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Adsorption Capacity Assessment of Advance Green Environmental Media to Remove Nutrients from Stormwater-Runoff

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ADSORPTION CAPACITY ASSESSMENT OF ADVANCED GREEN ENVIRONMENTAL MEDIA to REMOVE NUTRIENTS FROM STORMWATER-RUNOFF

by

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ABSTRACT

Best Management Practices (BMPs) in stormwater treatment are a suite of treatment alternatives to deal with pollutant removal problems from stormwater runoff. Biosorption-activated media (BAM) are green sorption media consists of recycled materials have shown excellent nutrient removal as an effective BMP by enhancing physicochemical and microbiological processes. In this study, Iron-Filling Green Environmental Media (denoted as IFGEM-3) and Advanced Green Environmental Media 1 and 2 (denoted as AGEM-1 and AGEM-2) were produced and tested for their adsorption capacities as well as removal and recovery potential for phosphate, nitrate, and ammonia against natural soil (baseline) collected from a stormwater retention basin in Ocala, FL. A set of isotherm and column tests were conducted at room temperature with varying contact times. Two media with the best adsorption performances were further tested to determine their life expectancy. The green sorption media characteristics and adsorption behaviors were further analyzed and realized by using a few existing isotherm models. The collected data on physical properties such as hydraulic conductivity, porosity, surface area, and density help justifying the comparative results. The results showed that AGEM-2 has the highest average nitrate removal efficiency (76.55%) when compared to IFGEM-3 (39.0%) and AGEM-1 (33.67%). Furthermore, IFGEM-3, AGEM-1 and AGEM-2 achieved the highest phosphate removals after only 30 minutes of contact time. It is indicative that IFGEM-3, AGEM-1 and AGEM-2 media all produced ammonia and the rates of production consistently increase as contact time increases. However, AGEM-2 generated an average of 35.22% more ammonia than IFGEM-3 and AGEM-1 suggesting it can be further utilized as a soil amendment. Natural soil showed no nutrient removal, however. The maximum adsorption capacities (q_{max}) derived by the isothermal test at high influent concentrations of 2mg/L phosphate and 2mg/L nitrate were found to be less than the q_{max} obtained from the column tests for IFGEM-3 and AGEM-2 with respect to nitrate. IFGEM-3 and AGEM-2 were further tested with respect to nitrate for their maximum adsorption capacities and their life expectancies based on column tests. The results indicated that AGEM-2 has a longer life expectancy and a higher adsorption capacity than IFGEM-3, in terms of nitrate removal, which is consistent with isotherm results. It is recommended that AGEM-2 be selected for nutrient removal in future stormwater treatment based on its better adsorption performance and recovery potential.

Key Words: Sorption media, Isotherm study, Column study, Equilibrium models, Breakthrough curves

Dedication

To my beloved brother; Ayman, husband; Hatim, son; Abdalla, and daughters; Reem and Maryam

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CHAPTER ONE: INTRODUCTION

1.1 Introductory Background

The demand for reducing stormwater runoff nutrient input into the downstream receiving waterbodies is increasing at a rapid pace due to lawn fertilization and agricultural crop production. Excessive nutrient depositions into the downstream receiving waterbodies from stormwater runoff might impact the ecosystem's integrity in the nutrient cycles (David and Masten 2009). Contaminated stormwater runoff with high levels of nutrient concentrations such as nitrogen and phosphorus can lead to the eutrophication and algal blooms, which threaten the existence of species within these environments (David and Masten 2009). The normal concentration ranges of nitrogen and total phosphorus in street and roof runoff of stormwater are from 0.03 to 1.97mg/L-N and from 0.14 to 2.78 mg/L-TP respectively (Yang and Toor 2017). A study on plots treated with poultry litter and inorganic fertilizers found that the total phosphorus concentrations in stormwater runoff was between 15.4 and 26.2 mg/L, respectively (Murray et al 2004). Also, fertilizer use, and spillage can play an essential role in increasing nitrogen concentrations to levels as high as 21 mg/L of nitrate and nitrite (Poe et al. 2003). Therefore, to control nutrient concentrations and limit the resulting eutrophication and algal blooms, the US Environmental Protection Agency (USEPA), under the Clean Water Act (CWA), regulates nutrient mass loading of stormwater runoff before it is discharged into waterbodies (White and Boswell 2006).

1.2 Problem Statement

High levels of nutrient depositions, mainly nitrogen and phosphorus, cause waterbodies to become eutrophied, which supports algal growth. Algal blooms eventually prevent sunlight penetration into water columns resulting in further ecological degradation. When algae die, it descends to the bottom of the waterbody where the benthic organisms utilize oxygen to decompose the algae. Algae decomposition reduces aeration of deep-water layers and contributes to the depletion of oxygen during summer stratification. These anaerobic conditions of water column forces cold water fish, that required at least 5-6mg/L of dissolved oxygen, to migrate in order to survive. Therefore, excess nutrient supply in waterbodies is undesirable and leads to excessive biomass concentrations that increase water turbidity affecting water odor and taste. Moreover, excessive biomass concentrations stimulate the growth of sludge worms, decreases dissolved oxygen levels and forces many species out of those water bodies causing a reduction in biodiversity within these ecosystems (Davis and Masten 2009).

