 RESULTS AND DISCUSSIONS

4.1 Determination of the Most Suitable Adsorbent

For the comprehensive preliminary batch experiment, Figure 4.1 shows the final PC to initial PC ratio for some selected adsorbents at an adsorbent dosage of 10 g/L. By comparing seashells to seashell powder and limestone aggregate to limestone powder, one can easily observe that higher surface area results in higher adsorption capacity. Contrary to findings in literature [12,19,23], electric arc furnace (EAF) slag (steel slag) was found to be ineffective in removing phosphorus. It may be due to differences in the properties of steel slag used in this study and the previous studies. Additionally, treating aggregate with alum proved to be very effective for phosphorus removal (more than 95% removal). Based on Figure 4.1, only four materials (limestone powder, smashed seashells, activated alumina, and alum treated aggregate) stood as possible adsorbents for phosphorus.

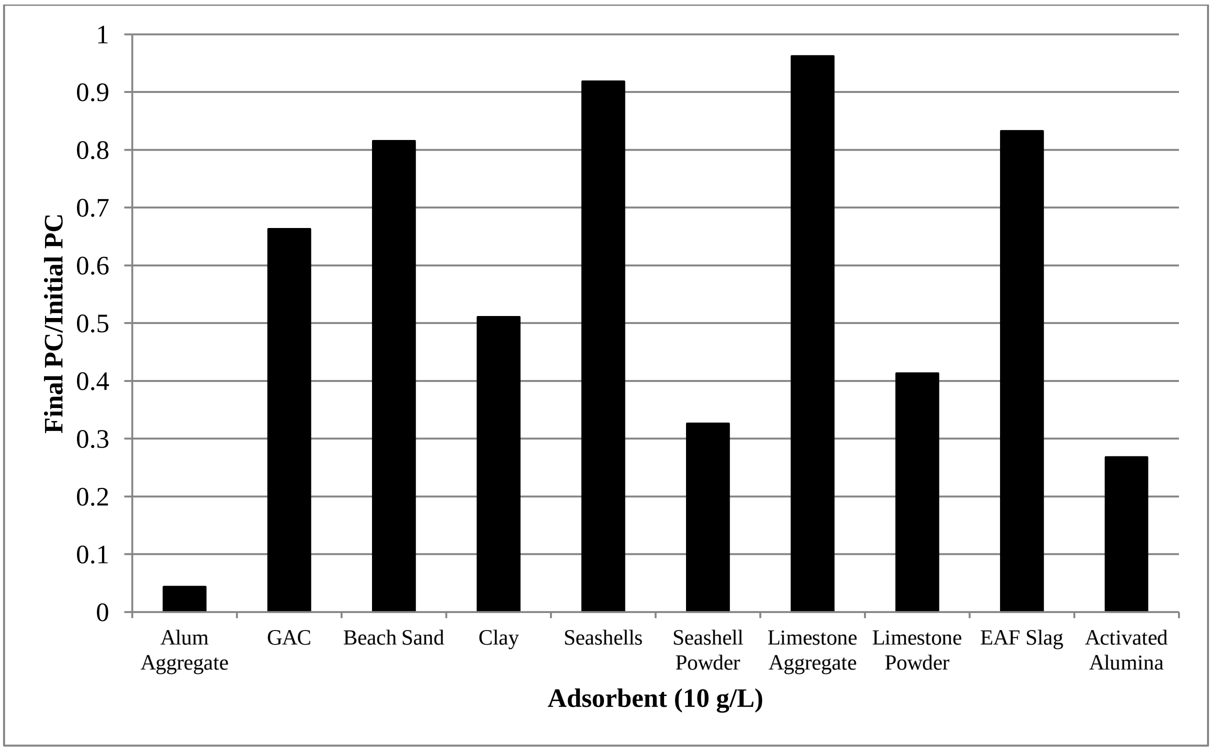

Figure 4.1: Preliminary batch test's results for 10 different adsorbents

Three of the five additional batch tests, which were conducted on synthetic water using limestone powder, smashed seashells, and activated alumina with an initial PC of 2.04 mg/L, showed superiority of activated alumina. Figure 4.2 shows final PC vs. adsorbent dosage for the three adsorbents. It was obvious that activated alumina was the best among these three with almost 90% removal at 10 g/L dosage and a particle size (4 to 5 mm) far greater than the particle sizes of the other two materials (less than 0.075 mm).

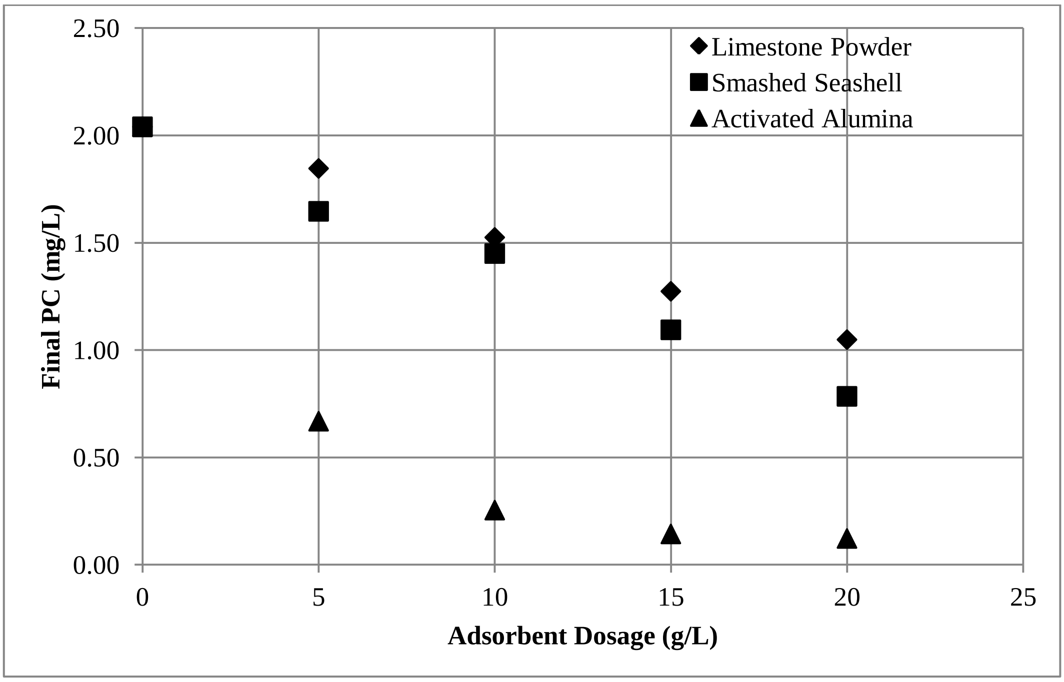

Figure 4.2: Comparison between three potential adsorbents

The other two additional batch tests, which were conducted on synthetic water using activated alumina and alum treated aggregate with an initial PC of 2.31 mg/L, indicated that both adsorbents had almost the same performance (Figure 4.3). The only difference was at 5 g/L dosage with a 50% phosphorus removal for alum aggregate and a 70% phosphorus removal for activated alumina. Nevertheless, activated alumina was selected as the best adsorbent due to the fact that alum aggregate required purchasing both aggregate and alum powder (cost ineffective) in addition to the need for at least one day for preparation of the adsorbent (time ineffective).

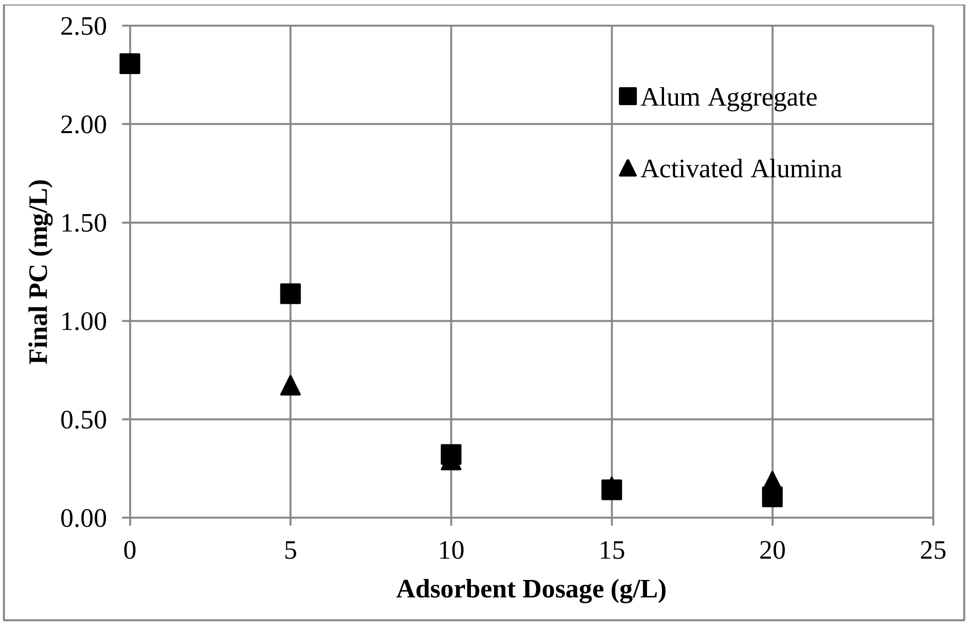

Figure 4.3: Comparison between alum aggregate and activated alumina

4.2 Repeatability of Experiments

The three identical batch tests conducted using activated alumina for repeatability studies showed reliability of the results (Figure 4.4). The range around each point in Figure 4.4 indicates the deviations of the two extreme values from the average of the three values. The maximum deviation from the average of the results obtained from the three tests was found to be less than 3%. It indicated that results from all the experiments were reliable and can be repeated with reasonable accuracy. Knowing that these differences are very small, the rest of the tests were conducted only once.

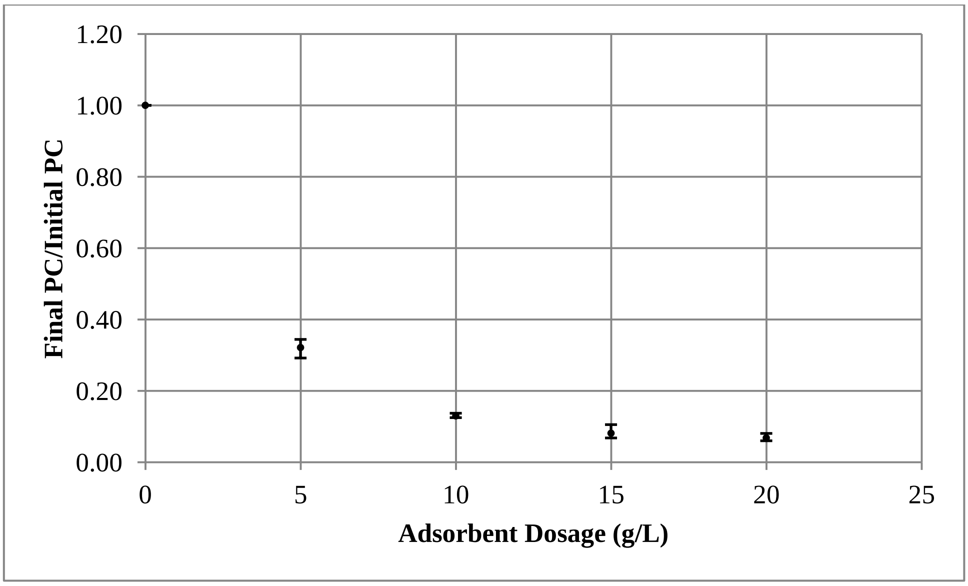

Figure 4.4: Repeated batch tests' results for activated alumina

4.3 Batch Tests

The sixteen batch tests conducted on cultivated seawater using activated alumina produced the following results.

4.3.1 Effect of pH on phosphorus removal

Looking into phosphorus removal, Figure 4.5 through Figure 4.8 show the percentage removal of phosphorus versus the particle size while varying the pH value and holding the initial PC constant. It can be clearly observed that, similar to what was found in the literature [22], acidic conditions (pH = 5) were the best for phosphorus removal on activated alumina while alkaline conditions (pH = 9) were the worst. This was due to the fact that, in acidic conditions, the high concentration of hydrogen cations in the solution stimulates the release of hydroxide anions from activated alumina by replacing them with orthophosphate anions. For instance, Figure 4.6 shows how the percentage removal of phosphorus at a particle size of 1.18 mm (as an example) reduced from 87% at a pH value of 5 to 75%, 73%, and 71% at pH values of 7, 8, and 9 respectively. Also, Figure 4.7 shows a reduction in the percentage removal of phosphorus, at a particle size of 0.6 mm, from 91% at a pH value of 5 to 85%, 82%, and 75% at pH values of 7, 8, and 9 respectively. This kind of reduction is apparent in all figures at all adsorbent particle sizes except for Figure 4.5 where it can be clearly observed that a pH value of 9 gave more phosphorus reduction than a pH value of 8. An example of that was the percentage removal of phosphorus at a particle size of 0.3 mm which came to be 94% for a pH value of 8 and 96% for a pH value of 9. This inconsistency can be attributed to the fact that Figure 4.5 is showing the results for an initial PC of 0.5 mg/L which was already a small value compared to the accuracy of measurement (0.01 mg/L). Thus, results would be very sensitive and such inconsistencies would be expected to occur. Another thing to observe is the fact that the removal percentages at different pH values were closing to each other as the particle size became smaller. For instance, Figure 4.8 shows how the difference in the removal percentages between a pH value of 5 and a pH value of 9 reduced from 27% at a particle size of 1.18 mm to 6% at a particle size of 0.075 mm. This observation was believed to be due to the fact that as the particle size decreased, the effect of the particle size became more apparent than the effect of the pH value and thus even a pH value of 9 would still provide a removal percentage close enough to that obtained at a pH value of 5.

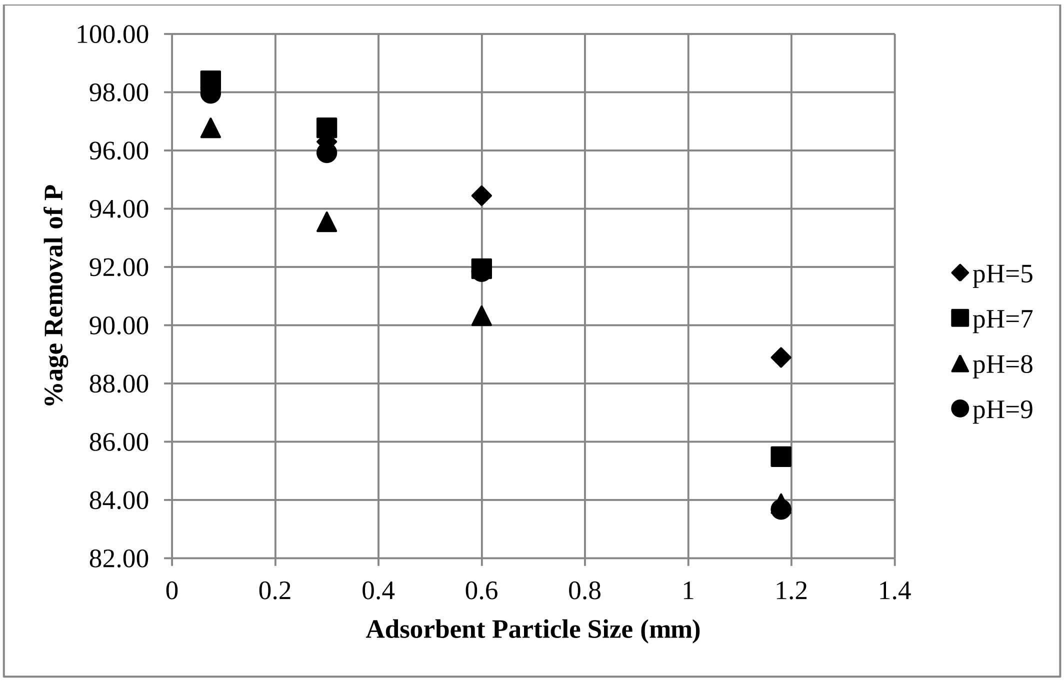

Figure 4.5: Four batch tests using activated alumina (P removal with initial PC = 0.5 mg/L)

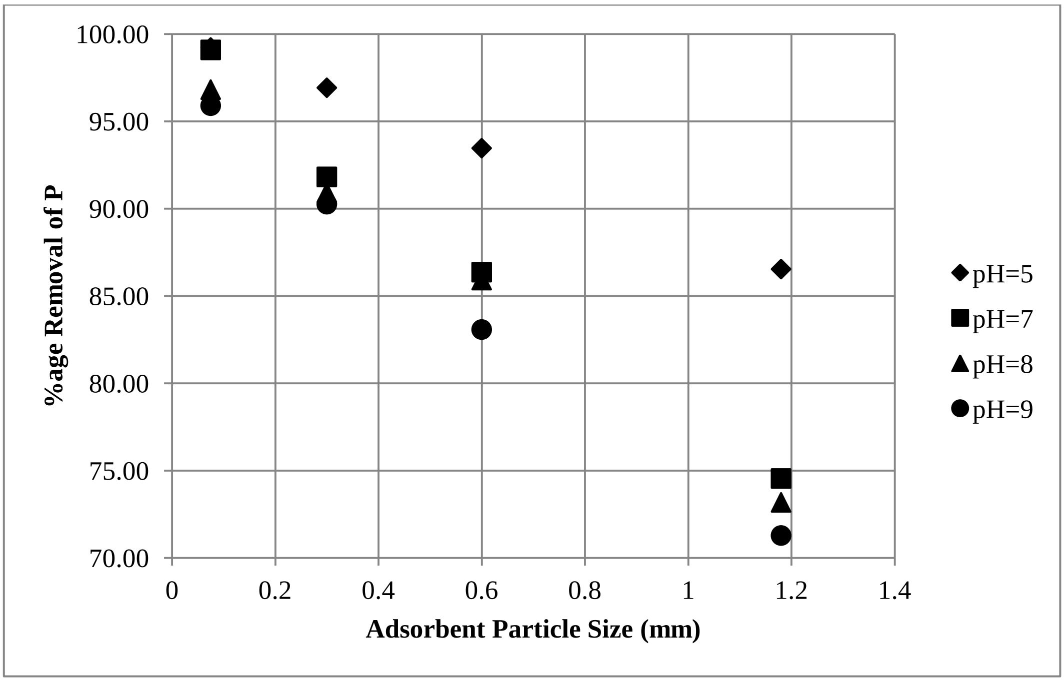

Figure 4.6: Four batch tests using activated alumina (P removal with initial PC = 2 mg/L)

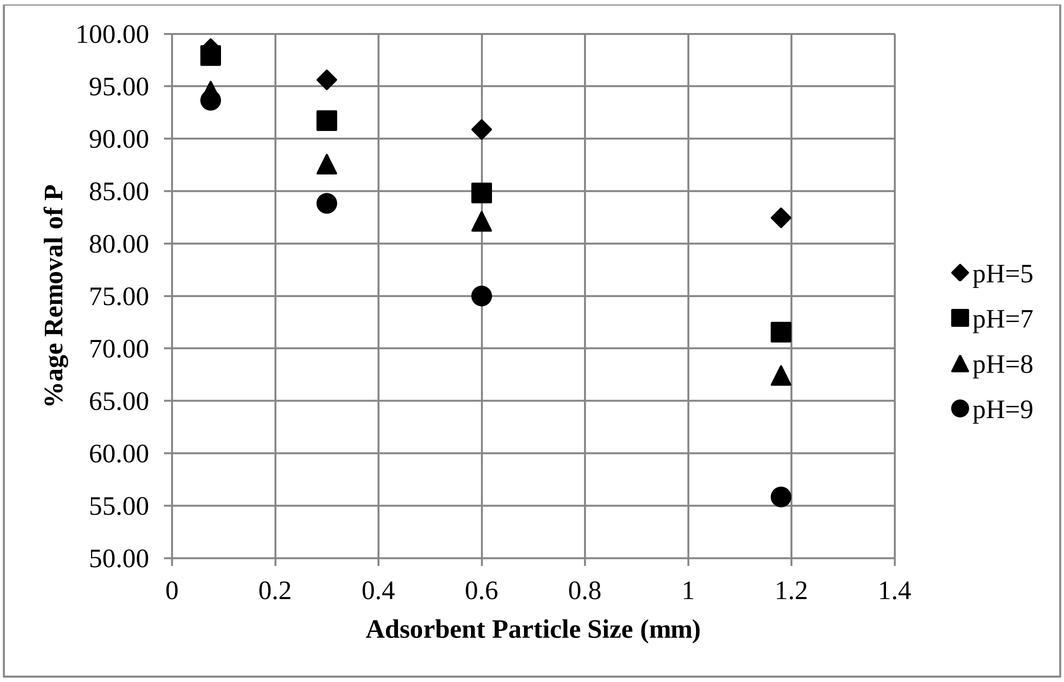

Figure 4.7: Four batch tests using activated alumina (P removal with initial PC =6 mg/L)

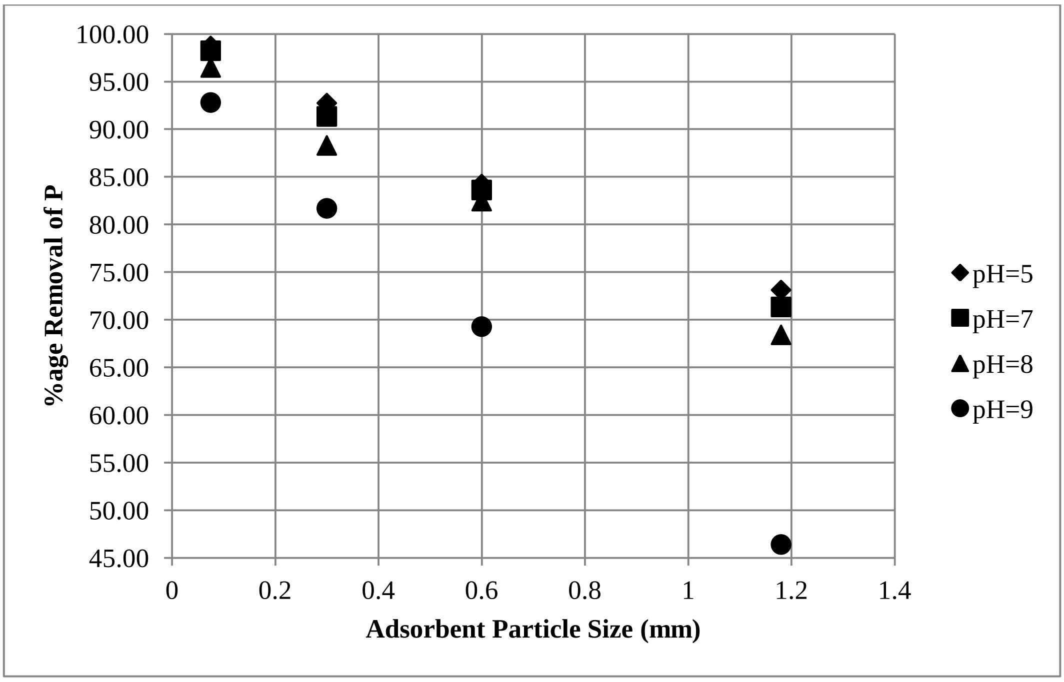

Figure 4.8: Four batch tests using activated alumina (P removal with initial PC = 8 mg/L)

4.3.2 Effect of initial phosphorus concentration on phosphorus removal

Looking from another aspect by varying the initial PC and holding the pH value constant, Figure 4.9 through Figure 4.12 show that the higher the initial PC was, the harder it was for activated alumina to maintain consistent phosphorus removal. For instance, even at a pH value of 9 (Figure 4.12) and a particle size of 1.18 mm, percentage phosphorus removal was well more than 80% for a 0.5 mg/L initial PC while it was less than 50% for an 8 mg/L initial PC. This also holds in the acidic condition (pH = 5) and with other adsorbent particle sizes and initial PCs. For example, Figure 4.9 shows that the percentage removal of phosphorus at a particle size of 0.6 mm was reduced from 93% at an initial PC of 2 mg/L to 91% at an initial PC of 6 mg/L. This observation agrees with the logical reasoning that a large amount of phosphorus is more difficult to be totally adsorbed than a small amount. Nevertheless, this relation failed to hold in some cases such as the case of Figure 4.11 (pH = 8) where the percentage removal at a particle size of 1.18 mm came to be 67% at an initial PC of 6 mg/L and 68% at an initial PC of 8 mg/L. Since the difference was very small, this disagreement can be regarded to the uncertainty that is usually associated with experimental studies. Another thing to observe is the fact that the removal percentages at different initial PCs were closing to each other as the particle size became smaller. An example of that can be observed from Figure 4.10 where the difference in the removal percentages between an initial PC of 0.5 mg/L and an initial PC of 8 mg/L reduced from 14% at a particle size of 1.18 mm to almost 0% at a particle size of 0.075 mm. This observation was believed to be due to the fact that as the particle size decreased, the effect of the particle size became more apparent than the effect of the initial PC and thus even an initial PC of 8 mg/L would still provide a removal percentage close enough to that obtained at an initial PC of 0.5 mg/L. Regardless of the experimental conditions, it was very obvious from the large removal percentages that activated alumina was removing phosphorus efficiently giving the fact that the adsorbent dosage used in all of these tests was only 4 g/L.

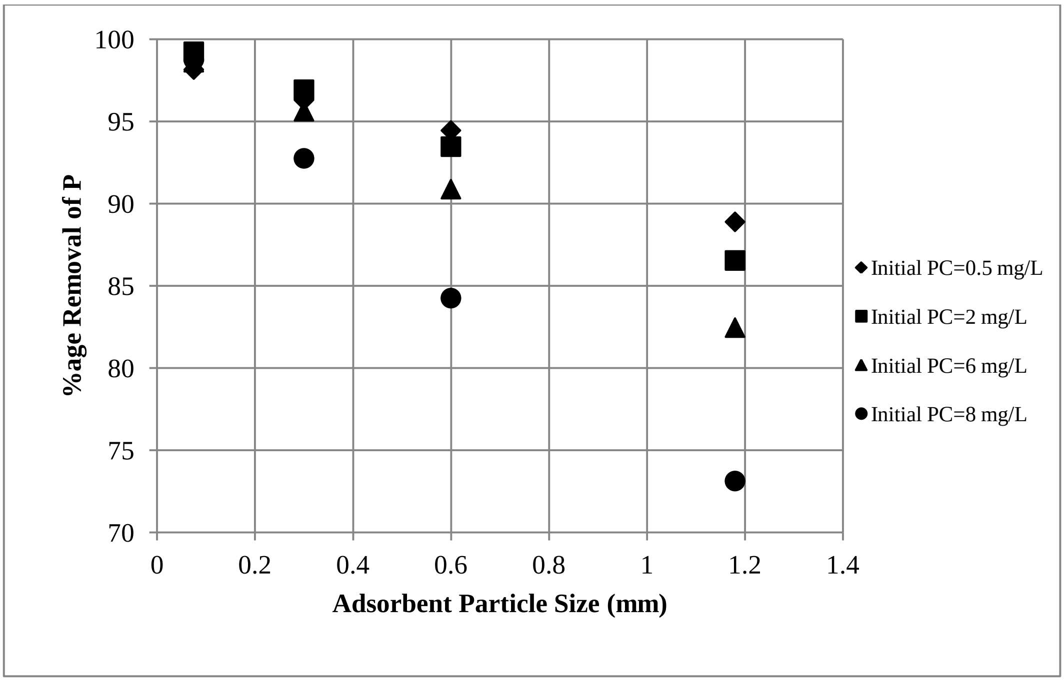

Figure 4.9: Four batch tests using activated alumina (P removal with pH = 5)

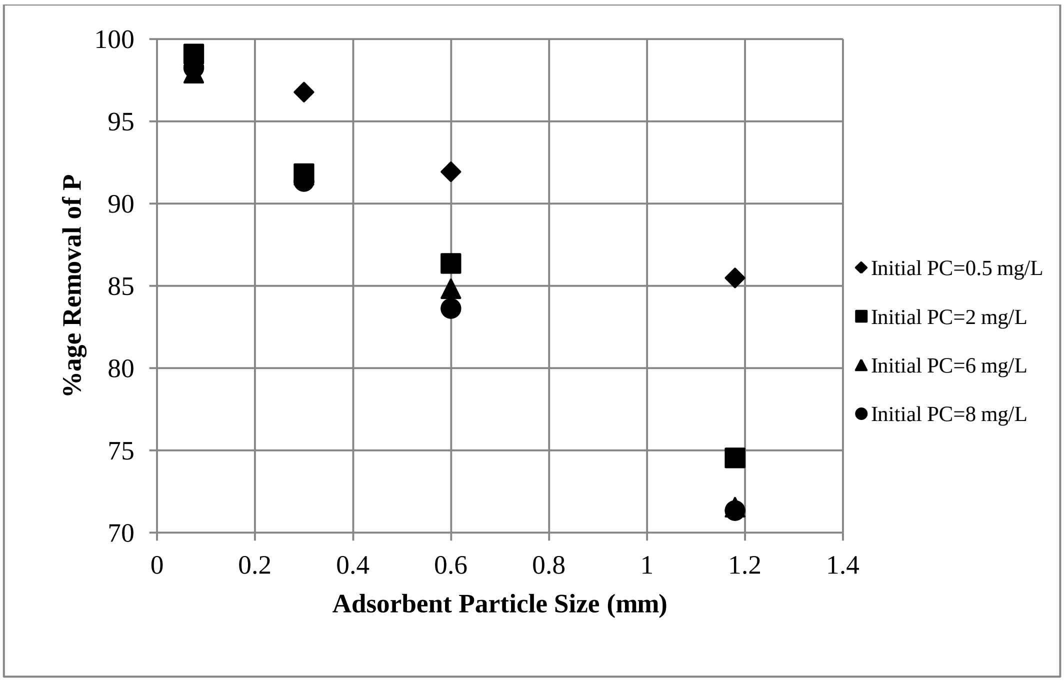

Figure 4.10: Four batch tests using activated alumina (P removal with pH = 7)

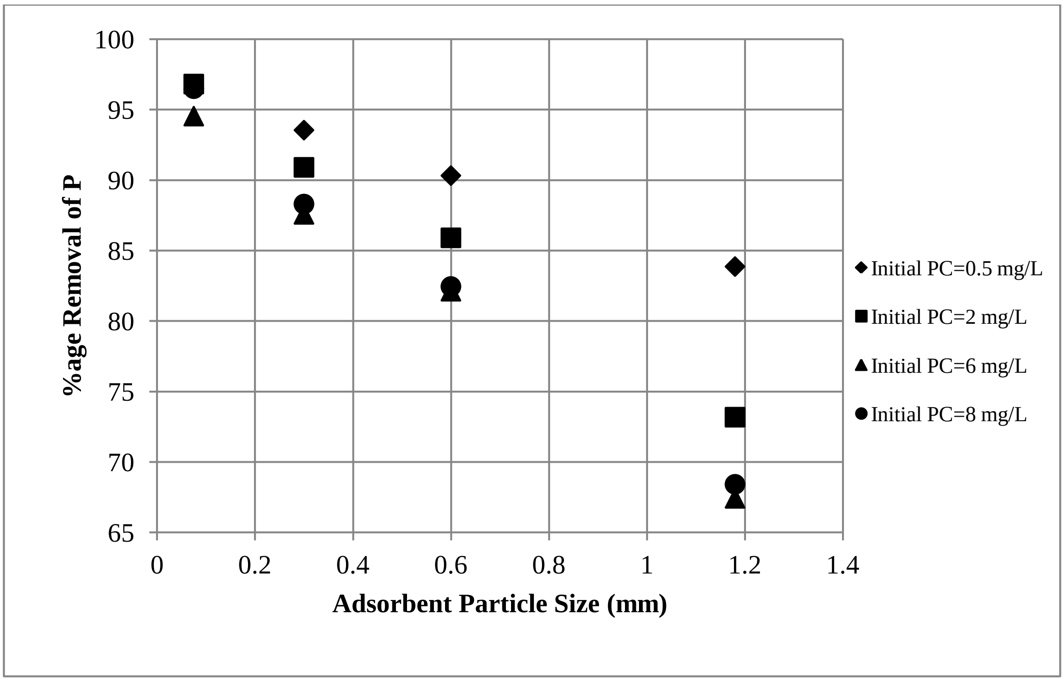

Figure 4.11: Four batch tests using activated alumina (P removal with original pH = 8)

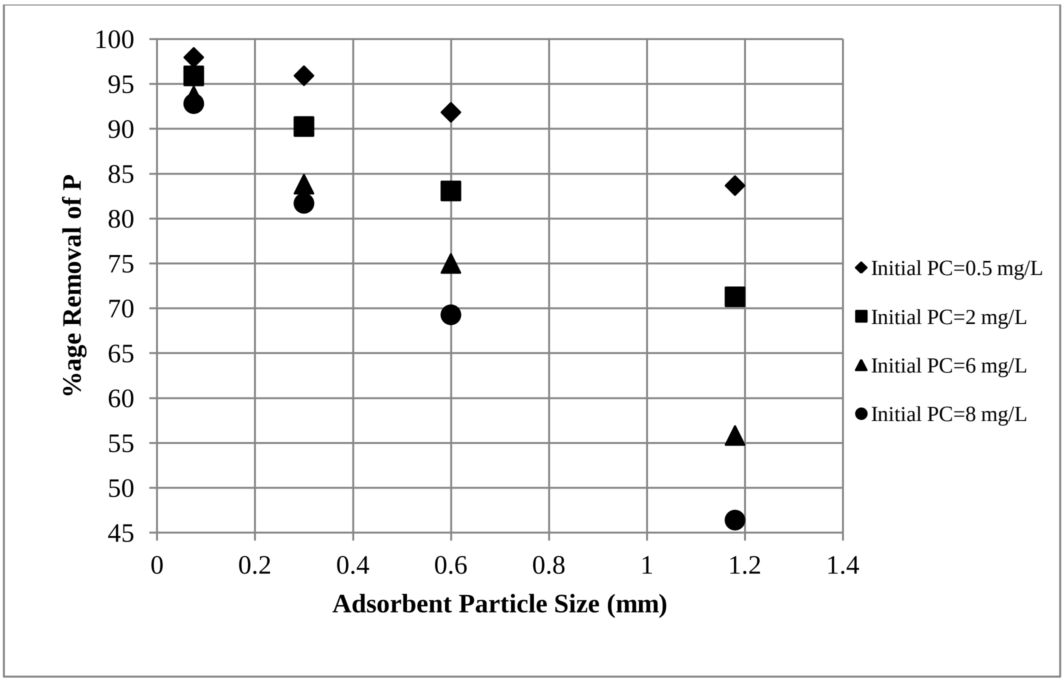

Figure 4.12: Four batch tests using activated alumina (P removal with pH = 9)

Even though percentage removal of phosphorus decreased as initial PC increased, Figure 4.13 shows clearly that the adsorption density or the uptake rate of phosphorus increased as the initial PC increased. This was expected since abundance of phosphorus at high initial PCs provided greater opportunities for each gram of activated alumina to become saturated with phosphorus while, at the same time, did not guarantee high removal percentages. The linear relation (between adsorption density and adsorbent particle size) with increased steepness as the initial PC increased can also be observed from Figure 4.13. These analyses were consistent at other pH values as shown in the appendix.

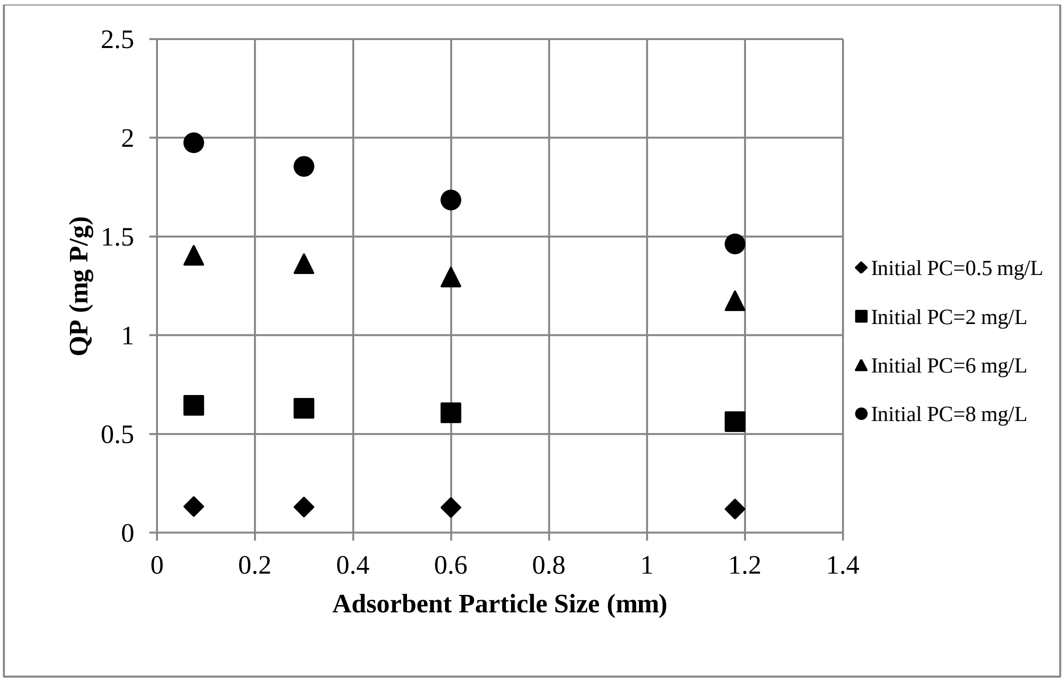

Figure 4.13: Phosphorus adsorption density versus adsorbent particle size (batch tests with pH = 5)

4.3.3 Effect of pH on microalgae removal

Shifting to the removal of microalgae, one can observe from Figure 4.14 through Figure 4.17 that the effect of pH variations was not as obvious as in the case of phosphorus especially when comparing neutral and alkaline conditions. For instance, Figure 4.14 shows that a pH value of 8 (9% chlorophyll-a removal) was better than a pH value of 9 (6% chlorophyll-a removal) at a particle size of 1.18 mm whereas the opposite was held for the rest of particle sizes. On the other hand, a pH value of 5 was always better than a pH value of 7. This inconsistency was believed to be due to the fact that initial chlorophyll-a concentrations (CCs) for the various batch tests were very different because of their dependency on the seawater condition at the time of collection. It can also be attributed to the possibility that coagulation might have been the main removal mechanism instead of adsorption. Nevertheless, it was quite observable that acidic conditions were slightly better almost at all initial PCs. Fortunately, this pH level matched the favorable pH conditions (pH = 5) for phosphorus removal as well. Also, the removal percentages of chlorophyll-a in the acidic condition (pH = 5) were on average 50% which were lesser than most of the percentages obtained from a previous study (99, 92, 71, and 33%) that involved coagulation by 4 g/L of kaolin clay [14]. These differences imply that kaolin clay was more efficient than activated alumina in terms of microalgae removal. Nevertheless, 50% removal is still considered sufficient to inhibit algal growth as discussed in section 4.3.4.