1.3 Objective and Scope of The Thesis

The objectives of the thesis are to: 1) to find the maximum adsorption capacities for IFGEM-3, AGEM-1 and AGEM-2; 2) to find their phosphorus, nitrogen removal efficiencies and ammonia recovery potentials; and 3) to compare the removal efficiencies and recovery potentials to that of natural soil (control media) collected from a stormwater retention basin in Ocala, FL. Furthermore, the media will be further tested for their life expectancy. Finally, the media with the highest adsorption capacity, the best nutrient removal performance, and the longest life expectancy will be recommended for stormwater runoff and wastewater treatment applications. The adsorption performance of these sorption media was evaluated under a constant flow rate and a constant temperature using various influent conditions and contact time. A series of isotherm and column tests were performed at the University of Central Florida Laboratories where water samples from both experiments were analyzed using HACH Kit products and methods and the results were recorded. Different isotherm and column models were applied, and their predicted theoretical parameter values were compared and evaluated against experimental results and the results from both tests were discussed.

1.4 Engineering Science Questions

The aim of this thesis is to explore the following engineering science questions: (1) what are the maximum adsorption efficiencies of IFGEM-3, AGEM-1, and AGEM-2 for phosphate, nitrate and ammonia compared to that of natural soil? (2) what are the maximum adsorption capacities of IFGEM-3, AGEM-1 and AGEM-2 for phosphorus, nitrate and ammonia under different influent concentrations? (3) what are the sorption life expectancy of IFGEM-3 and AGEM-2 media with respect to nitrate removals? (4) What are the possible interactions between clay particles and iron/ aluminum ions? (5) What are the differential effects of nitrate and phosphate removal and recovery due to the inclusion of aluminum ions in AGEMs relative to IFGEM-3?

CHAPTER TWO: LITERATURE REVIEW

Solving potential surface and groundwater contamination problems associated with stormwater runoff and infiltration is an acute need. Stormwater runoff increases due to urbanization, and thus, pervious surfaces through which stormwater infiltration could occur are reduced. This results in higher quantities of pollutants in stormwater runoff which become discharged into water bodies. Therefore, many artificial stormwater infiltration mechanisms have been introduced and used in urbanized areas as an initial step to decrease the volume of stormwater runoff into surface water and to increase stormwater infiltration for groundwater recharge. Some of these infiltration techniques including surface infiltration devices such as grass filters and grass-lined drainage swales into which stormwater runoff can be captured to ensure proper drainage. Also, French drains and soak-ways, porous pavements, drainage trenches, infiltration wells and dry wells are used to provide better infiltration and stormwater drainages, and to redirect stormwater runoff to sub-surface environments (Pitt et al. 1999). The capture and management of stormwater runoff on-site via retention and treatment processes would be a further step towards stormwater runoff pollution control where runoff and pollutant characteristics largely impact the efficiency of the treatment processes such as settling, adsorption, or filtration (Sage et al. 2015). The pollutant removal efficiency of detention ponds, for example, is noticeably impacted by the pollutant's particle size distribution (Erickson et al. 2012). Other criteria such as sufficient residence time, sufficient adsorption capacity and pollutant concentration are among the important factors that affect the treatment processes. The adsorption process is the most efficient and promising approach where cost and technical procedures are affordable and easily handled (Foo and Hameed 2010). In this process, a fluid mixture of component of gas or liquid adheres to either the interior or immediate exterior surface of a solid adsorbent forming flocs that can be further removed and/or recovered (Hossain et al. 2010). The effectiveness of the adsorption treatment process largely depends on the use of proper filter media that have effective adsorption capacity and can promote pollutant removal, improve solid-liquid contact, provide sufficient infiltration in wet and dry bio-retention ponds, and enhancing both physio-chemical and microbiological processes.

Several studies have introduced various types of natural sorption media used to treat stormwater runoff and wastewater effluents by physical, chemical and biological means before discharge (Xuan et al. 2009). This approach of treatment processes has ‘green’ implications because of the use of natural and recycled materials such as clay, sand, iron filling, and tire crumb within the sorption media mixtures to increase treatment efficiency and efficacy (Jones et al. 2015). The sorption media mixture matrix provides maximum sorption capacity, promotes sufficient infiltration rates, and increases the moisture retention time for the media (O’Reilly et al 2012). A sorption media mixture matrix that operates under various temperatures and pH to remove nutrients, TOC, and metals from water is yet to be fully discovered, but many media mixture matrices demonstrate promising results.

Sand filters were used before 1995 to remove nutrients from contaminated stormwater. For example, Delaware sand filter demonstrated 71.1% , 6.7%, and 59.9 % removal efficiency for total phosphorus (TP), NH_3-N, and total Kjeldahl nitrogen (TKN), respectively (Bell et al. 1995). The problem associated with sand filters is their limitation to remove all nutrients. Therefore, sorption media were found to be better alternatives in removing nutrients from waterbodies. Compost was discovered, by Richman (1997), to remove 90% solids, 82-98% heavy metals and 85% oil and greases by adsorption. Wallastonite calcium inosilicate ($CaSiO3$) was discovered, by DeBusk et al. (1997), to remove 87.8% phosphorus, 97.7% cadmium (Cd), 81.4% copper (Cu), and 80.3% nickel (Ni). Sand, peat and lime-rock demonstrated phosphorus removal of 41.4%, 44%, and 41.4% by adsorption, respectively. The study concluded that Wallastonite is more effective in removing phosphorus because it contains calcium and ferrous ions that can precipitate and absorb phosphorus from contaminated stormwater (DeBusk et al. 1997). Filter media such as alfalfa, leaf, newspaper, wheat straw and wood chips were used to remove nitrate from stormwater by biological means. Kim et al. (2000) found that 100 % nitrate removal efficiency can be obtained using alfalfa and newspaper, while wheat straws and wood chips were found to have > 95% nitrate removal. The authors concluded that these media were electron donors and were considered good sources of carbon that promote denitrification and enhance nitrate removal.