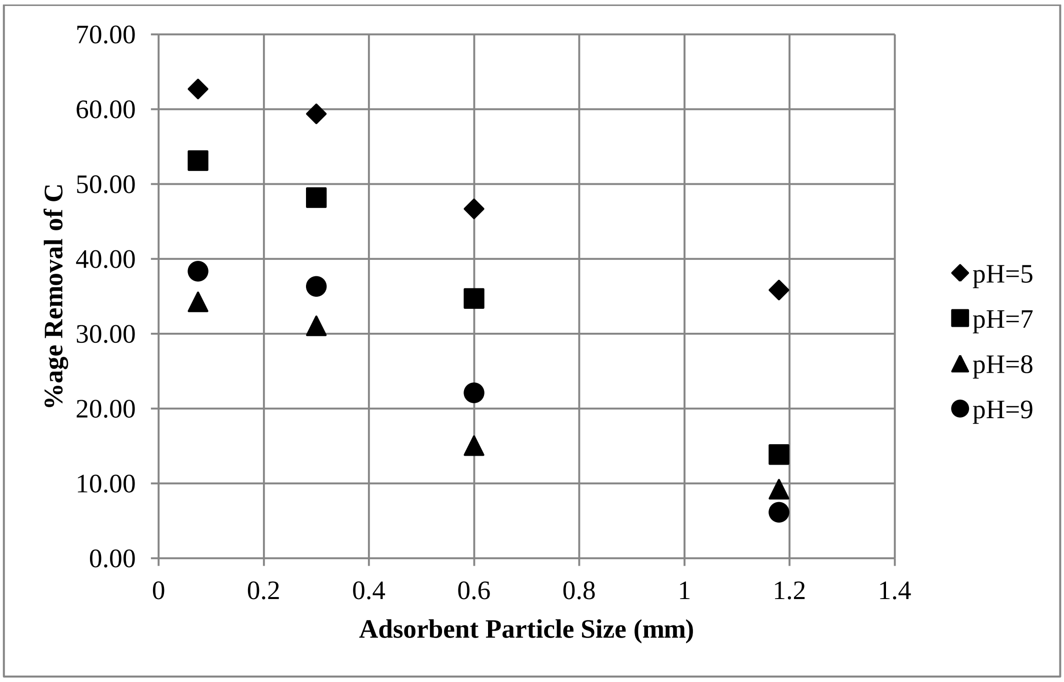

Figure 4.14: Four batch tests using activated alumina (C-a removal with initial PC = 0.5 mg/L)

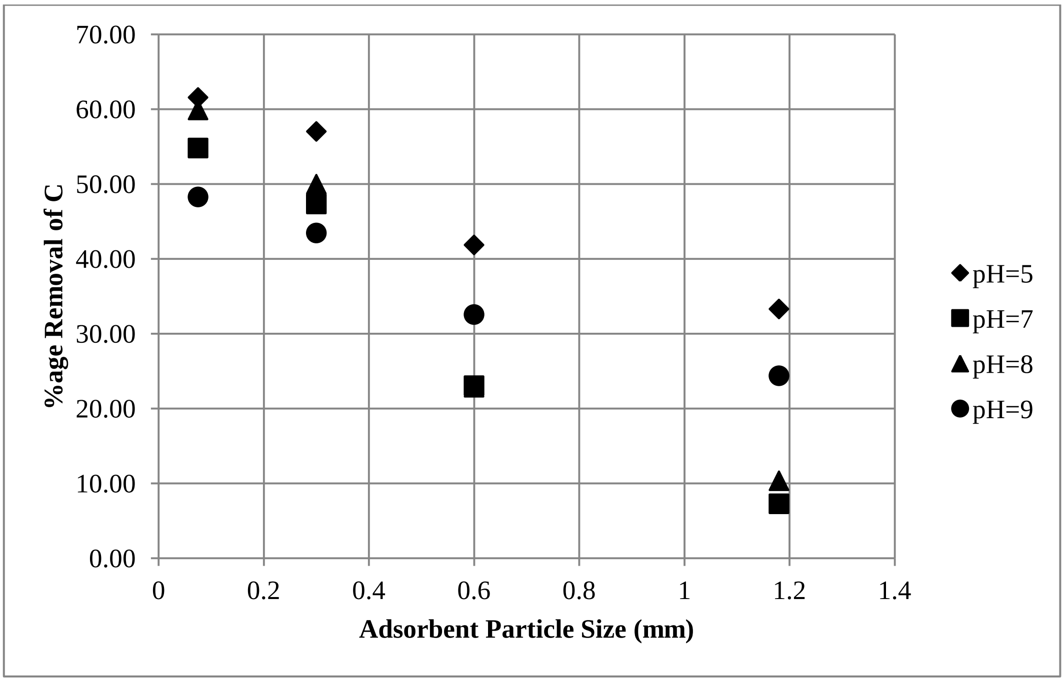

Figure 4.15: Four batch tests using activated alumina (C-a removal with initial PC = 2 mg/L)

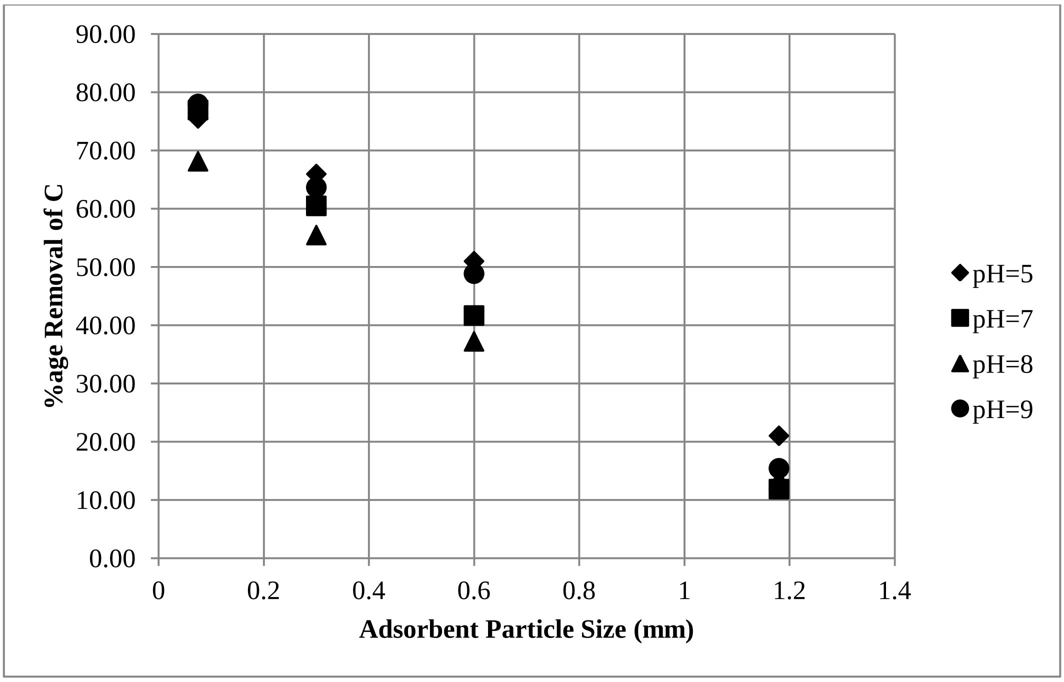

Figure 4.16: Four batch tests using activated alumina (C-a removal with initial PC = 6 mg/L)

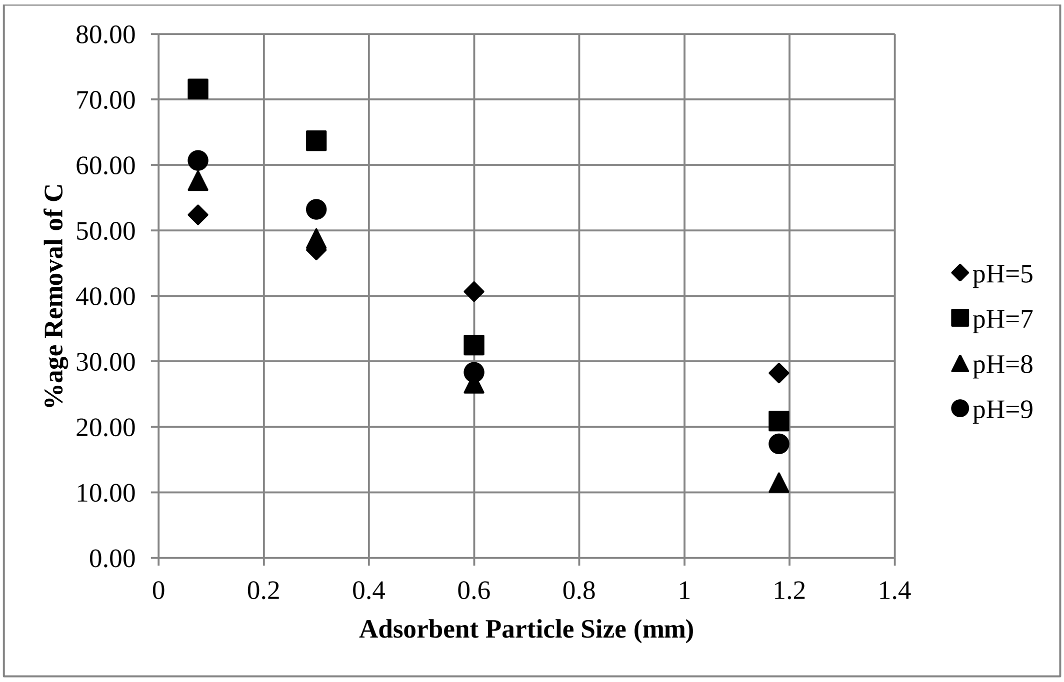

Figure 4.17: Four batch tests using activated alumina (C-a removal with initial PC = 8 mg/L)

4.3.4 Effect of initial phosphorus concentration on microalgae removal

Although phosphorus is considered a limiting factor of algal growth, it is pretty obvious from Figure 4.18 that the initial PC variation does not have any clear effect on chlorophyll-a removal. This conclusion holds even when looking at the removal density of chlorophyll-a as shown in Figure 4.19 (see the appendix for the rest of the figures at other pH values). This opposed the initial intuitive guess that higher initial PCs should produce lower chlorophyll-a removal. However, this observation was in fact logical since activated alumina proved to be very efficient in removing phosphorus which means that microalgae would not be able to have the luxury of consuming phosphorus in the presence of activated alumina. Regardless of the experimental conditions, it was rather obvious that chlorophyll-a was removed less efficiently as compared to phosphorus. However, the obtained removal percentages at a pH level of 5 and an adsorbent particle size of 0.6 mm or less which ranged between 40% and 60% were considered sufficient to inhibit algal growth. For instance, if a chlorophyll-a concentration of 136 µg/L is enough to cause algal bloom as mentioned in the literature [13], then reducing chlorophyll-a concentrations from 200 µg/L to 100 µg/L while maintaining low concentrations of phosphorus can be sufficient to stop the red tide and ensure prohibition of regrowth.

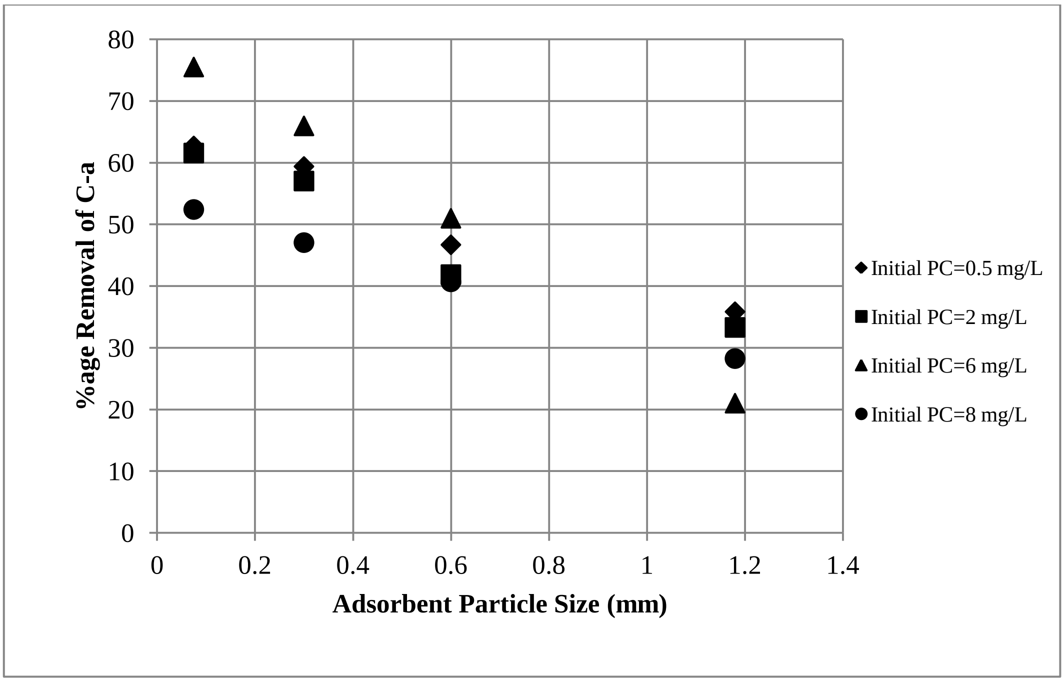

Figure 4.18: Four batch tests using activated alumina (C-a removal with pH = 5)

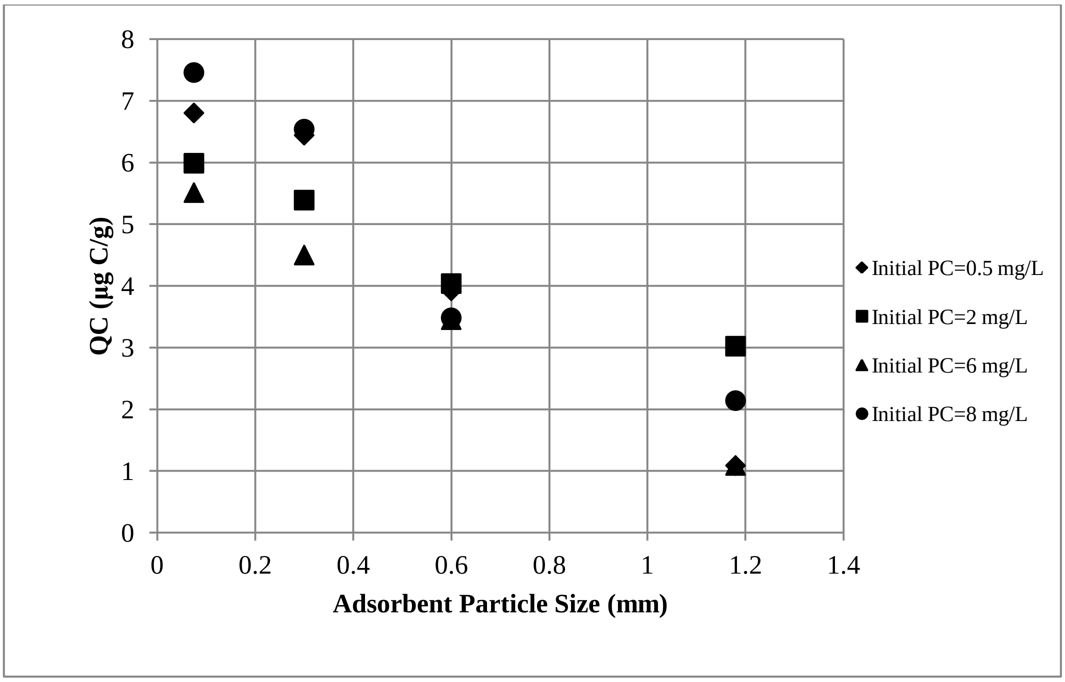

Figure 4.19: Chlorophyll-a removal density versus adsorbent particle size (batch tests with pH = 9)

4.3.5 Effect of initial chlorophyll-a concentration on microalgae removal

Plotting the several graphs of removal density versus adsorbent particle size for the various initial CCs (Figure 4.20 & Figure 4.21) gave an indication of its effect on the removal of microalgae. Of course, similar to the case of phosphorus removal, looking at the removal percentages was not meaningful (see the appendix). It was rather clear from Figure 4.20 & Figure 4.21 that the removal density of chlorophyll-a increased as the initial CC increased. This observation has the same explanation as the one observed while studying the adsorption density of phosphorus. Also, it can be seen that the decrease of the removal density as the adsorbent particle size increased became overall more rapid at higher initial CCs similar to the case of phosphorus adsorption density. This could be due to the fact that higher initial CCs resulted in higher orders of magnitude for the values of removal densities and thus gave rise to higher reductions in the removal density as the particle size increased. Similar observations were also noticed at other pH values as shown in the appendix.

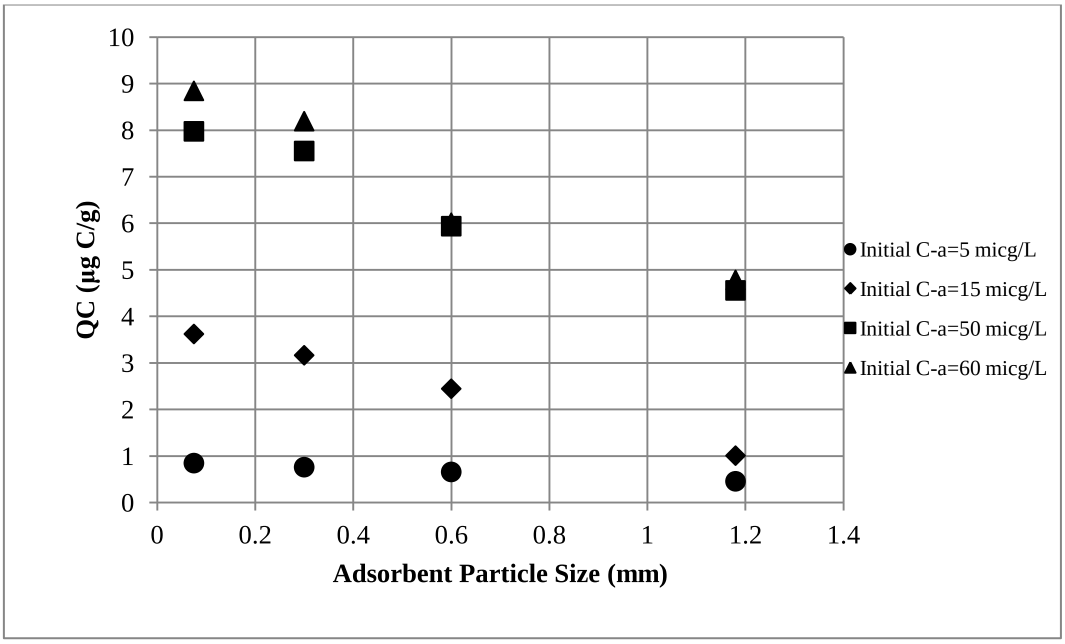

Figure 4.20: Effect of initial Chlorophyll-a variation (C-a removal density with pH=5)

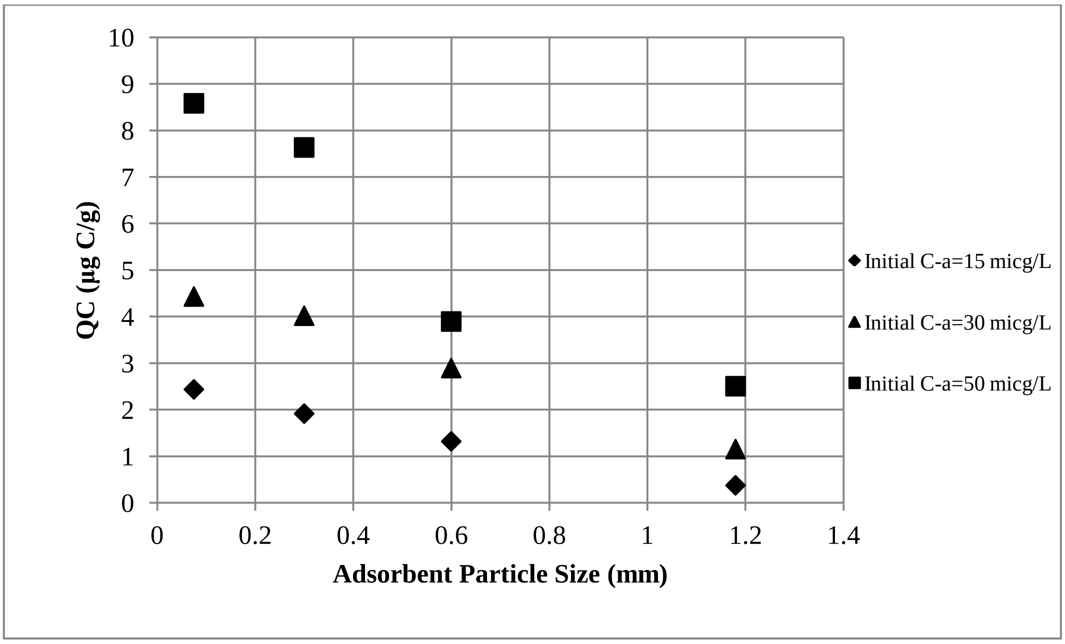

Figure 4.21: Effect of initial Chlorophyll-a variation (C-a removal density with pH=7)

4.3.6 Effect of adsorbent particle size on both phosphorus and microalgae removal

All figures presented in section 4.3 had adsorbent particle size as their x-axes. It can be clearly observed from all of them that, under any circumstances, both phosphorus and chlorophyll-a removals were decreasing as the adsorbent particle size increased. This follows the logical reasoning that a smaller particle size provides higher surface area which in turn promotes increased removal. For the case of phosphorus (see Figure 4.7 & Figure 4.12 as examples), the relation between the percentage removal of phosphorus and the particle size of activated alumina was always relatively linear. Also, the decrease in the removal percentage became more rapid as both pH and initial PC increased. On the other hand, for the case of chlorophyll-a (see Figure 4.14 as an example), the nature of the relation between the percentage removal and the particle size was different since the linear relation was absent and the slope was changing rather erratically as the adsorbent particle size changed. One explanation for that could be attributed to the sensitive nature of the fluorometric method used for chlorophyll-a measurement. It can also be regarded to the fact that coagulation might have been the main removal mechanism instead of adsorption.

4.4 Column Tests

After the thorough investigation of the results obtained from the batch tests, it was concluded that the best experimental conditions for both chlorophyll-a and phosphorus removal are acidic conditions (pH = 5) and adsorbent particle sizes of 0.6 mm or less. A trial column test was conducted in order to see whether 0.3 mm particle size is suitable for phosphorus and microalgae removal without operational issues. However, it was found that 0.3 mm particle size was small enough to cause clogging and continuous leakage from the column assembly. As a result, 0.6 mm particle size was adopted as the best adsorbent particle size for the treatment system and thus was used for the two column tests conducted for this study. The two column tests were conducted with an influent seawater of 0.5 mg/L phosphorus concentration since this value was considered to be the most realistic value and high enough to cause algal bloom in seawater [2]. However, the influent chlorophyll-a concentration (ICC) was very hard to control since it depended on the conditions of the seawater in Sharjah beaches. Therefore, ICC varied a lot during the operation of the two column experiments. The pH values of the influent seawater in the column tests were chosen to be 5 and the original pH of seawater (about 8.3) in order to justify that going through the effort of reducing the pH value was worth it. The two column tests of pH 8.3 and pH 5 were conducted at flow rates of approximately 11.2 and 20 mL/min respectively. The influent temperatures were about 22.7 ^{o}C for both columns.

4.4.1 Effluent pH and temperature

Starting with effluent pH values, it can be noticed from Figure 4.22 that, in both tests, the effluent pH values tended to initially come out as 7.5 whether by an increase from acidity or a reduction from alkalinity. This observation indicated that, regardless of the initial pH level of the water, the reaction between activated alumina and water altered the pH level of the water and brought it towards neutrality. However, as time passed, the effect of activated alumina on the pH level withered away and the effluent pH level started diverging from neutrality towards values closer and closer to the influent pH value. The effluent pH level stabilized after the processing of about 1000 pore volumes. Figure 4.23 shows that the effluent temperatures were almost constant (about 24 ^{o}C) and the same for both tests. This increase in the effluent temperature from 22.7 to 24 ^{o}C indicated that the reaction with activated alumina produced only little heat which did not create any undesirable effects on the treated water in terms of temperature.

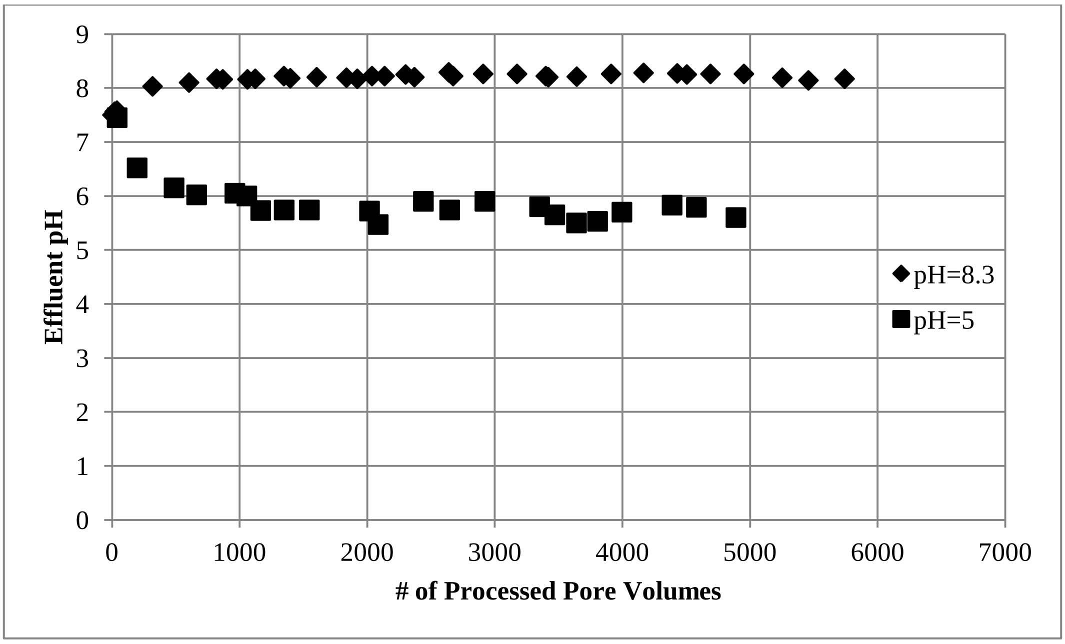

Figure 4.22: Effluent pH values of the two column tests

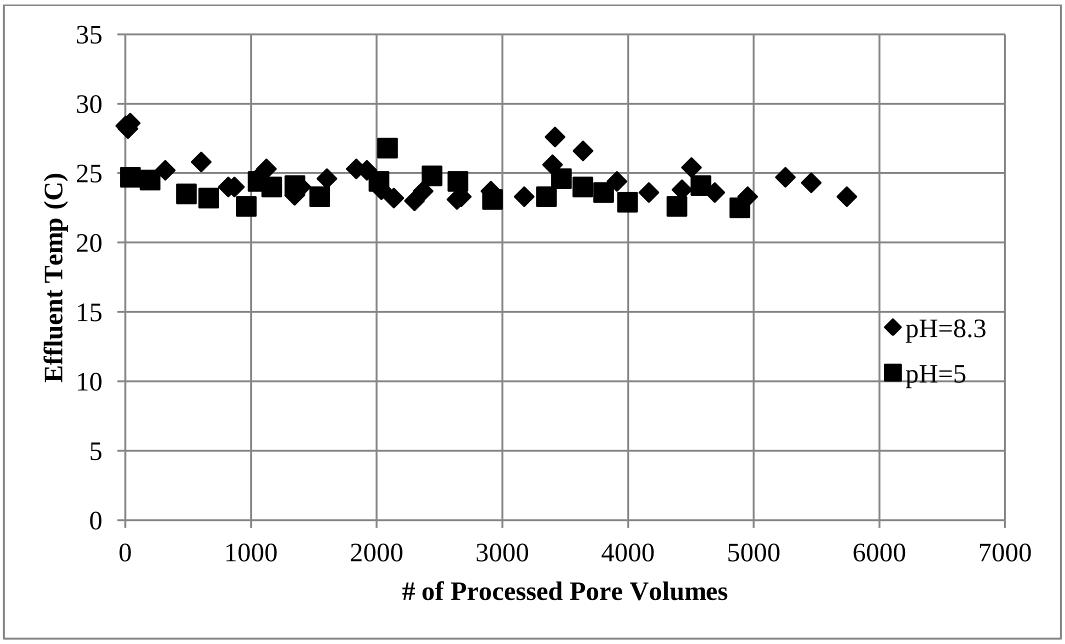

Figure 4.23: Effluent temperature values of the two column tests

4.4.2 Effluent phosphorus concentration

For phosphorus removal, the results came to agree with those obtained from the batch tests (Figure 4.24) in terms of the fact that the acidic condition (pH = 5) was better suited for phosphorus removal than the original (alkaline) condition of the seawater. There is a horizontal gap between the two data sets in Figure 4.24 of about 1000 pore volumes and a vertical gap of about 0.1 EPC to IPC ratio. Also, the breakthrough point (EPC/IPC = 0.05) for the original test occurred after processing less than 300 pore volumes whereas it occurred after 1000 pore volumes for the acidic test. This further supported the finding that phosphorus removal was more efficient in acidic than in alkaline conditions. It can also be observed from Figure 4.24 that the rate at which EPC to IPC ratio increased with respect to the number of processed pore volumes was almost the same for both tests with some minor erratic behavior. Overall, the treatment efficiency for both tests was considered very good since the percentage removal of phosphorus was still 40% for the original test and 50% for the acidic test even after processing 5000 pore volumes. It should also be noted that the empty bed contact times (EBCTs) were only 5.5 and 3 min for the original and the acidic tests respectively. Comparing these results with those obtained from the literature [22], one can see that the breakthrough point appeared there later than here but this can be regarded to the fact that the experimental conditions were extremely different. For instance, their particle size, flow rate, and EBCT were 0.065 mm, 2.7 mL/min, and 11.4 min respectively. Therefore, this difference in the breakthrough timing was logically expected.

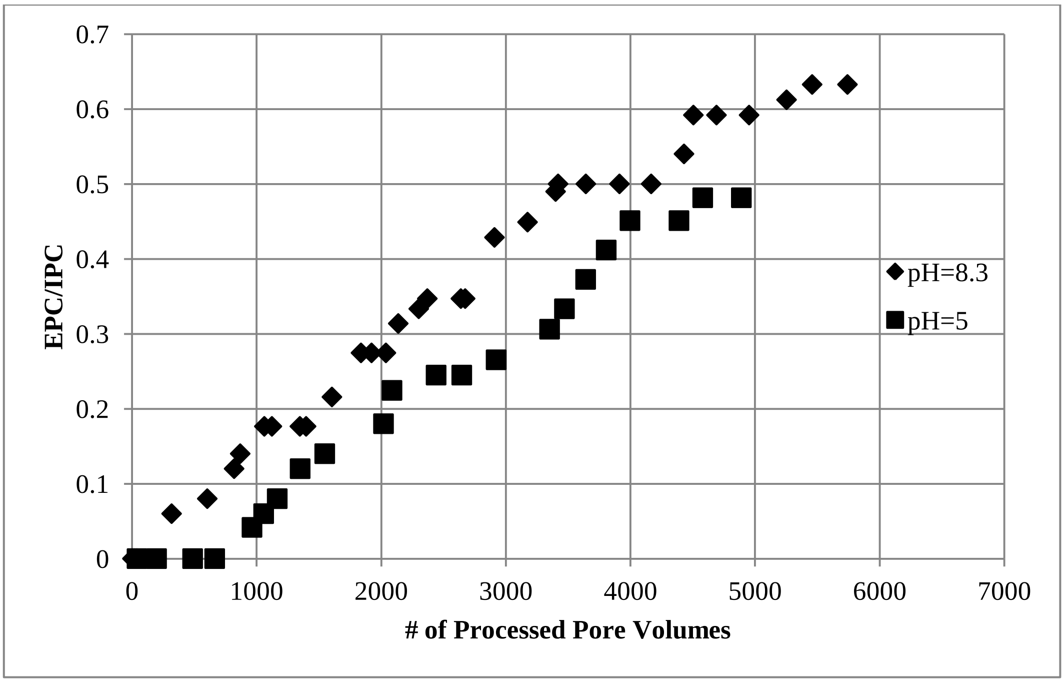

Figure 4.24: Phosphorus removal for the two column tests

4.4.3 Influent chlorophyll-a concentration

Figure 4.25 shows the ICC versus the number of processed pore volumes for the two column tests. As can be detected from the figure, there were some jumps in the values of ICC because the influent seawater samples were actually replaced or mixed with new batches of water every few days. This was done to ensure the availability of the required water volume since the container that was used to hold the influent seawater had a limited capacity (100 L). It can be observed that there was quite a big difference in the ICC values between the acidic test and the original test. This was due to the fact that the influent seawater samples were brought from Sharjah coasts at different times and thus the ICC values would depend on the conditions of these water samples at the time of collection. The ICC values for the original test were mostly between 50 and 60 µg/L while they were between 30 and 40 µg/L for the acidic test. Also, a decrease in the ICC values (for a given influent seawater sample) with time can be observed in both tests owing to the fact that the removal of seawater from the coast resulted in a less favorable conditions for microalgae to continue growing or at least remain constant. However, it is rather clear from Figure 4.25 that the acidic conditions resulted in a less rapid decrease compared to the original conditions. Nevertheless, since the initial ICC values were different, this conclusion might not be true all the time. Due to all of these differences in the conditions of the influent seawater samples, the comparison between the chlorophyll-a removal efficiencies of the two columns would not be fair and might not be easy to conduct. This claim can be supported by the findings obtained from the batch tests which showed that removal efficiencies of chlorophyll-a were highly dependent on the initial CCs especially when dealing with removal percentages.

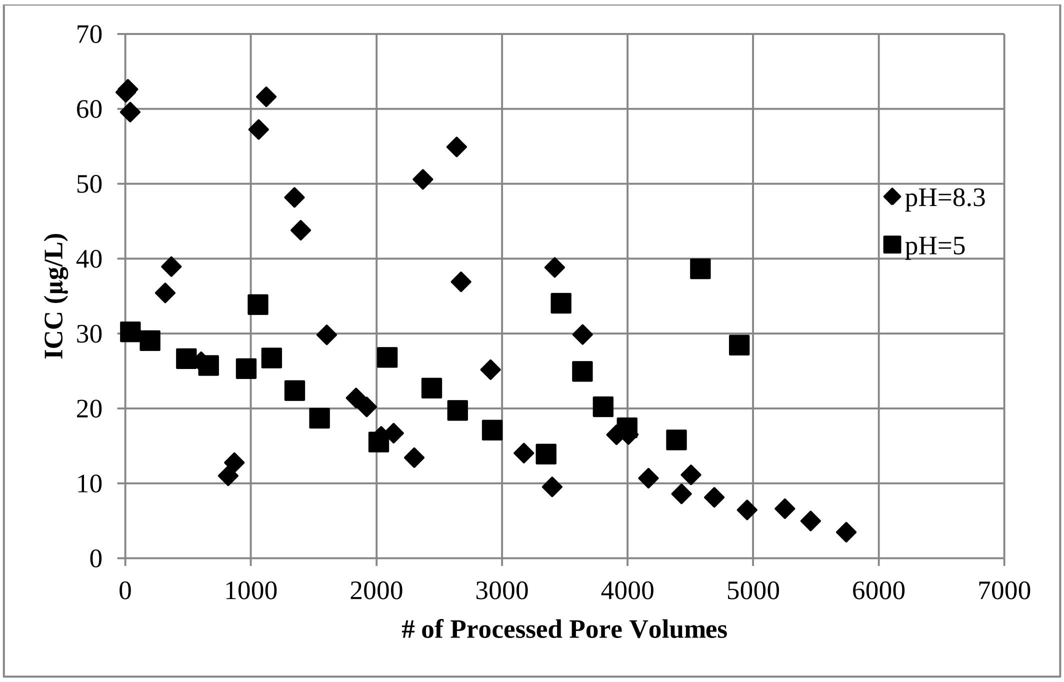

Figure 4.25: ICC for the two column tests

4.4.4 Effluent chlorophyll-a concentration

For removal of microalgae (chlorophyll-a), it can be observed from Figure 4.26 that there was no clear detection of superiority of one test over the other (i.e. no apparent effect of pH). For instance, the acidic test appeared to be better in the first 1000 pore volumes whereas the original test took the lead after that till the processing of about 4500 pore volumes. This kind of inconsistency was to be expected since, as mentioned in section 4.4.3, initial conditions were very different. Therefore, it would be expected to find that the two tests performed very closely in terms of microalgae removal. Also, it was observed that the results from both tests did not appear to follow the pattern of a typical fixed bed column adsorption experiment where the effluent concentration starts very small and continue increasing continuously (rather than behaving erratically) till it reaches a value close enough to the influent concentration. This also could be attributed to the big differences in the ICC values among the two tests as well as the continuous changes in the ICC values because of the death of microalgae and the sudden replacements of the influent seawater. Also, it is most likely that coagulation and filtration were the main removal mechanism instead of adsorption which might have changed the behavior of the results. The removal percentages of chlorophyll-a during the operation of the two column tests were on average less than those obtained from a previous pilot test (87% to 97%) conducted via microfiltration [13]. However, Figure 4.26 shows that, during the processing of about 5000-6000 pore volumes, the ECC/ICC ratio almost never exceeded 0.5 which was considered a very good value indicating that percentage removal of chlorophyll-a concentration can continue exceeding 50% during algal bloom for a long period of time. Therefore, as both phosphorus and microalgae were removed quite efficiently, the proposed treatment system can be declared as a very good treatment system for microalgae and phosphorus removal from seawater.

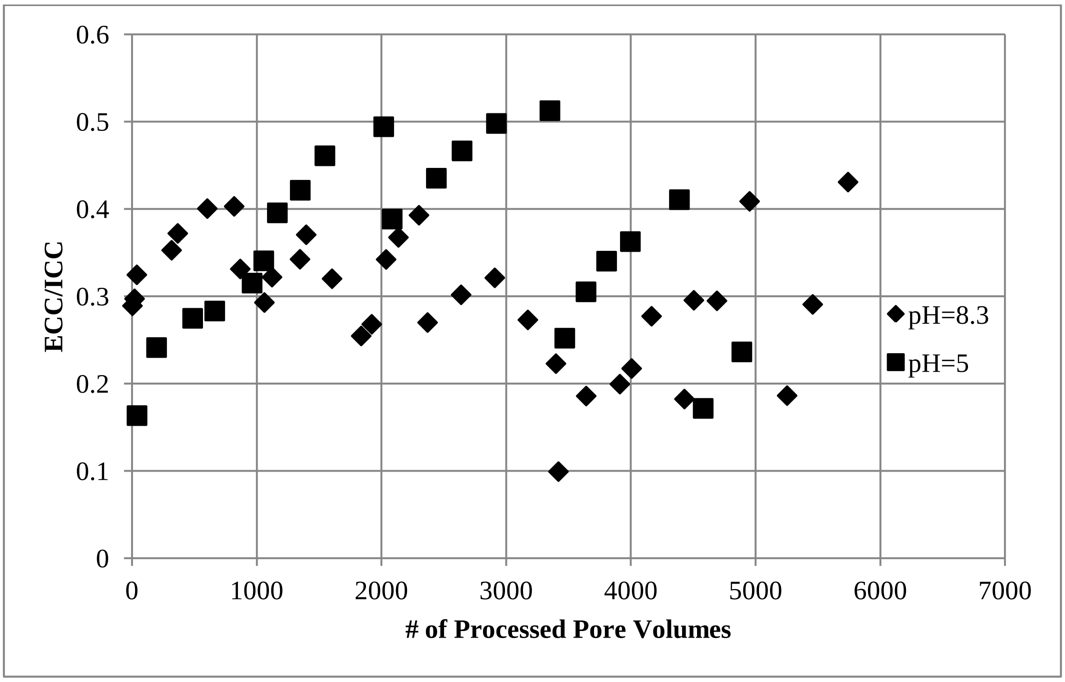

Figure 4.26: Chlorophyll-a removal for the two columns

4.4.5 The batch tests associated with the column tests

For the two batch tests associated with each column test, the following results were obtained. For phosphorus removal, the superiority of the acidic test over the original test can be clearly observed from Figure 4.27 & Figure 4.28. As the adsorbent dosage increased, the final PC to initial PC ratio for both tests decreased nonlinearly at a decreasing rate and both values got closer and closer to each other being almost equal (about 0.05) at an adsorbent dosage of 8 g/L (Figure 4.27). Figure 4.28 shows how the adsorption density increased as the final PC increased and shows how both Freundlich and Langmuir isotherm models were able to sufficiently fit the experimental data. However, statistical analysis suggested that the Freunlich isotherm model was much better at representing the experimental results and this can be ascertained by comparing the coefficients of determination presented in Table 4.1. It is also observed from Figure 4.28 that the rate of increase in the adsorption density with respect to the final PC was greater for the case of the acidic test than for the case of the original test. This can also be deduced from the kinetic parameters shown in Table 4.1 since the values of both (1/n) and (a) for the acidic test were greater than those for the original test. Also, the average slopes of the Freundlich curves in Figure 4.28 were calculated and found to be 981 cm^3/g for the original test and 1711 cm^3/g for the acidic test. These values were used to calculate the retardation factors for the column tests. The retardation factors came to be 975 and 1797 for the original and acidic tests respectively. These values agreed with the results obtained in Figure 4.24 which showed about 1000 pore volumes gap between the two tests.