Boving and Zhang (2004) utilized aspen wood filters to remove polynuclear aromatic hydrocarbons (PAH) in aqueous phase and the results indicated that hydrophobicity and PAH's molecular weight impacted its sorption. The authors stated that the sorption rate decreased over time and that smaller particles had a greater sorption capacity when compared to larger ones. In a batch study on urban stormwater runoff, by Hsieh and Davis (2005), 18 columns were filled with different media mixtures containing mulch, soil, and sand were tested for nitrate, total phosphorus (TP) and ammonium removal efficiencies. The results demonstrated that 43% nitrate removal was achieved using a mulch and sand mixture, but only 4% total phosphorus removal was attained. In addition, the ammonium removal for all the media mixtures tested were between 2% to 26%. The authors concluded that soils containing higher silt/clay, cations (Mg, Ca, K) and organic matter contents tend to have greater cation exchange capacity and thus, are more efficient in removing nutrients. Also, they concluded that in repetitive nutrient loading, coarse media might not be able to hold nutrients due to the small surface area available for adsorption. Also, stormwater with a pH > 7 would provide the best removal of metals by sorption media that otherwise, would be quickly released (Chang et al. 2010).

Hardwood mulch was used by Ray et al. (2006) to remove some metals such as Cu, Cd, Cr, Pb and Zn and other organic materials from urban stormwater runoff. The researchers indicated that metal concentration and pH impact the sorption capacity and metal removal. While acidic pH increases metal ion dispersion in solution, alkaline pH enhances ion removal by precipitation or adsorption. Also, metal removal most likely occurs via adsorption or ion exchange and less likely via biological processes. In another study, heavy metals were removed from stormwater using fine glass, sand, coarse glass, ash compost, packing wood and zeolite (Seelsaen et al. 2006). Clinoptilolite was used by Huang et al. (2007) to remove nitrate with metallic iron, and ammonium [NH_4^+ + NH_3] and ferrous ions [Fe (II)]. Huang et al. (2007) also found that clinoptilolite was very active in removing nitrate in the presence of Fe^0 when pH is between 2.2 and 4.5, and that nitrate removal was inversely related to both pH and nitrate loading. The study showed that increasing nitrate loading allowed more insufficient iron sites to absorb more nitrates, thus, nitrate removal was increased. It also showed that, in the presence of Fe, the redox reaction of nitrate resulted in ammonium/ammonia production and that the removal of Fe (II) and ammonium/ammonia by clinoptilolite were dependent on the F/N ratio and pH value.

In Chang et al. 2018b and Wen et al. 2018, a new bio-sorption activated media (BAM) was developed, which consists of 85% poorly graded sand, 5% clay, and 10% tire crumb by volume. Iron filling-based green environmental media; IFGEM-1, consists of 96.2% fine sand, and 3.8%

ground iron fillings while IFGEM-2 consists of 80% sand, 5% pure clay, 10% tire crumb and 5% ground iron fillings by volume (Chang et al. 2018b; Wen et al. 2018). A new sorption media (IFGEM-3) is also developed based on the constituents of IFGEM-2 with a refined percentage of 2 % clay, and 83% sand. IFGEM-3 also has 5% iron filings, and 10% tire crumb, by volume to obtain the Optimum IFGEM-3 sorption media, (herein referred to as IFGEM-3). Valencia et al (2019) demonstrated that varying ratios of IFGEM-3 components significantly impact their nutrient removal capacities and nutrient recovery potential.

BAM, and iron filling-based green environmental media, (e.g.; IFGEM-1 and IFGEM-2,) were tested through isotherm and column study experiments and the results demonstrated successful nutrient reduction, recovery, and reuse potential (Chang et al. 2018). BAM has shown to promote nitrification and denitrification, enhancing stormwater treatment procedures whereas IFGEM-1 and IFGEM-2 demonstrated effective nutrient removal and reuse potential within varying temperature conditions (Chang et al. 2011). IFGEM-3 has been tested and demonstrated the best performance for stormwater and wastewater treatment for phosphorus and nitrogen removal with low effluent iron concentration (Chang et al. 2018). IFGEM-3 adsorption media absorbed chemical substances by physical and chemical means until they became saturated when the equilibrium point is reached. In this study, the Advance green environmental media, AGEM-1 and AGEM-2, were produced and are amongst the current media under investigation for their nitrogen, phosphorus, and ammonia removal efficiencies. AGEM-1 contains 5% iron, 78% sand, 10% tire crumb, and 2% clay, whereas AGEM-2 consists of 3% clay, 7.5% iron filling, 4.5% aluminum powder, and 85% fine sand. At varying influent conditions, AGEM-1 and AGEM-2 maximum adsorption capacities and nutrient removal efficiencies were compared against IFGEM-3 (optimum), and natural soil (control).