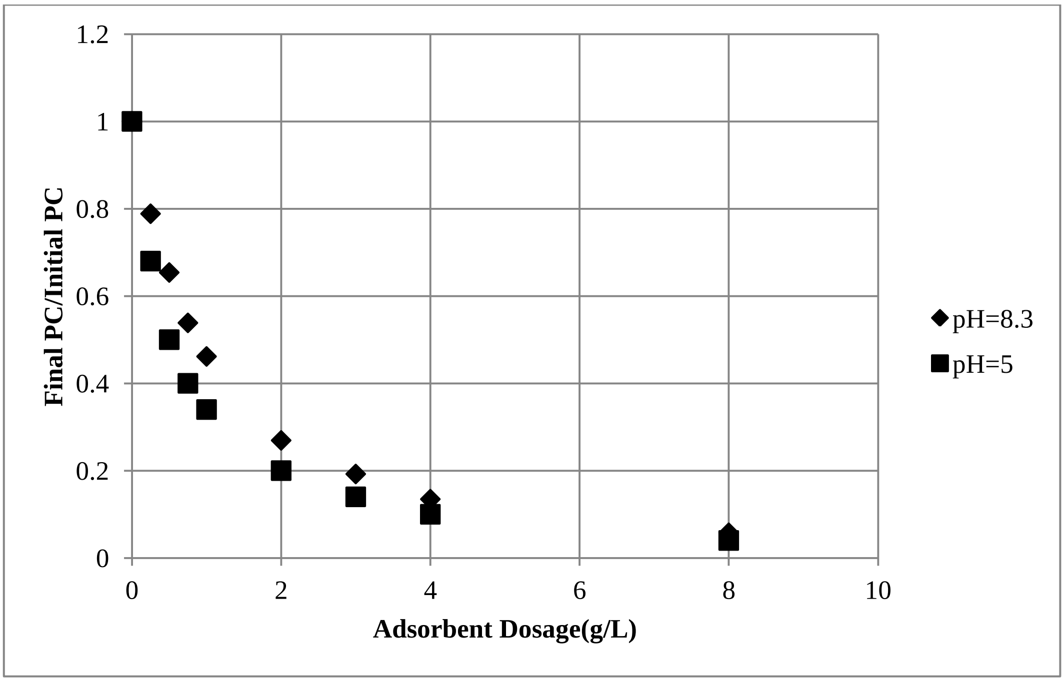

Figure 4.27: The batch tests associated with the column tests for phosphorus removal

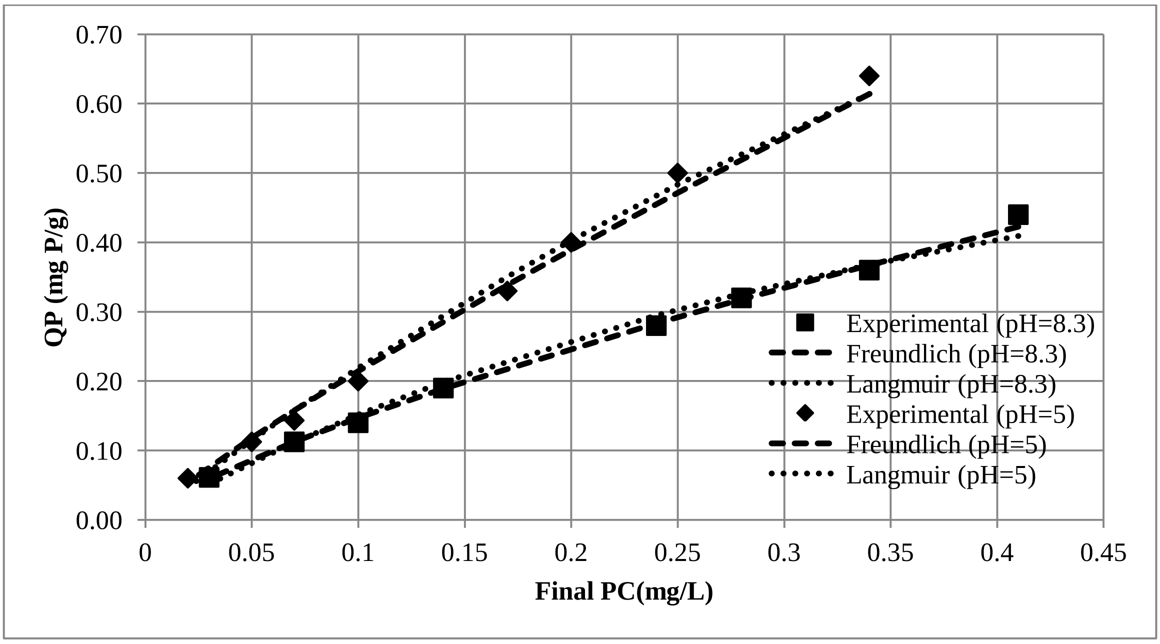

Figure 4.28: Comparisons between the isotherm models and the experimental results obtained from the phosphorus batch tests associated with the column tests

Table 4.1: Kinetic parameters for the phosphorus batch tests associated with the column tests

Srl. No.	**Influent pH Value**	**Isotherm Model**					
		Freundlich			**Langmuir**		
		K_d	**1/n**	**R^2**	**a**	**b**	**R^2**
1	8.3	0.82395	0.7488	0.9971	0.90604	2.00928	0.9877
2	5	1.5531	0.86	0.9966	2.46548	0.9757	0.9942

For the batch tests associated with chlorophyll-a removal, Figure 4.29 & Figure 4.30 show relatively the same results obtained for the phosphorus removal batch tests. Unlike the results obtained from the column test itself, the superiority of the acidic test to the original test was very obvious from the batch tests' results. This was due to the fact that at the time of execution of the two batch tests, the initial CCs were fortunately almost the same (20 µg/L). As the adsorbent dosage increased, the final CC to initial CC ratio for both tests decreased nonlinearly at a decreasing rate (Figure 4.29). Figure 4.30 shows how the removal density increased as the final CC increased and shows how both Freundlich and Langmuir isotherm models were able to sufficiently fit the experimental data. However, statistical analysis suggested that the Langmuir isotherm model was slightly better at representing the experimental results and this can be ascertained by comparing the coefficients of determination presented in Table 4.2. It is also observable from Figure 4.30 that the rate of increase in the removal density with respect to the final CC was greater for the case of the acidic test than for the case of the original test. This can also be deduced from the kinetic parameters shown in Table 4.2 since the values of both (1/n) and (a) for the acidic test were greater than those for the original test.

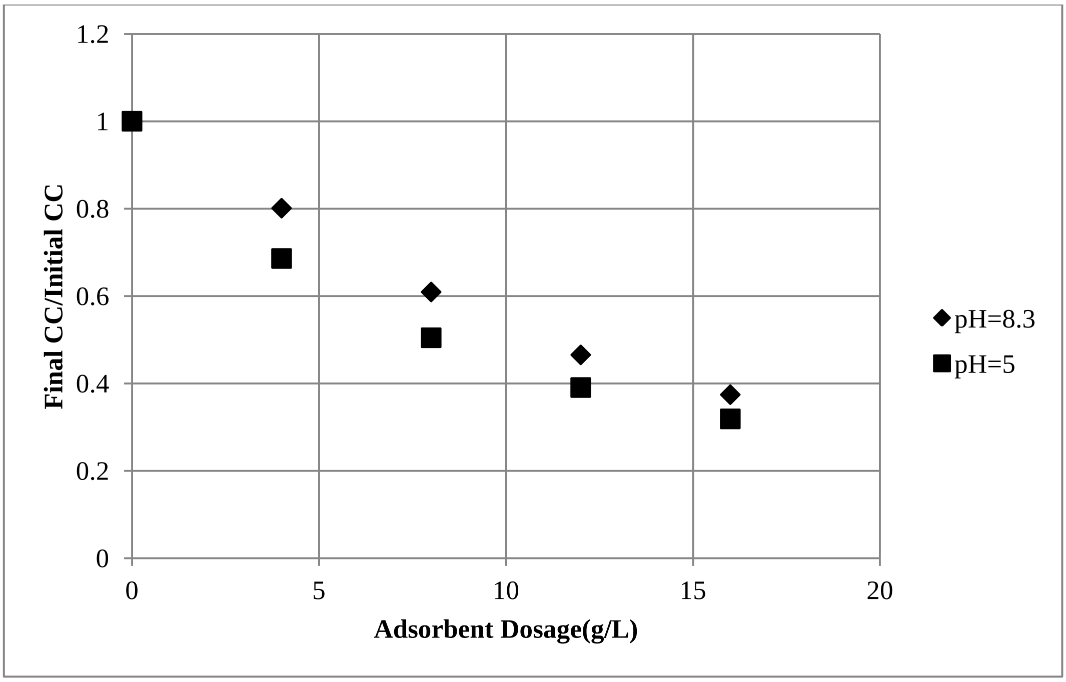

Figure 4.29: The batch tests associated with the column tests for chlorophyll-a removal

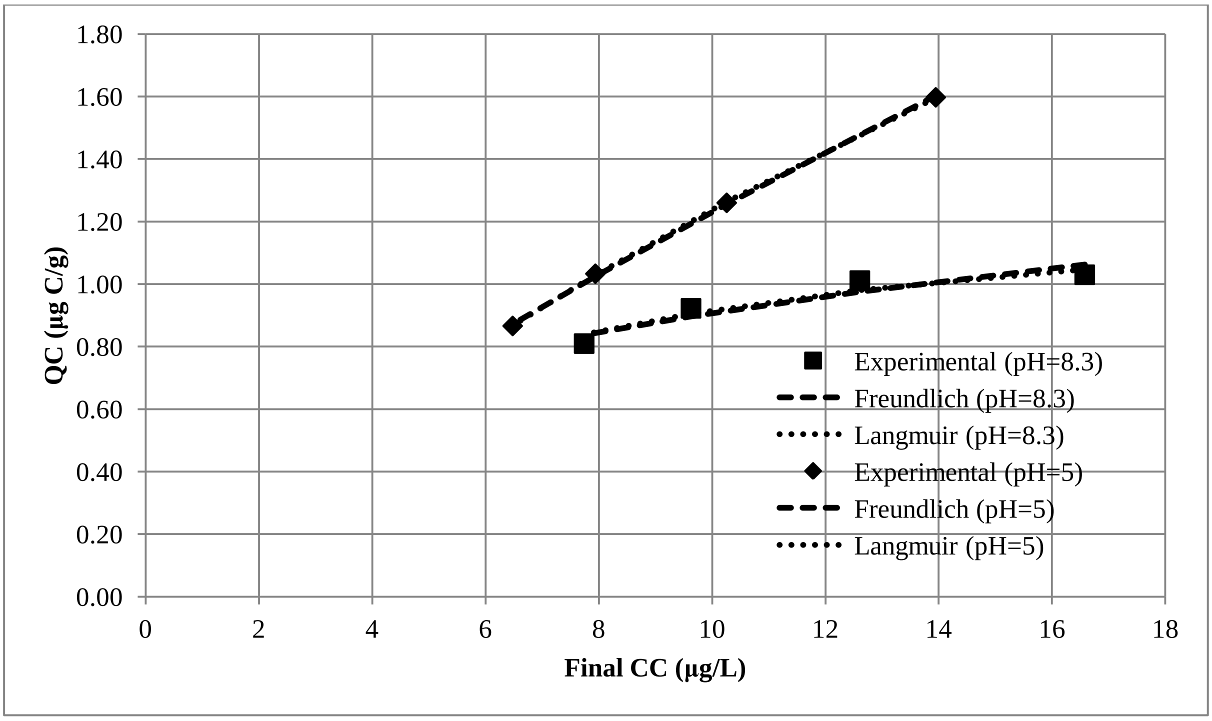

Figure 4.30: Comparisons between the isotherm models and the experimental results obtained from the chlorophyll-a batch tests associated with the column tests

Table 4.2: Kinetic parameters for the chlorophyll-a batch tests associated with the column tests

Srl. No.	**Influent pH Value**	**Isotherm Model**					
		Freundlich			**Langmuir**		
		K_d	**1/n**	**R^2**	**a**	**b**	**R^2**
1	8.3	0.44096	0.3132	0.9979	1.33726	0.21757	0.9987
2	5	0.19751	0.7946	1	5.88582	0.02667	1

4.5 Desorption Batch Test

For the desorption test, it can be observed from Figure 4.31 how the final (desorbed) PC increased as the adsorbent dosage increased reaching a value of about 3 mg/L at an adsorbent dosage of 16 g/L. The relationship seemed to be slightly nonlinear with a reduction in the rate of increase in the desorbed phosphorus concentration as the adsorbent dosage increased. As expected, Figure 4.32 shows how the desorption density of phosphorus decreased as the desorbed phosphorus concentration increased. It also shows that both isotherm models were able to sufficiently fit the experimental data except for the case of a desorbed phosphorus concentration of 0.3 mg/L where it could not be properly fit by the Langmuir isotherm model. The Freundlich isotherm model was much better in representing the experimental data than the Langmuir isotherm model as can be deduced from the coefficients of determination (Table 4.3). Also, it can be noted from Table 4.3 that the (1/n) and (b) values are actually negative thus implying that desorption was taking place in this test. The ability to recover phosphorus at a pH value of 13.1 was due to the fact that, in alkaline conditions, the abundance of hydroxide anions in the solution stimulates the desire of activated alumina to adsorb hydroxide by releasing the previously adsorbed orthophosphate.

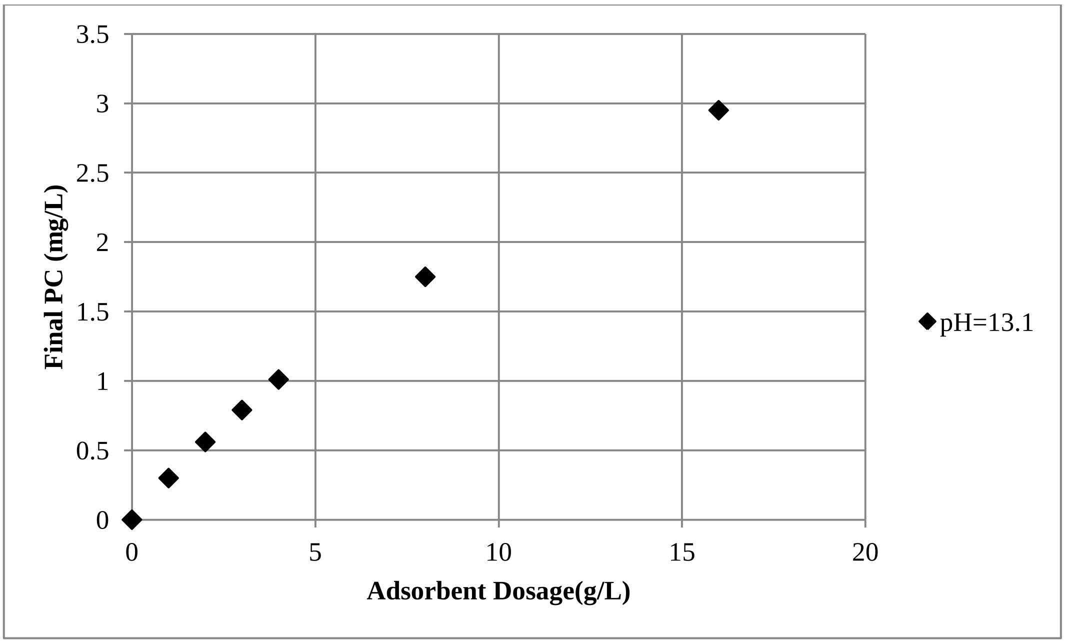

Figure 4.31: Desorption batch test for phosphorus recovery

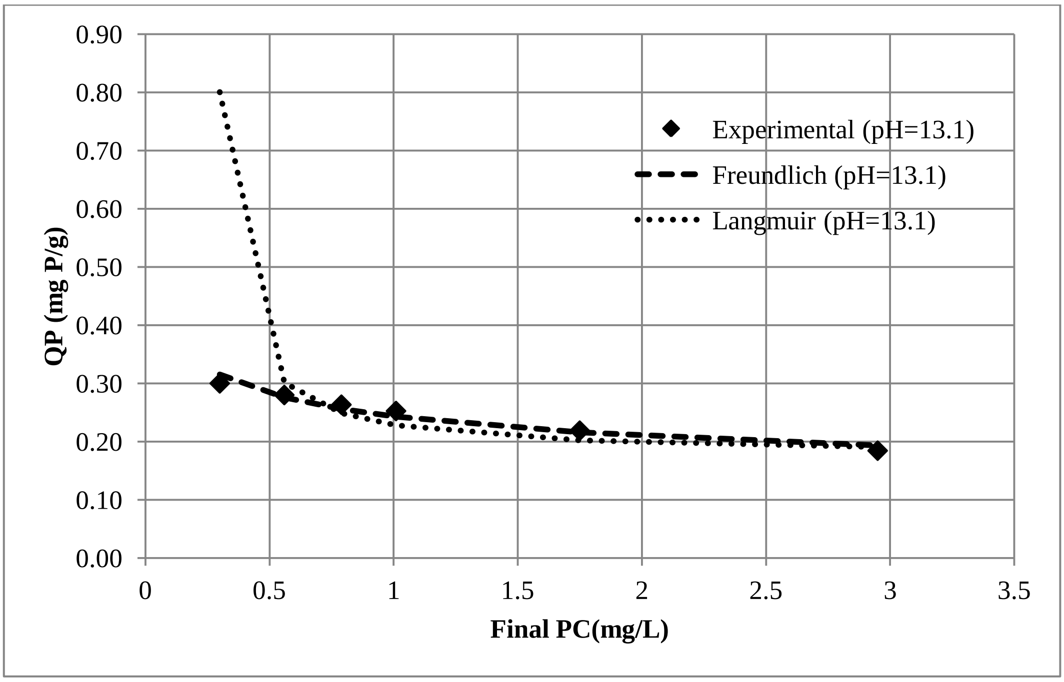

Figure 4.32: Comparisons between the isotherm models and the experimental results obtained from the desorption batch test

Table 4.3: Kinetic parameters for the desorption batch test

Srl. No.	pH Level	Isotherm Model					
		Freundlich			Langmuir		
		K_d	1/n	R^2	a	b	R^2
1	13.1	0.24344	-0.2139	0.9494	0.17511	-4.26657	0.5546

5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Among the different materials tested, activated alumina (even with a particle size of 4-5 mm) was the most suitable adsorbent for phosphorus removal from synthetic water. Further batch experiments conducted on actual seawater using activated alumina showed that acidic conditions (pH = 5) and a particle size of 0.6 mm were the most feasible conditions to achieve maximum removal of phosphorus and microalgae (chlorophyll-a) from algal contaminated seawater. The removal percentages for both phosphorus and chlorophyll-a were high enough (more than 84% for phosphorus and more than 40% for chlorophyll-a) considering the fact that only 4 g/L of activated alumina was used in all of these experiments. These experiments also showed how the removal density increases with the increase of initial phosphorus and chlorophyll-a concentrations while the percentage removal decreases. Two column experiments were then conducted with an adsorbent particle size of 0.6 mm and pH levels of 8.3 and 5 in order to investigate the feasibility of the treatment system and the superiority of the acidic conditions over the original seawater conditions. These experiments showed good results even after the processing of 5000 pore volumes. The removal percentages remained more than 50% for both phosphorus and chlorophyll-a without affecting the temperature of effluent seawater (only an increase of 2^{o} C). The comparisons between the original and the acidic experiments for phosphorus removal ensured the superiority of the acidic conditions with horizontal and vertical gaps of 1000 pore volumes and 0.1 EPC to IPC ratio respectively. However, the comparisons between the original and the acidic experiments for microalgae removal were inconclusive. Nevertheless, these comparisons were believed to be unfair due to extreme differences (the ICCs for the original test were almost twice the ICCs for the acidic test) in the characteristics of the two influent seawater samples. Also, the main mechanism for microalgae removal was believed to be coagulation and filtration instead of the intended adsorption. A desorption batch test proved that phosphorus can be recovered from activated alumina in the presence of extreme alkaline conditions (pH = 13.1). These recovered phosphorus-rich solutions can be later reused for the preparation of fertilizers that can be utilized in agriculture.

This dissertation was able to prove that activated alumina in particular, with acidic conditions (pH = 5) and 0.6 mm particle size, is a very good material for phosphorus and microalgae removal from seawater.

5.2 Recommendations

It is recommended, for future studies, to conduct additional batch and column experiments under various acidic conditions in order to further investigate the optimum acidic pH value. Also, the different species of microalgae and whether they can all be removed using the same treatment system adopted in this dissertation should be investigated. Moreover, investigating the extreme conditions of algal contamination (algal blooms or red tides) is a must before these treatment systems can be adopted for use in desalination plants. Further investigations via pilot tests are also required in order to ascertain the feasibility of such treatment systems for real life applications. It is also recommended to attempt modeling of the column experiments using black box tools such as artificial neural networks in order to assess their feasibility especially for the chlorophyll-a data which are highly erratic. Most importantly, other types of experiments should be conducted to further ascertain the removal mechanism of microalgae.

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APPENDIX

Additional Figures and Tables for the Experimental Data

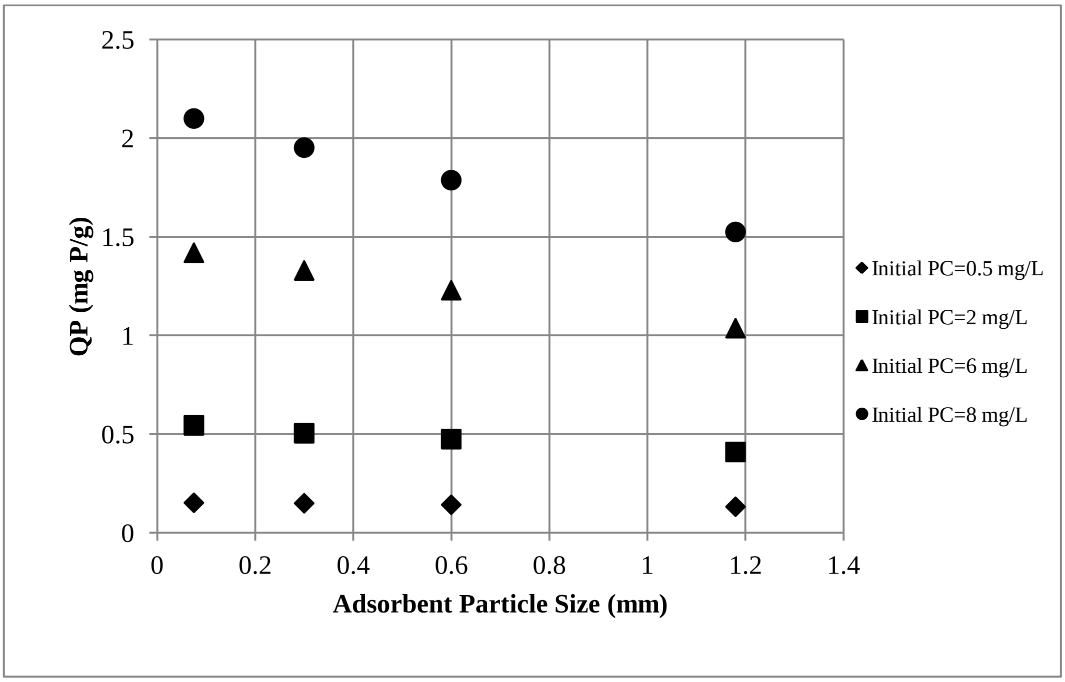

Figure A.1: Phosphorus adsorption density versus adsorbent particle size (batch tests with pH = 7)

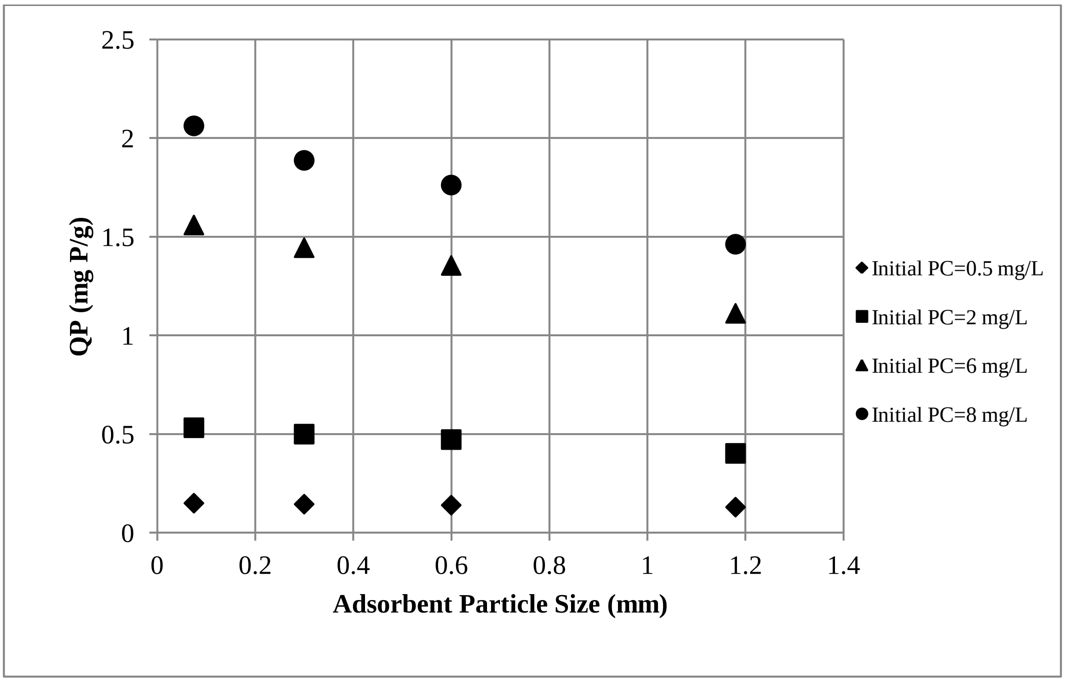

Figure A.2: Phosphorus adsorption density versus adsorbent particle size (batch tests with original pH = 8)

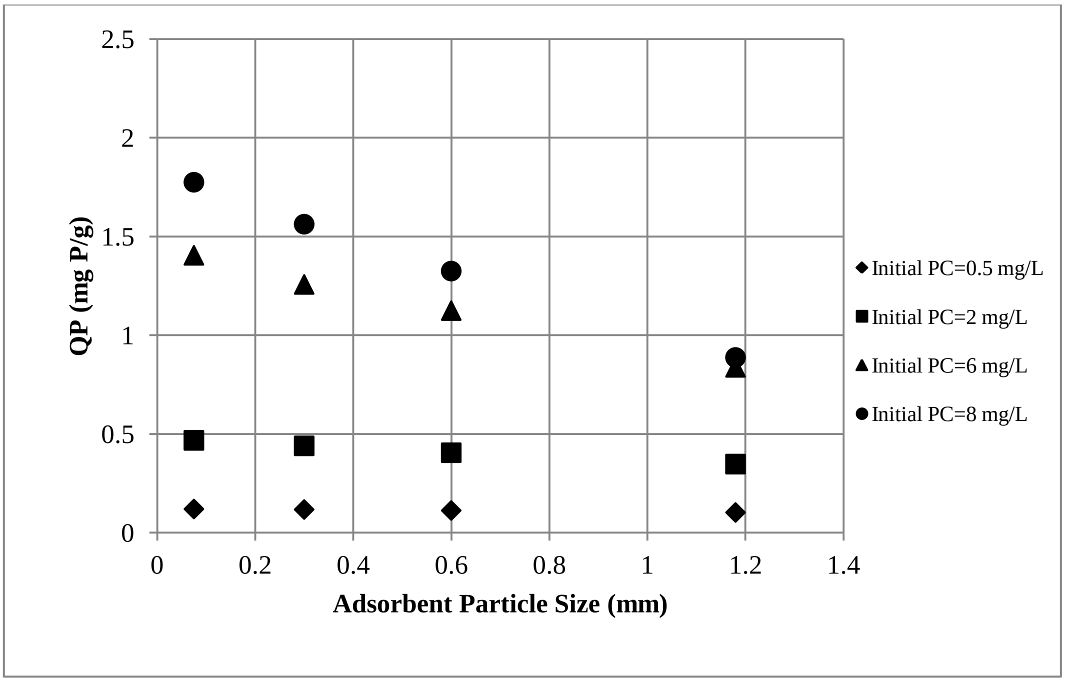

Figure A.3: Phosphorus adsorption density versus adsorbent particle size (batch tests with pH = 9)

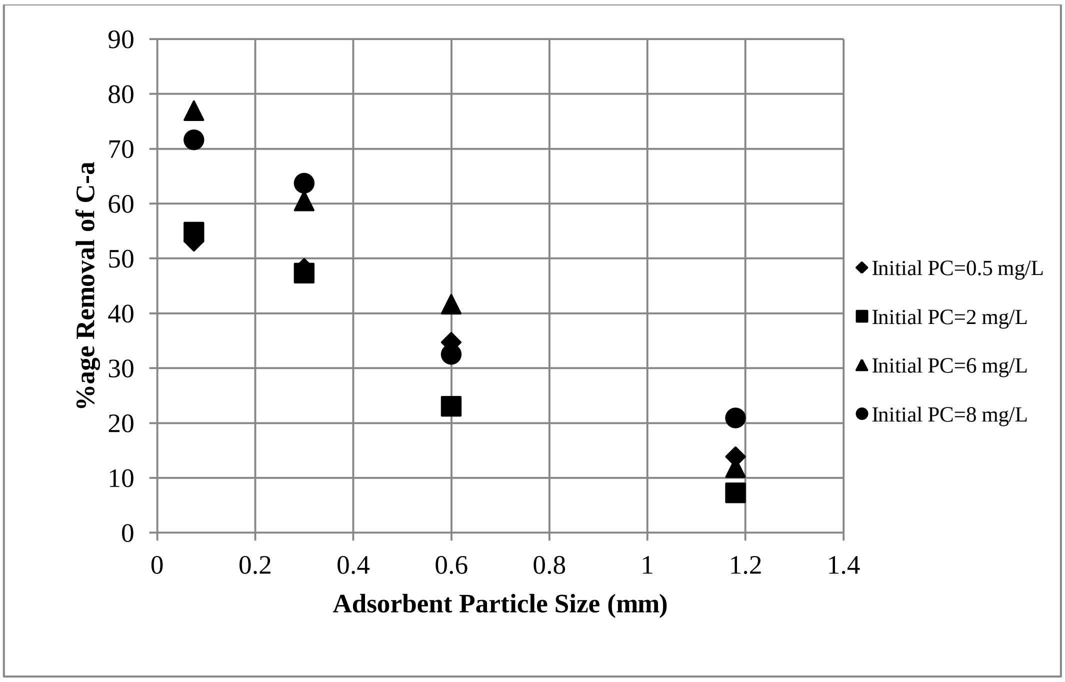

Figure A.4: Four batch tests using activated alumina (C-a removal with pH = 7)

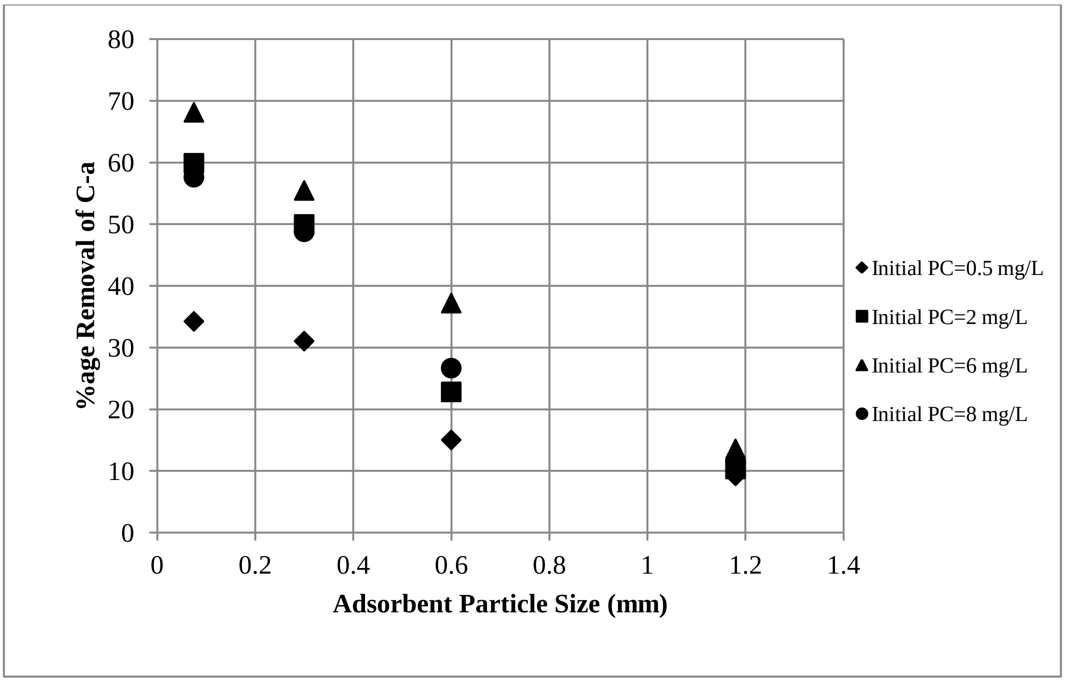

Figure A.5: Four batch tests using activated alumina (C-a removal with original pH = 8)

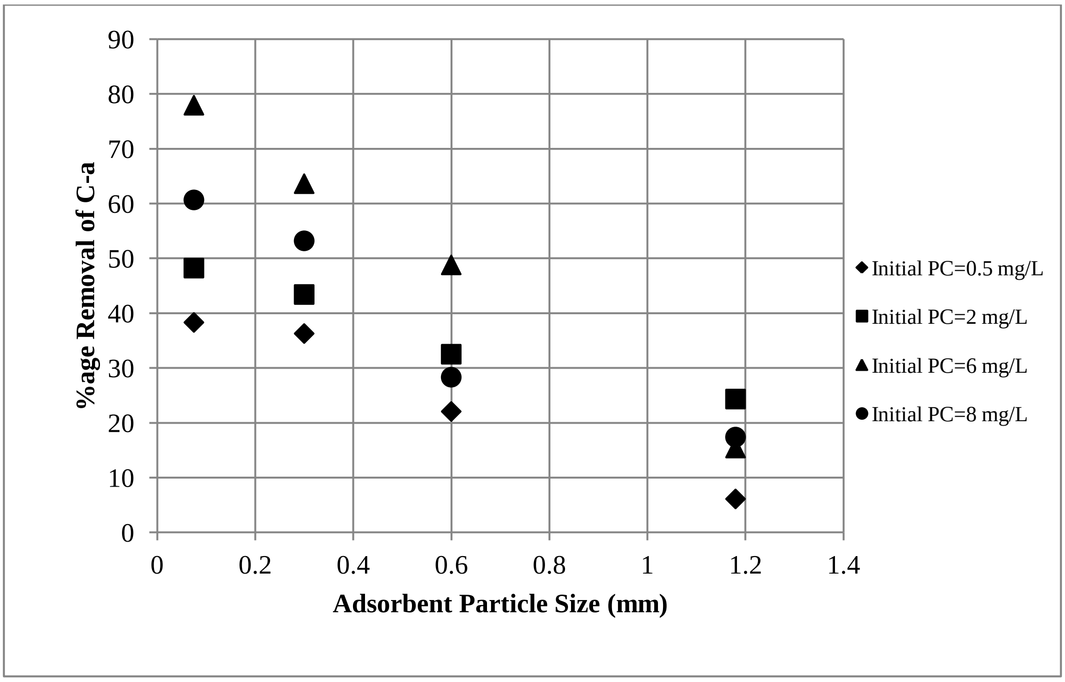

Figure A.6: Four batch tests using activated alumina (C-a removal with pH = 9)

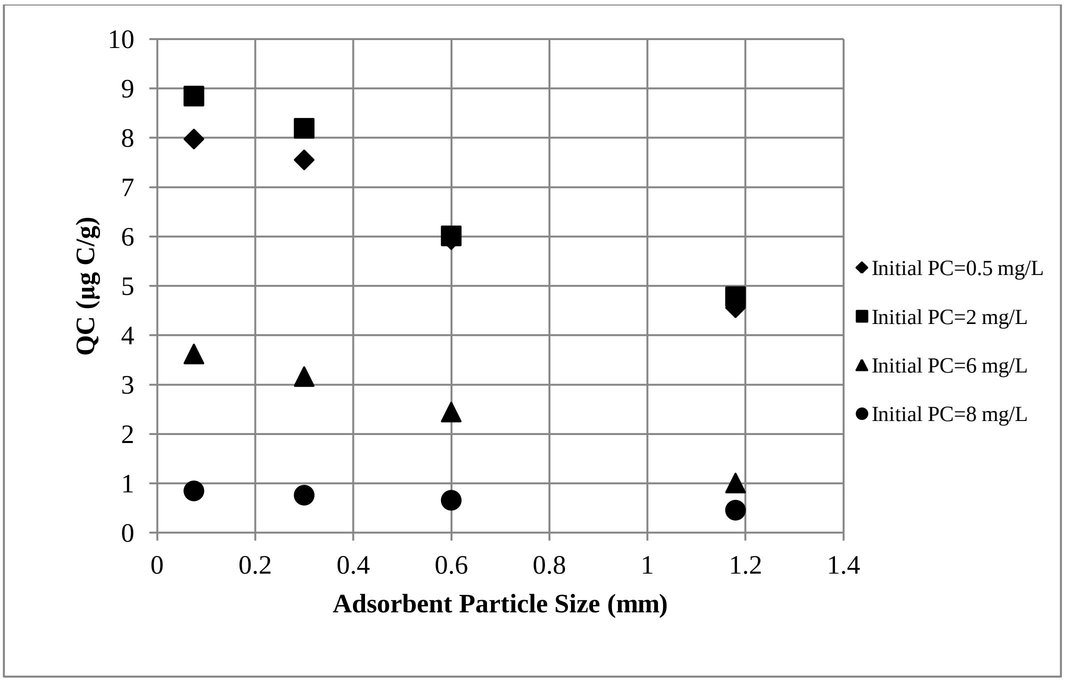

Figure A.7: Chlorophyll-a removal density versus adsorbent particle size (batch tests with pH = 5)