Best management practices (BMPs) were used in controlling urban runoff and decreasing corrosion and sediment transport from urbanized and agricultural areas. They also demonstrated to be effective in reducing high nutrient concentrations as a step towards meeting EPA regulations. These practices include, but are not limited to, the use of sediment retention ponds, conservation tillage, and filter strips for agricultural fields and infiltration devices, ponds, filters, and constructed wetlands for urban runoff pollution control (Chang et al. 2010). The use of low-impact development (LID) such as rain gardens and permeable pavements are among the non-structural BMPs practices in treating contaminated stormwater. Physio-chemical and microbiological treatment processes are essential parts of both BMPs and LID that have been used to remove excess nutrients in contaminated stormwater and wastewater. The utilization of effective filter media in wet and dry bio-retention ponds is also appealing to BMPs. Biofiltration processes with varying effective sorption media are also popular due to their reasonable cost. Finally, the development of a proper sorption media mixture matrix that results in the best adsorption capacities and the longest life expectancies is an area of research that warrants further investigation. Further investigation into this area is also warranted because it would sustain the renewed interest for biological and physio-chemical processes as essential parts of BMPs in stormwater and wastewater management.

CHAPTER THREE: METHODOLOGY

3.1 Research Methodology

Isotherm and column tests were applied to Natural Soil, IFGEM-3, AGEM-1, and AGEM-2 under varying contact time and influent conditions: condition 1 (0.9 mg/L NO_3^- and 0.3 mg/L PO_4^{-3}), condition 2 (1.5 mg/L NO_3^- and 0.9 mg/L PO_4^{-3}) and condition 3 (2 mg/L NO_3^- and 2 mg/L PO_4^{-3}) referred to as C_1 C_2 C_3 hereafter. The optimum influent condition, the performance efficiency, and the maximum adsorption capacity for these media were obtained via a series of isotherm and column tests. AGEM-2 and IFGEM-3 were further tested via column tests and the results were compared and discussed. The optimum influent concentration was utilized in the column tests as the only influent condition under constant flow rate and temperature. Thus, the results from the isotherm and column tests were more reliable and can be utilized for a possible recommendation for sorption media to be used for future stormwater and wastewater treatment applications.

Natural soil, IFGEM-3, AGEM-1, and AGEM-2 act as adsorbents during the adsorption process where dissolved nutrient species adhere to their surface or near the inner porous surface. When the media reaches its maximum adsorption capacity, it becomes saturated and is no longer absorbing nutrients. This process is called equilibrium and it is when nutrient influent concentrations are the same as the effluent concentrations. Physical and chemical reactions that occur between adsorbents (IFGEM-3 and AGEMs) and adsorbates (nutrient species) leads to phosphorus and nitrogen removal via adsorption or/and precipitation. Precipitation occurs when phosphate reacts with iron and aluminum in the media forming precipitates. The precipitates formed have a solid component [$Fe_3(PO_4)_2$* $8H_2O$] and an insoluble salt [$AlPO_4$] following Equation 1 (Fredrickson et al. 1998) and Equation 2 (Martin, 1986), respectively.

$$3Fe^{2+} + 2HPO_4^{2-} + 8H_2O \rightarrow Fe_3(PO_4)_2 * 8H_2O + 2H^+ \quad (1)$$

$$Al^{3+} + H_3PO_4^{-} \rightarrow AlPO_4 + 2H^+ \quad (2)$$

Also, nitrate reacts with iron and aluminum in the media to produce ammonium, ammonia and base species following Equation 3 (Choe et al. 2004) and Equation 4 (Murphy, 1991), respectively. The production of base (OH^-) consumes the acidity in the solution resulting in a pH increase. Thus, the redox reaction of nitrate results in ammonia production for recovery and reuse or in nitrate removal to the atmosphere as nitrogen gas as shown in Equation 5 (Luk and Au-Yeung, 2002) below:

$$NO_3^- + 10H^- + 4Fe \rightarrow NH_4^+ + 3H_2O + 4Fe^{2+} \quad (3)$$

$$3NO_3^- + 4Al + 8H_2O \rightarrow NH_3 + 4Al(OH)_3 + OH^- + 2NO_2^- \quad (4)$$

$$3NO_3^- + 4Al + 7H_2O \rightarrow N_{2\,(g)} + 4Al(OH)_3 + 2OH^- + NO_2^- \quad (5)$$

3.2 Physical Characteristics of The Media

In this study, IFGEM-3, AGEM-1 and AGEM-2 are the sorption media that were tested and analyzed for their performance efficiency and adsorption capacity. All the media have iron filings, clay and sand within their media mixture matrix at varying ratios. IFGEM-3 media consists of 83% sand, 10% tire crumb, 2% clay, and 5% iron fillings. AGEM-1 media consists of 78% fine sand and 5% grinded iron fillings, 5% aluminum filling, 2% clay and 10% tire crumb, while AGEM-2 consists of 83% fine sand, 7.5% grinded iron, 7.5% aluminum powder filling, 2% clay by volume

(Chang et.al. 2018). The aluminum within the AGEM-1 and AGEM-2 mix have aluminum flasks produced from a recycled rod and aluminum power produced from ground aluminum foil, respectively. IFGEM-3 and AGEM-1 have tire crumb obtained from recycled tires. The nutrient removal performances of IFGEM-3, AGEM-1 and AGEM-2 were compared to natural soil that was used as a baseline and collected from a stormwater retention basin in Ocala, Florida.

All the media components were carefully selected to enhance the physio-chemical adsorption of phosphate, nitrate and ammonia. For example, while tire crumb enhances the hydraulic conductivity of the sorption media allows contaminated water to infiltrate easily through pore spaces in the media. Sand ensures better water distribution by increasing void spaces within the media. Some of physio-chemical characteristics that impact the adsorption processes were explored and measured. Porosity and hydraulic conductivity of the studied media were measured at the Geotechnical laboratory at the University of Central Florida, while BET surface area and bulk density were measured at the EMSL Analytical, Inc laboratories.

3.3 Isotherm Tests

Isotherm tests were a series of experiments applied to natural soil, IFGEM-3, AGEM-1, and AGEM-2 to test their performance efficiency and to determine their experimental adsorption capacity under different influent conditions and contact times. The experimental adsorption capacities (q_e) were compared to that of the maximum adsorption capacities obtained from isotherm models. Isotherm tests were performed three times for each media to ensure reliable results. Effluent water samples were collected from each media after 30 minutes, 1 hour, 1.5 hours, 3 hours and 5 hours, and then analyzed for phosphate, nitrate and ammonia concentrations. All analyses of the effluent samples were performed at the University of Central Florida Laboratories via Hach test 'n' tube $^{TM-}$. The pH DO and ORP were measured via Waterproof Double Junction pH Test® 30 and HACH HQ40D IntelliCAL/MTC101.The total average effluent concentration value of the triplicate for each contact time was calculated and compared to that of the influent to determine the removal efficiency of the media for phosphorus, nitrate and ammonia. Isotherm tests were followed with column tests and the media with the highest adsorption capacity and the longest life expectancy is recommended for full-scale operations for stormwater runoff and wastewater nutrient control applications.

3.3.1 Isotherm Experiment Setup

The adsorption capacity and nutrient removal efficiency of the Natural Soil, IFGEM-3, AGEM-1 and AGEM-2 were explored via isotherm tests. Prior to conducting the experiment, the tested media contents were flushed with DI water for 24 hours and then oven-dried at 90 ^{0}C for 24 hours to eliminate any bacterial growth in the media and to limit the test to the media's capability in removing nitrate and phosphate by physical and chemical means. Distilled water was spiked with three different influent concentrations of nitrate and phosphate (0.9 mg/L NO_3^- and 0.3 mg/L PO_4^{-3}), (1.5 mg/L NO_3^- and 0.9 mg/L PO_4^{-3}), and (2 mg/L NO_3^- and 2 mg/L PO_4^{-3}). Each of Five 500 mL flasks were filled with 300 mL of spiked solution under each of the influent concentrations and then 50g of a media recipe was added to each flask in triplicates. All flasks used in this experiment were washed with 10 % hydrochloric acid and oven dried for 24 hours at 180 ^{0}C. The flasks with the distilled water and media samples were covered with parafilm to avoid outsides disturbances and they were constantly mixed for 30 min,1 hr., 1.5 hr., 3 hr., and 5hr. on a shaking platform at 200 rpm.

The solutions were removed from the media using 0.45 μm filters and analyzed 5 times in triplicate for total phosphate, nitrate and ammonia removal and recovery. At room temperature and a pH around neutral, influent and effluent concentrations were tested via in house-analysis using Hach kits for each media in triplicates (Table 1). The results from the isotherm experiment were fit into the Langmuir isotherm and the Freundlich isotherm equations as well as other isotherm equations to obtain the maximum nutrient adsorption capacity per gram of media.

Table 1: Analysis Methods and Measuring Range

Chemical Species	Product Number	Measuring Rang (mg L^{-1})
Phosphate	TNT 843	0.15-4.5 mg PO_4^{-3}/L
Nitrate	TNT 835	0.2-13.5 mg NO_3-N/L
Ammonia	TNT 830	0.015-2.mg NH_3-N/L
Aluminum	TNT 848	0.02-0.5 mg AL_3/L
Iron	TNT 858	0.2-6 mg Fe_3^{+2}/L

3.3.2 Isotherm Models

The adsorption isotherm models were useful in describing the removal or the mobility of a substance from the aqueous porous media to a solid phase at a constant temperature and pH (Limousin et al. 2007). Adsorption equilibrium occurs when an adsorbate is in contact with adsorbent for a sufficient amount of time to allow the adsorbate concentration in the aqueous solution to reach a dynamic balance with the interface concentration (Foo and Hameed 2010). A wide variety of existing isotherm models have been formulated and their mathematical correlation was demonstrated graphically depicting the solid phase concentration versus the residual concentration. Some of these models include the Langmuir, Freundlich, Temkin, Harkin-Jura, Halsey, Redlich-Peterson, Elovich and Jovanovic isotherm models. Some of these models were used to determine the mechanisms of a sorption media and some were used to estimate the optimum adsorption capacity of the sorption media. Also, the isotherm models were used to determine the relation curves between adsorption equilibrium capacity and equilibrium concentration.