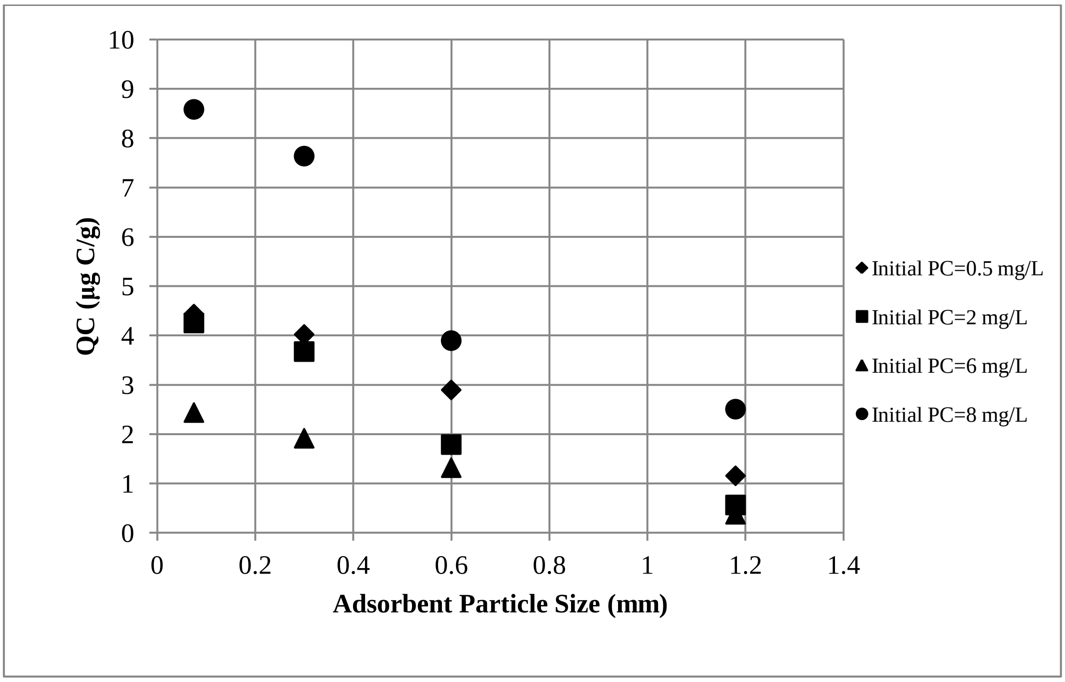

Figure A.8: Chlorophyll-a removal density versus adsorbent particle size (batch tests with pH = 7)

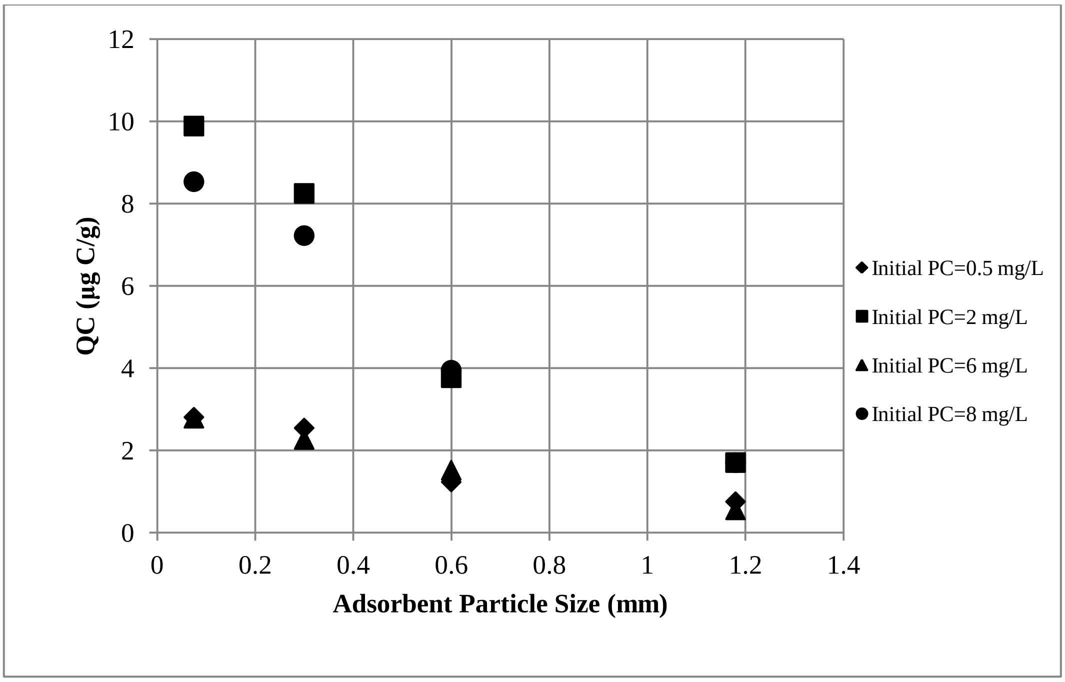

Figure A.9: Chlorophyll-a removal density versus adsorbent particle size (batch tests with original pH = 8)

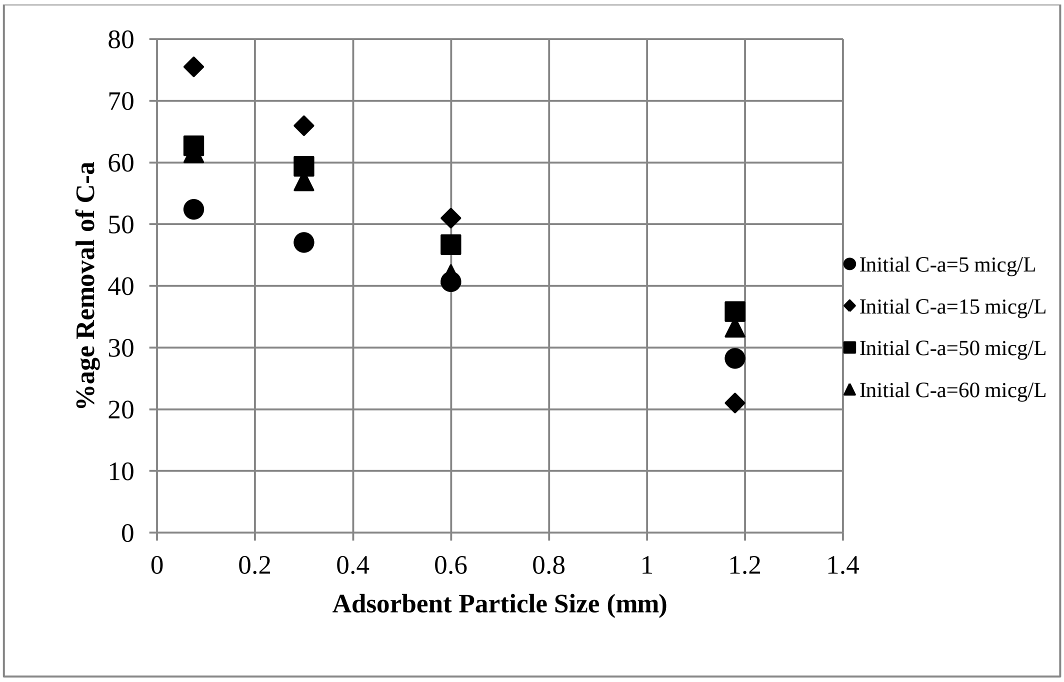

Figure A.10: Effect of initial Chlorophyll-a variation (C-a % age removal with pH=5)

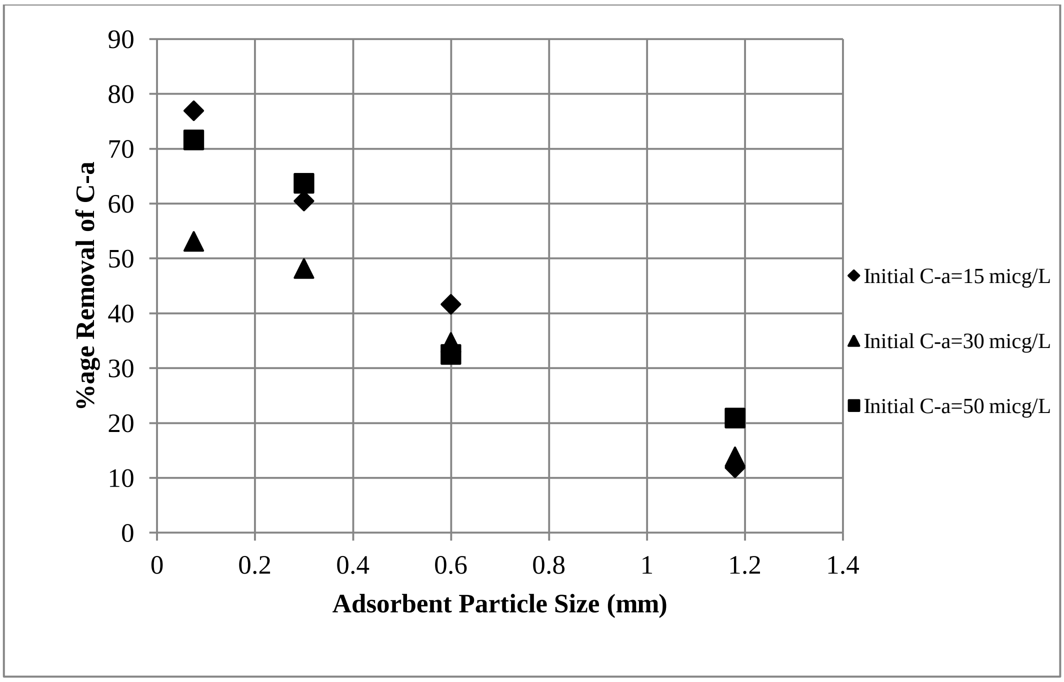

Figure A.11: Effect of initial Chlorophyll-a variation (C-a %age removal with pH=7)

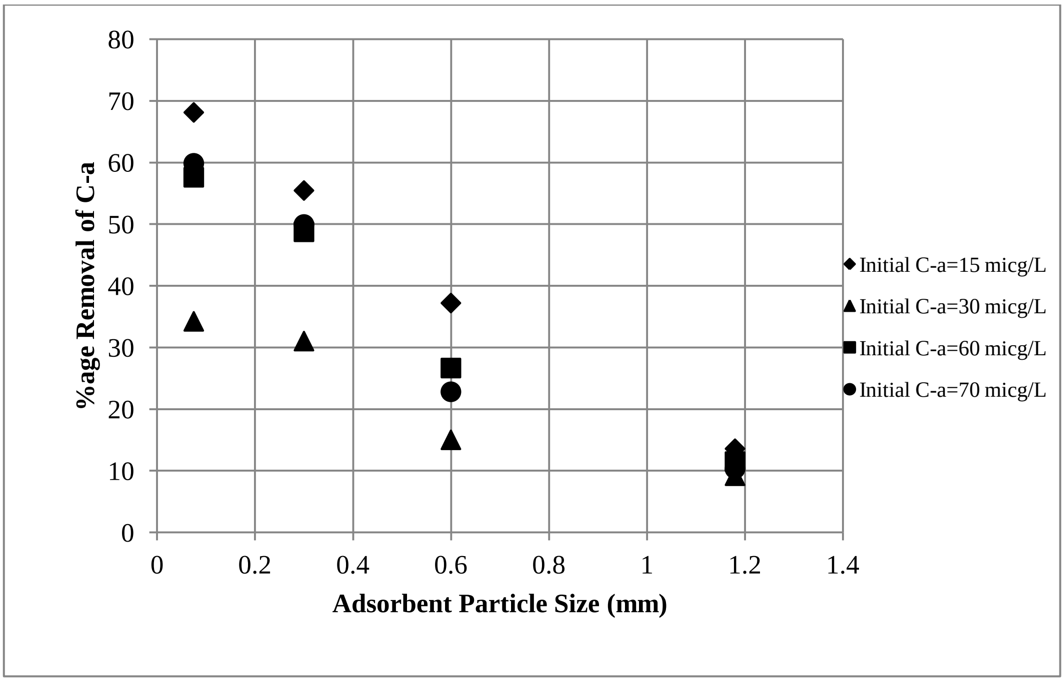

Figure A.12: Effect of initial Chlorophyll-a variation (C-a %age removal with original pH=8)

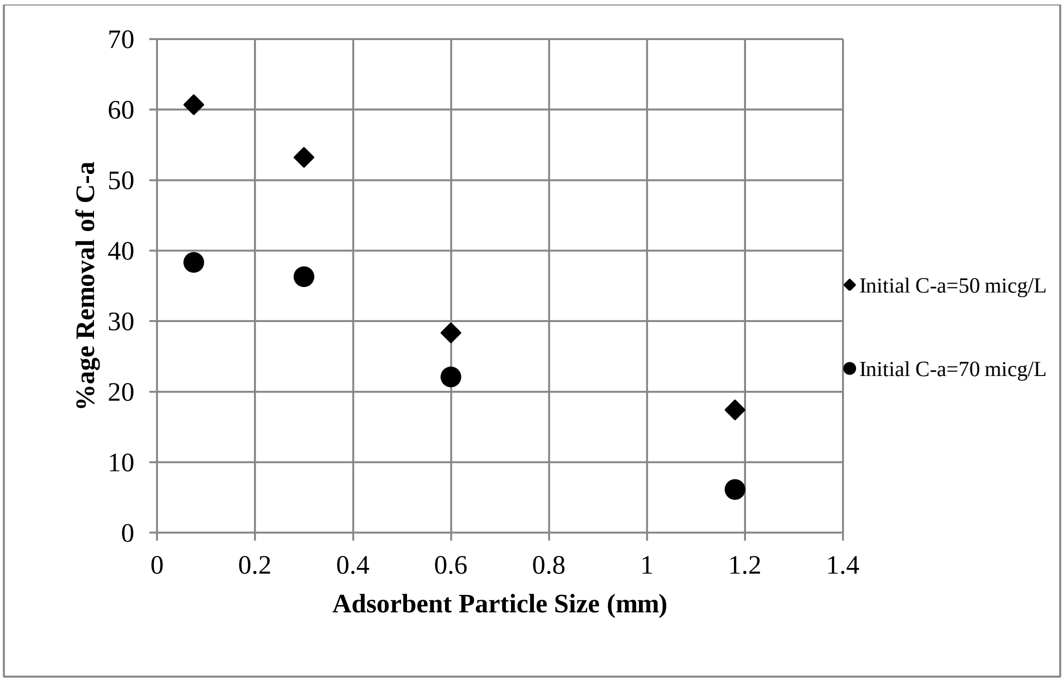

Figure A.13: Effect of initial Chlorophyll-a variation (C-a %age removal with pH=9)

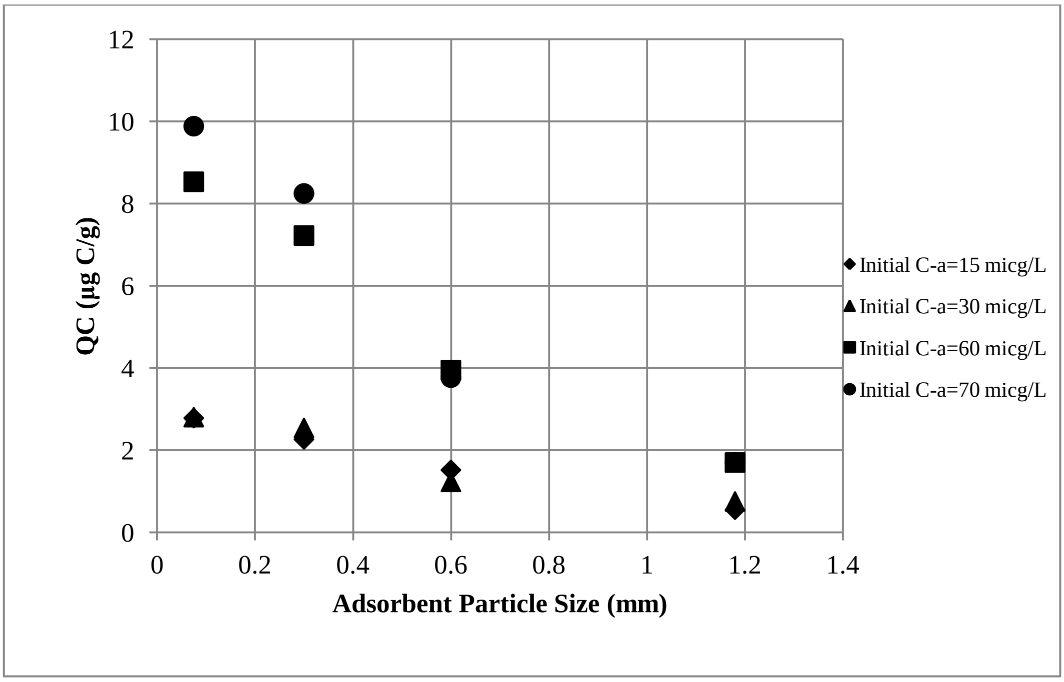

Figure A.14: Effect of initial Chlorophyll-a variation (C-a removal density with original pH=8)

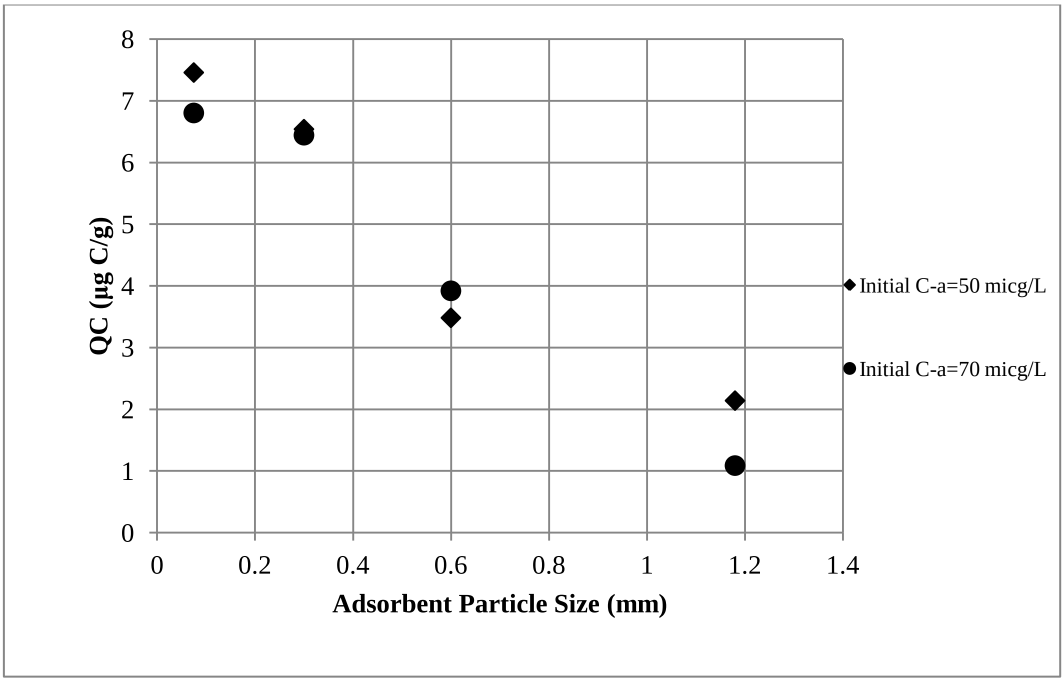

Figure A.15: Effect of initial Chlorophyll-a variation (C-a removal density with pH=9)

Table A.1: Raw experimental data for the four batch tests of 0.5 mg/L initial PC

Group	**Blank**	**Activated Alumina**			
Sample No.	**1**	**2**	**3**	**4**	**5**
Particle Size (mm)	**None**	**1.18**	**0.6**	**0.3**	**0.075**
Duration of Shaking (hr)	**3**				
Static Time Duration (hr)	**72**				
Date	**2-Oct-11**				
pH	4.94	5.03	4.95	5.04	5.04
Temp	28.3	27.5	28.3	27.4	28.2
Chlorophyll-a (µg/L)	50.89	32.66	27.14	20.68	18.99
%age C removed	None	35.82	46.67	59.36	62.68
QC (µg C/g)	None	4.56	5.94	7.55	7.98
P(mg/L)	0.54	0.06	0.03	0.02	0.01
%age P removed	None	88.89	94.44	96.30	98.15
QP (mg P/g)	None	0.1200	0.1275	0.1300	0.1325
Date	**16-Oct-11**				
pH	7.1	6.97	6.97	6.96	6.97
Temp	24.9	25	24.9	24.9	24.7
Chlorophyll-a (µg/L)	33.38	28.76	21.8	17.3	15.65
%age C removed	None	13.84	34.69	48.17	53.12
QC (µg C/g)	None	1.16	2.90	4.02	4.43
P(mg/L)	0.62	0.09	0.05	0.02	0.01
%age P removed	None	85.48	91.94	96.77	98.39
QP (mg P/g)	None	0.1325	0.1425	0.1500	0.1525
Date	**16-Oct-11**				
pH	8.14	7.83	7.74	7.74	7.66
Temp	25	25.1	25.1	25	24.8
Chlorophyll-a (µg/L)	32.79	29.77	27.86	22.61	21.56
%age C removed	None	9.21	15.04	31.05	34.25
QC (µg C/g)	None	0.76	1.23	2.55	2.81
P(mg/L)	0.62	0.10	0.06	0.04	0.02
%age P removed	None	83.87	90.32	93.55	96.77
QP (mg P/g)	None	0.1300	0.1400	0.1450	0.1500
Date	**2-Oct-11**				
pH	9.08	8.95	8.98	8.94	8.96
Temp	28.3	28.2	28.2	28.2	28.2
Chlorophyll-a (µg/L)	70.98	66.63	55.3	45.21	43.77
%age C removed	None	6.13	22.09	36.31	38.33
QC (µg C/g)	None	1.09	3.92	6.44	6.80
P(mg/L)	0.49	0.08	0.04	0.02	0.01
%age P removed	None	83.67	91.84	95.92	97.96
QP (mg P/g)	None	0.1025	0.1125	0.1175	0.1200

Table A.2: Raw experimental data for the four batch tests of 2 mg/L initial PC

Group	**Blank**	**Activated Alumina**			
Sample No.	**1**	**2**	**3**	**4**	**5**
Particle Size (mm)	**None**	**1.18**	**0.6**	**0.3**	**0.075**
Duration of Shaking (hr)	**3**				
Static Time Duration (hr)	**72**				
Date	**3-Oct-11**				
pH	4.9	4.94	5.03	4.96	5.01
Temp	27	27.1	27	26.9	26.7
Chlorophyll-a (µg/L)	57.49	38.36	33.44	24.72	22.11
%age C removed	None	33.28	41.83	57.00	61.54
QC (µg C/g)	None	4.78	6.01	8.19	8.85
P(mg/L)	2.60	0.35	0.17	0.08	0.02
%age P removed	None	86.54	93.46	96.92	99.23
QP (mg P/g)	None	0.5625	0.6075	0.6300	0.6450
Date	**16-Oct-11**				
pH	7.1	7.01	6.9	6.95	6.91
Temp	24.8	25	24.9	25	24.9
Chlorophyll-a (µg/L)	31.05	28.8	23.9	16.36	14.04
%age C removed	None	7.25	23.03	47.31	54.78
QC (µg C/g)	None	0.56	1.79	3.67	4.25
P(mg/L)	2.20	0.56	0.30	0.18	0.02
%age P removed	None	74.55	86.36	91.82	99.09
QP (mg P/g)	None	0.4100	0.4750	0.5050	0.5450
Date	**18-Oct-11**				
pH	8.14	7.79	7.72	7.78	7.7
Temp	26.4	26.3	26.3	26.3	26.4
Chlorophyll-a (µg/L)	66.04	59.22	50.97	33.05	26.5
%age C removed	None	10.33	22.82	49.95	59.87
QC (µg C/g)	None	1.71	3.77	8.25	9.89
P(mg/L)	2.20	0.59	0.31	0.20	0.07
%age P removed	None	73.18	85.91	90.91	96.82
QP (mg P/g)	None	0.4025	0.4725	0.5000	0.5325
Date	**3-Oct-11**				
pH	8.93	9.08	9.03	9.01	9.1
Temp	26.9	26.8	25	25	25
Chlorophyll-a (µg/L)	49.64	37.55	33.49	28.08	25.69
%age C removed	None	24.36	32.53	43.43	48.25
QC (µg C/g)	None	3.02	4.04	5.39	5.99
P(mg/L)	1.95	0.56	0.33	0.19	0.08
%age P removed	None	71.28	83.08	90.26	95.90
QP (mg P/g)	None	0.3475	0.4050	0.4400	0.4675

Table A.3: Raw experimental data for the four batch tests of 6 mg/L initial PC

Group	Blank	Activated Alumina			
Sample No.	1	2	3	4	5
Particle Size (mm)	None	1.18	0.6	0.3	0.075
Duration of Shaking (hr)	3				
Static Time Duration (hr)	72				
Date	22-Sep-11				
pH	4.9	5.01	4.97	4.9	5.05
Temp	25	25	25	25	25
Chlorophyll-a (µg/L)	19.19	15.16	9.41	6.536	4.705
%age C removed	None	21.00	50.96	65.94	75.48
QC (µg C/g)	None	1.01	2.45	3.16	3.62
P(mg/L)	5.70	1.00	0.52	0.25	0.08
%age P removed	None	82.46	90.88	95.61	98.60
QP (mg P/g)	None	1.1750	1.2950	1.3625	1.4050
Date	18-Sep-11				
pH	6.98	7.09	7.07	7.01	7.04
Temp	26.9	25	25	25	25
Chlorophyll-a (µg/L)	12.67	11.17	7.394	5.008	2.923
%age C removed	None	11.84	41.64	60.47	76.93
QC (µg C/g)	None	0.38	1.32	1.92	2.44
P(mg/L)	5.80	1.65	0.88	0.48	0.12
%age P removed	None	71.55	84.83	91.72	97.93
QP (mg P/g)	None	1.0375	1.2300	1.3300	1.4200
Date	18-Sep-11				
pH	7.95	7.78	7.74	7.73	7.74
Temp	26.6	26.6	25	26.6	26.7
Chlorophyll-a (µg/L)	16.34	14.12	10.26	7.277	5.208
%age C removed	None	13.59	37.21	55.47	68.13
QC (µg C/g)	None	0.56	1.52	2.27	2.78
P(mg/L)	6.60	2.15	1.18	0.82	0.36
%age P removed	None	67.42	82.12	87.58	94.55
QP (mg P/g)	None	1.1125	1.3550	1.4450	1.5600
Date	22-Sep-11				
pH	9.01	8.92	8.92	8.96	9
Temp	25	25	25	25	25
Chlorophyll-a (µg/L)	28.28	23.92	14.47	10.28	6.232
%age C removed	None	15.42	48.83	63.65	77.96
QC (µg C/g)	None	1.09	3.45	4.50	5.51
P(mg/L)	6.00	2.65	1.50	0.97	0.38
%age P removed	None	55.83	75.00	83.83	93.67
QP (mg P/g)	None	0.8375	1.1250	1.2575	1.4050

Table A.4: Raw experimental data for the four batch tests of 8 mg/L initial PC

Group	**Blank**	**Activated Alumina**			
Sample No.	**1**	**2**	**3**	**4**	**5**
Particle Size (mm)	**None**	**1.18**	**0.6**	**0.3**	**0.075**
Duration of Shaking (hr)	**3**				
Static Time Duration (hr)	**72**				
Date	**4-Oct-11**				
pH	4.9	4.97	4.97	5.02	4.98
Temp	28	28	28	28	28
Chlorophyll-a (µg/L)	6.465	4.64	3.836	3.425	3.078
%age C removed	None	28.23	40.67	47.02	52.39
QC (µg C/g)	None	0.46	0.66	0.76	0.85
P(mg/L)	8.00	2.15	1.26	0.58	0.10
%age P removed	None	73.13	84.25	92.75	98.75
QP (mg P/g)	None	1.4625	1.6850	1.8550	1.9750
Date	**18-Oct-11**				
pH	6.9	6.9	6.9	7.07	7.02
Temp	26.5	26.5	26.5	26.6	26.7
Chlorophyll-a (µg/L)	47.94	37.92	32.36	17.4	13.61
%age C removed	None	20.90	32.50	63.70	71.61
QC (µg C/g)	None	2.51	3.90	7.64	8.58
P(mg/L)	8.55	2.45	1.40	0.74	0.15
%age P removed	None	71.35	83.63	91.35	98.25
QP (mg P/g)	None	1.5250	1.7875	1.9525	2.1000
Date	**18-Oct-11**				
pH	7.77	7.71	7.62	7.65	7.73
Temp	26.4	26.4	26.4	26.4	26.5
Chlorophyll-a (µg/L)	59.24	52.43	43.44	30.35	25.11
%age C removed	None	11.50	26.67	48.77	57.61
QC (µg C/g)	None	1.70	3.95	7.22	8.53
P(mg/L)	8.55	2.70	1.50	1.00	0.30
%age P removed	None	68.42	82.46	88.30	96.49
QP (mg P/g)	None	1.4625	1.7625	1.8875	2.0625
Date	**20-Oct-11**				
pH	9.04	8.97	8.97	8.94	8.95
Temp	25.9	26.1	25.9	25.8	26.1
Chlorophyll-a (µg/L)	49.15	40.59	35.22	22.99	19.32
%age C removed	None	17.42	28.34	53.22	60.69
QC (µg C/g)	None	2.14	3.48	6.54	7.46
P(mg/L)	7.65	4.10	2.35	1.40	0.55
%age P removed	None	46.41	69.28	81.70	92.81
QP (mg P/g)	None	0.8875	1.3250	1.5625	1.7750

Table A.5: Raw data for the first column test (original pH = 8.3, bulk density = 0.7697 g/cm^3, Q = 11.197 mL/min, Porosity = 0.7749)

Date	**Time of sample collection**	**Influent pH**	**Influent Temperature**	**IPC(mg/L)**	**ICC(μg/L)**	**Effluent pH**	**Effluent Temperature**	**EPC(mg/L)**	**ECC(μg/L)**
5-Nov-11	1:30 PM	8.34	22.7	0.5	62.2	7.5	28.4	0	17.98
5-Nov-11	3:05 PM				62.6	7.56	28.2	0	18.6
5-Nov-11	4:45 PM				59.55	7.58	28.6	0	19.33
6-Nov-11	6:20 PM				35.41	8.03	25.2	0.03	12.49
6-Nov-11	10:50 PM				38.92	None	None	None	14.48
7-Nov-11	8:35 PM				26.22	8.1	25.8	0.04	10.5
8-Nov-11	4:20 PM				10.99	8.17	24	0.06	4.429
8-Nov-11	8:50 PM				12.75	8.16	24	0.07	4.224
9-Nov-11	2:35 PM	8.3	22.1	0.51	57.23	8.16	24.7	0.09	16.76
9-Nov-11	8:10 PM				61.6	8.17	25.3	0.09	19.83
10-Nov-11	4:45 PM				48.16	8.22	23.4	0.09	16.49
10-Nov-11	9:20 PM				43.78	8.18	24	0.09	16.22
11-Nov-11	4:20 PM				29.81	8.2	24.6	0.11	9.543
12-Nov-11	1:45 PM				21.38	8.19	25.3	0.14	5.442
12-Nov-11	9:30 PM				20.19	8.17	25.2	0.14	5.41
13-Nov-11	8:05 AM				16.26	8.22	23.8	0.14	5.564
13-Nov-11	5:10 PM				16.68	8.22	23.2	0.16	6.129
14-Nov-11	8:15 AM				13.41	8.25	23	0.17	5.268
14-Nov-11	2:35 PM	8.33	22.4	0.49	54.9	8.2	23.7	0.17	14.82
15-Nov-11	3:15 PM				36.89	8.29	23.1	0.17	11.13
15-Nov-11	6:25 PM				None	8.22	23.3	0.17	9.989
16-Nov-11	4:00 PM				25.16	8.26	23.7	0.21	8.08
17-Nov-11	4:20 PM				14.02	8.26	23.3	0.22	3.827
18-Nov-11	1:00 PM				9.508	8.22	25.6	0.24	2.119
18-Nov-11	2:50 PM	8.32	23.8	0.5	38.81	8.2	27.6	0.25	3.85
19-Nov-11	11:15 AM				29.85	8.21	26.6	0.25	5.545

Table A.5: continued

Date	**Time of sample collection**	**Influent pH**	**Influent Temperature**	**IPC(mg/L)**	**ICC(µg/L)**	**Effluent pH**	**Effluent Temperature**	**EPC(mg/L)**	**ECC(µg/L)**
20-Nov-11	12:00 PM	8.32	23.8	0.5	16.47	8.26	24.4	0.25	3.284
20-Nov-11	8:40 PM				16.5	None	None	None	3.585
21-Nov-11	11:20 AM				10.67	8.28	23.6	0.25	2.957
22-Nov-11	11:30 AM				8.578	8.27	23.8	0.27	1.564
22-Nov-11	6:25 PM	8.26	23.3	0.49	11.12	8.25	25.4	0.29	3.285
23-Nov-11	11:25 AM				8.114	8.26	23.6	0.29	2.392
24-Nov-11	11:25 AM				6.432	8.26	23.3	0.29	2.629
25-Nov-11	3:00 PM				6.599	8.19	24.7	0.3	1.229
26-Nov-11	9:50 AM				4.957	8.14	24.3	0.31	1.441
27-Nov-11	11:50 AM				3.461	8.17	23.3	0.31	1.491

Table A.6: Raw data for the second column test (pH = 5, bulk density = 0.7736 g/cm^3, Q = 19.957 mL/min, Porosity = 0.7372)

Date	Time of sample collection	Influent pH	Influent Temperature	IPC(mg/L)	ICC(μg/L)	Effluent pH	Effluent Temperature	EPC(mg/L)	ECC(μg/L)
28-Nov-11	2:25 PM	4.93	22.1	0.48	30.21	7.45	24.7	0	4.935
28-Nov-11	10:05 PM				29.04	6.52	24.5	0	7.007
29-Nov-11	12:15 PM				26.63	6.15	23.5	0	7.318
29-Nov-11	8:55 PM				25.72	6.02	23.2	0	7.283
30-Nov-11	11:35 AM				25.3	6.05	22.6	0.02	7.972
30-Nov-11	4:10 PM	4.87	22.6	0.5	33.85	6	24.4	0.03	11.53
30-Nov-11	9:30 PM				26.72	5.73	24	0.04	10.57
1-Dec-11	6:30 AM				22.37	5.74	24.1	0.06	9.428
1-Dec-11	4:10 PM				18.68	5.74	23.3	0.07	8.61
2-Dec-11	3:15 PM				15.5	5.72	24.4	0.09	7.66
2-Dec-11	6:35 PM	5.18	23.1	0.49	26.8	5.47	26.8	0.11	10.41
3-Dec-11	11:55 AM				22.7	5.9	24.8	0.12	9.88
3-Dec-11	10:00 PM				19.72	5.74	24.4	0.12	9.2
4-Dec-11	11:30 AM				17.09	5.9	23.1	0.13	8.51
5-Dec-11	8:30 AM				13.89	5.8	23.3	0.15	7.12
5-Dec-11	2:20 PM	5.08	22.2	0.51	34.03	5.65	24.6	0.17	8.576
5-Dec-11	10:40 PM				24.93	5.5	24	0.19	7.607
6-Dec-11	6:45 AM				20.21	5.53	23.6	0.21	6.876
6-Dec-11	4:05 PM				17.4	5.7	22.9	0.23	6.31
7-Dec-11	11:20 AM				15.78	5.83	22.6	0.23	6.48
7-Dec-11	8:40 PM	5.01	22.9	0.54	38.63	5.79	24.1	0.26	6.63
8-Dec-11	11:50 AM				28.44	5.6	22.5	0.26	6.72

Table A.7: Raw data for the chlorophyll-a batch tests associated with the column tests

Group	**Blank**	**Activated Alumina**			
Sample No.	**1**	**2**	**3**	**4**	**5**
Adsorbent Dosage (g/L)	**0**	**4**	**8**	**12**	**16**
Duration of Shaking (hr)	**1**				
Date	**19-Nov-11**				
pH	8.3	8.17	8.03	7.96	7.99
Temp	26.1	26.1	26.1	26.1	26.4
Chlorophyll-a (µg/L)	20.7	16.58	12.61	9.63	7.744
%age C removed	None	19.90	39.08	53.48	62.59
QC (µg C/g)	None	1.0300	1.0113	0.9225	0.8098
Freundlich QC	None	1.0626	0.9753	0.8963	0.8372
Langmuir QC	None	1.0470	0.9800	0.9052	0.8392
Date	**1-Dec-11**				
pH	4.98	6.15	6.61	6.77	6.75
Temp	23.2	23.2	23.3	23.1	23.4
Chlorophyll-a (µg/L)	20.34	13.95	10.26	7.942	6.482
%age C removed	None	31.42	49.56	60.95	68.13
QC (µg C/g)	None	1.5975	1.2600	1.0332	0.8661
Freundlich QC	None	1.6035	1.2562	1.0249	0.8721
Langmuir QC	None	1.5960	1.2645	1.0288	0.8675

Table A.8: Raw data for the phosphorus batch tests associated with the column tests

Group	**Blank**	**Activated Alumina**							
Sample No.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Adsorbent Dosage (g/L)	**0**	**0.25**	**0.5**	**0.75**	**1**	**2**	**3**	**4**	**8**
Duration of Shaking (hr)	**3**								
Static Duration (hr)	**72**								
Date	**19-Nov-11**								
pH	8.29	8.25	8.22	8.19	8.14	8.03	8	7.9	7.74
Temp	24.3	24.6	24.4	24.4	24.3	24.3	24.4	24.5	24.4
P(mg/L)	0.52	0.41	0.34	0.28	0.24	0.14	0.1	0.07	0.03
%age P removed	None	21.15	34.62	46.15	53.85	73.08	80.77	86.54	94.23
QP (mg P/g)	None	0.4400	0.3600	0.3200	0.2800	0.1900	0.1400	0.1125	0.0613
Freundlich QP	None	0.4226	0.3673	0.3176	0.2830	0.1890	0.1469	0.1125	0.0596
Langmuir QP	None	0.4093	0.3677	0.3262	0.2948	0.1989	0.1516	0.1117	0.0515
Date	**1-Dec-11**								
pH	5.01	5.76	6.06	6.24	6.35	6.59	6.85	6.98	7.3
Temp	23.4	23.4	23.4	23.4	23.4	23.4	23.6	23.6	23.6
P(mg/L)	0.5	0.34	0.25	0.2	0.17	0.1	0.07	0.05	0.02
%age P removed	None	32.00	50.00	60.00	66.00	80.00	86.00	90.00	96.00
QP (mg P/g)	None	0.6400	0.5000	0.4000	0.3300	0.2000	0.1433	0.1125	0.0600
Freundlich QP	None	0.6141	0.4714	0.3891	0.3384	0.2144	0.1578	0.1181	0.0537
Langmuir QP	None	0.6142	0.4835	0.4026	0.3508	0.2192	0.1576	0.1147	0.0472

Table A.9: Raw data for the desorption batch test

Group	**Blank**	**Activated Alumina**					
Sample No.	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Adsorbent Dosage (g/L)	**0**	**1**	**2**	**3**	**4**	**8**	**16**
Duration of Shaking (hr)	**3**						
Static Duration (hr)	**72**						
Date	**8-Dec-11**						
pH	13.13	13.14	13.12	13.11	13.09	13.09	13.07
Temp	22.5	22.6	22.7	22.8	22.8	22.8	22.7
P(mg/L)	0	0.3	0.56	0.79	1.01	1.75	2.95
QP (mg P/g)	None	0.3000	0.2800	0.2633	0.2525	0.2188	0.1844
Freundlich QP	None	0.3150	0.2756	0.2560	0.2429	0.2160	0.1932
Langmuir QP	None	0.8006	0.3011	0.2490	0.2280	0.2022	0.1902

VITA

Ahmad Adel Ghadban was born on March 11, 1989, in Dubai, United Arab Emirates (UAE). He studied in Al Ahlia Private School in Sharjah, UAE from elementary throughout secondary education. He graduated from high school in 2006. He was awarded the Bachelor of Science degree in Civil Engineering with MAGNA CUM LAUDE institutional honors from the American University of Sharjah, UAE on December 31, 2009. He immediately began his Master's program in Civil Engineering at the American University of Sharjah in 2010. He is expected to earn his Master's degree on January 21, 2012. During his graduate studies at the American University of Sharjah, he worked as a graduate teaching and research assistant and got involved with variety of research activities and lab duties.