3.3.2.1 Langmuir model

The model describes a monolayer adsorbate formation where the adsorbed layer's thickness is one molecule on the interface of the adsorbent (Foo and Hameed 2010). The adsorbent contains a constant number of identical adsorption sites where each site is capable of binding only one molecule of the adsorbate, and that the adsorption to each adsorption site has the same free-energy change. Thereby, the Langmuir model demonstrates the equilibrium distribution of metal ions between liquid and solid phases (Rahel and Bhatnagar 2014). Based on these assumptions, the linear form of the Langmuir isotherm equation is represented as follows (Chang et al. 2018):

$$\frac{1}{q_e} = \frac{1}{(q_{max}K_L)} * \left(\frac{1}{C_e}\right) + \frac{1}{q_{max}} \qquad (6)$$

Where:

C_e = the residual pollutant concentration left in the solution after binding (mg/L)

q_e = the amount of pollutant bound to the adsorbent (mg/g)

q_{max} = the maximum monolayer coverage capacity (mg/g)

K_L = Langmuir adsorption constant, L/mg

q_{max} and K_L were calculated by plotting 1/ q_e versus 1/C_e from the slope and intercept values, respectively (Chang et al. 2018). The dimensionless equilibrium constant R_L is one of the significant parameters of the Langmuir isotherm model and is referred to as separation factor or equilibrium parameter (Dada et al. 2012).

$$\mathbf{R_L = \frac{1}{1+(1+K_L\,C_0)}} \qquad (7)$$

Where:

C_0= initial Concentration

K_L = Langmuir Constant related to the energy of adsorption

R_L represents the nature of the adsorption to be either favorable if $0 < R_L < 1$, unfavorable if $R_L > 1$, Linear if $R_L = 1$ and irreversible if $R_L = 0$ (Dada et al. 2012).

3.3.2.2 Freundlich model

This model describes the adsorption characteristics for heterogeneous surfaces (Dada et al. 2012). The data is fitted into the empirical linear form of Freundlich isotherm equation (Chang et al. 2018):

$$\mathbf{\log q = \log K + \frac{1}{n}\log C} \qquad (8)$$

Where:

K = Freundlich isotherm constant ($mg^{1-(1/n)}\ L^{1/n}\ g^{-1}$)

C= equilibrium concentration of adsorbate (mg/L)

n = measures the affinity or the intensity of the adsorption

q = measures the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g)

K and n are determined by fitting the data into the linear form of Freundlich equation whereas, a linear regression is used to determine the parameters of the isotherm models (Guadalupe et al. 2008). Also, 1/n and K are calculated by plotting log (q) versus log (C) from the slope and intercept values, respectively. The adsorption capacity can be approximately estimated by K, while 1/n measures the strength of adsorption process (Voudrias et al. 2002). 1/n less than one ($1/n<1$) indicates a normal adsorption, while 1/n greater than one ($1/n>1$) indicates cooperative adsorption (Mohan and Karthikeyan 1997). Furthermore, 1/n is the heterogeneity parameter, and as 1/n decreases, the heterogeneity increases and when $1/n = 1$ the expression then describes a linear isotherm. If $10>n>1$, the adsorption process will be favorable (Goldberg 2005).

3.3.2.3 Elovich isotherm Model

The model equation is based on a kinetic principle assuming that the sides of the adsorption exponentially increases with the adsorption for a multilayer adsorption (Ayawei et al. 2017).

The linear form of the Elovich model is as follows:

$$\ln \frac{q_e}{C_e} = \ln K_e q_{max} - \frac{q_e}{q_{max}} \qquad (9)$$

Where q_{max} and K_e are the maximum adsorption capacity and Elovich constant respectively. Both parameters can be obtained from the slope and intercept of plotting Ln (q_e/C_e) versus q_e.

3.3.2.4 Redlich-Peterson Model

This model is considered to be a combination of the Langmuir and Freundlich equations and does not follow the monolayer adsorption principle that the Longmuir model assumes. The model linear equation is presented as follows:

$$\ln \frac{C_e}{q_e} = \beta \ln C_e - \ln A \qquad (10)$$

Where A is the Redlich-Peterson isotherm constant (Lg^{-1}), and β is the exponent that lies between 0 and 1. When β = 1, it shows the Langmuir equation and when β = 0, it demonstrates Henry's equation (Ayawei et al. 2017). β and A are calculated from plotting Ln (C_e/q_e) versus Ln C_e where β is the slope and Ln A is the intercept. The model is concentration dependent in the numerator and is an exponential function in the denominator that has the ability to describe a wide range of the adsorbate concentrations in both homogeneous and heterogeneous systems (Gimbert et al. 2008).

3.3.2.5 Jovanovic Isotherm Model

The model demonstrates some mechanical contacts between the adsorbate and the adsorbent. The linear equation of the model is shown as follows:

$$\ln q_e = \ln q_{max} - K_J C_e \qquad (11)$$

Where q_{max} and K_J are found from plotting Ln(q_e) versus C_e where q_{max} is the maximum adsorption (µg g^{-1}) and K_J is the Jovanovic constant (Ayawei et al. 2017).

3.3.2.6 Temkin Model

The interactions between the adsorbent and adsorbate are explicitly represented by a factor in this isotherm model. The model assumes that the adsorption heat of all molecules in a layer is a function of temperature and is decreasing linearly, rather than logarithmically, with coverage. The Temkin isotherm model equation's derivation is characterized by a uniform distribution of binding energies and its parameters are found by fitting the data into a linear form of the equation that is given as follows (Dada et al. 2012):

$$\mathbf{q_e = \frac{RT}{b_T} lnA_T + \frac{RT}{b_T} lnC_e} \qquad (12)$$

Where :

$$\mathbf{B = \frac{RT}{b_T}} \qquad (13)$$

$$\mathbf{q_e} = \mathrm{B\ ln\ A_T + B\ ln\ C_e} \qquad (14)$$

A_T = Temkin isotherm equilibrium binding constant (L/g)

b_T = Temkin isotherm constant

R = universal gas constant (8.314J/mol/K)

T = Temperature at 298 K

B = Constant related to heat of the sorption (J/mol)

3.3.2.7 Harkin-Jura Isotherm Model

This model conveys the possibility of multilayer adsorption on the surface of sorption media with heterogeneous pore distribution. The linear form of the model is expressed as follows:

$$\mathbf{\frac{1}{q_e^2} = \frac{B}{A} - \left(\frac{1}{A}\right) \log C_e} \tag{15}$$

B and A are Harkin- Jura constants that can obtained from plotting $\frac{1}{q_e^2}$ versus log C_e (Foo and Hameed 2010).

3.3.2.8 Halsey Isotherm Model

This model is used to evaluate the multilayer adsorption when there is a relatively large distance from the adsorbates to the adsorbents. The model conveys the heterosporous nature of the adsorbents at high coefficient of determination (R^2) (Ayawei et al. 2017). The linear equation of the model is expressed as follows:

$$\mathbf{q_e = \frac{1}{n_H} \mathit{I_n} K_H - \frac{1}{n_H} \ln C_e} \tag{16}$$

Where K_H and n_H are the Halsey isotherm constants and are obtained from plotting Ln q_e versus Ln C_e.

3.4. Column Tests

Column tests were conducted to demonstrate the adsorption potential in the field, to determine optimized adsorption capacity, and to identify the life expectancy of the sorption media utilized. The adsorption capacity of both media, IFGEM-3 and AGEM-2, were examined in triplicates under different conditions where a series of columns were fed with a constant flow rate of 3 mL/min with identical influent conditions of 2mg/L as PO_4^{-3} and 2mg/L as NO_3^- in distilled water. The effluent samples from both media were constantly collected within the same collection time interval and analyzed for their total phosphate, nitrate and ammonia using the chemical methods outlined in Table 2. The column tests data for both media, IFGEM-3 and AGEM-2, were fitted into the Bohart-Adams (B-A) model and the Modified Dose-Response (MDR) model to account for different adsorption capacities and break-through curves. The models' parameters were obtained by performing linear regressions within the linear form of both models, and the results were interpreted accordingly.

3.4.1 Method and Materials

The sorption media used were IFGEM-3 and AGEM-2. IFGEM-3 is a media mix of 83%, 10%, 5%, and 2% by volume of sand, tire crumb, iron filings, and clay, respectively. AGEM-2 is a media mix of 85%, 7.5%, 3%, and 4.5 % by volume of sand, iron filings, clay and aluminum powder, respectively. IFGEM-3 and AGEM-2's adsorption performances were verified via a series of column tests where effluent samples were constantly examined for their phosphate, nitrate and ammonia concentrations. The results obtained were fitted into the Bohart-Adams (B-A) and the Modified Dose-Response (MDR) models to determine the maximum adsorption capacities and the life expectancies for both studied media.

3.4.2 Column Experiment Step-up

Six columns were used and set up as an upward flow system and were tightened to a wooden board; each column is 2.5 inches in diameter and 7 inches in height. Each column was filled with 500g of a media recipe in triplicates. Prior to utilization, IFGEM-3 and AGEM-2 media were flushed with distilled water for 24 hours and then oven-dried for another 24 hours to ensure no biological activity would disturb the adsorption processes. Distilled water was spiked with nitrate and phosphate standard solution to obtain an identical influent condition of 2mg/L as PO_4^{-3} and 2mg/L as NO_3^- that was previously selected as the optimum concentration with the highest adsorption capacities for all the studied media.

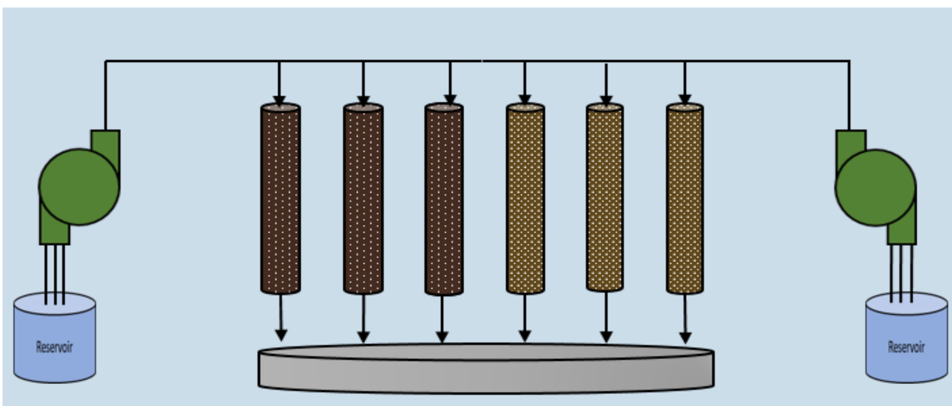


Figure 1 Six columns each with a diameter of 2.5 inches and a height of 7 inches filled with IFGEM-3 and AGEM-2 in triplicates

Six columns are constantly fed with the influent concentration at a flow rate of 3 mL/min to provide identical conditions for the triplicate measurements for each test. To ensure good dispersion and to prevent outflow of fine particles, a filter fabric was placed on the bottom of each column and the top of the column was covered with pebbles. Water samples from both influent and effluent were collected and analyzed within the same time interval waiting for the media to reach the breakthrough point (BTCs) that is also known as a point of exhaustion, where both influent and effluent concentrations are almost the same.

3.4.3 Column Breakthrough Models

Column experimental data for IFGEM-3 and AGEM-2 were fitted into two different dynamic adsorption models to develop the breakthrough curves, based on the Bohart-Adams (B-A) and Modified Dose-Response (MDR) models as described below:

3.4.3.1 Bohart-Adams (B-A)

The Bohart-Adams (B-A) model assumes pseudo- first-order reversible reaction kinetics and an asymmetrical breakthrough curve. The model has reflected good correlation to data from column studies of heavy metals sorption (Chu, 2010). The nonlinear and linear equations are shown below:

$$\frac{C_e}{C_0} = \frac{1}{1+\exp\left(K_{BA}\left(\frac{q_{max}\, m - C_0 V}{Q}\right)\right)} \tag{17}$$

$$\ln\left(\frac{C_0}{C_e} - 1\right) = \frac{K_{BA} q_{max} m}{Q} - K_{BA} C_0 t \tag{18}$$

C_o and C_e are the influent and effluent concentrations in mg/mL, K_{BA} is the rate constant in the B-A model in unit of mL/mg min, q_{max} is the equilibrium media uptake when C_e/C_0 reaches an asymptotic value, m is the total media mass in the column in g and V is the throughput volume in mL. m, Q, t, Ce are known parameters calculated from the column test and design. Plotting ln [(C_0/C_e)-1] vs. t and by using a linear regression, the rate constant K_{BA} and q_{max} are derived, and the model parameters are estimated.

3.4.3.2 Modified Dose-Response (MDR)

The Modified Dose-Response (MDR) model minimizes the error presented by the Thomas model at the lower and higher time periods of the breakthrough curve of the adsorption media that demonstrates asymmetrical behavior. MDR is an empirically derived model that has specifications for reaction kinetics. The linear and non-linear forms are shown below, respectively:

$$\ln\left(\frac{C_e}{C_0 - C_e}\right) = a_{mdr}\ln(C_0 Qt) - a_{mdr}\ln(q_{max} m) \quad (19)$$

$$\frac{C_e}{C_0} = 1 - \frac{1}{1+\left(\frac{C_0 Qt}{q_{max} m}\right)^{a_{mdr}}} \quad (20)$$

a_{mdr} is the modified dose-response model constant in mL /mg min. The input parameters m, Q, t, C_e, and C_0 are known quantities, and a_{mdr} and q_{max} are obtained by conducting a linear regression with the linear form of the model.

3.4.4 Life-Expectancy of Media Recipes

The life expectancy of the adsorption media is calculated using q_{max}, which is the equilibrium media uptake when C_1/C_0 reaches an asymptotic value, which is obtained from the column adsorption study using the following equation:

3.4.4.1 Life-Expectancy Usage Rate Equation

$$\text{Usage rate} = \frac{C_0 - C_1}{q_{max}} \quad (21)$$

Where:

C_0 is the influent concentration in mg/L

C_1 is the average target influent for the entire column in mg/L

q_{max} is $(x/m)_o$ in mg/g where $C_0=C_1$

The life expectancies of the IFGEM-3 and AGEM-2 sorption media are important parameters in estimating the operational time and the efficiency of an adsorption treatment before replacement. The determination of the nutrients absorbed by each media at equilibrium are used to obtain an equilibrium media uptake (q_{max}) based on either the Bohart-Adams (B-A) model or the Modified Dose Response Model. Obtaining q_{max} and calculating the usage rate values using Equation 23 make it possible to graph the life expectancy curves and therefore, calculate the life expectancy of a sorption media (Jones et al. 2015).

CHAPTER FOUR: ISOTHERM STUDY RESULTS AND DISCUSSION

4.1 Sorption Efficiency of the Media

The experimental amount of nutrient absorbed by the sorption media was calculated using the following mass balance equation (Howe et al. 2012):

$$\mathbf{m}(\mathbf{q_e} - \mathbf{q_i}) = \mathbf{V}(\mathbf{C_i} - \mathbf{C_e}) \qquad (22)$$

where q_i is the initial nutrient concentration in the sorbent and is normally assumed to be zero; q_e is the final nutrient concentration in the sorbent.

And:

$$\mathbf{q_e} = \frac{\mathbf{V}(\mathbf{C_i} - \mathbf{C_e})}{\mathbf{m}} \qquad (23)$$

C_i, and C_e are the initial and final concentrations of nutrients in solution (mg/L); V is the volume of the solution (L); m is the dry weight of the sorbent (g).

The sorption efficiency of each media is calculated from the following equation:

$$\% \text{ nutrient removal} = \left[\frac{\mathbf{C_i} - \mathbf{C_e}}{\mathbf{C_i}}\right] \times \mathbf{100} \qquad (24)$$

The calculated average removal efficiency for phosphate (PO_4^{-3}), nitrate (NO_3^-), and ammonia (NH_3) removed by Natural Soil, IFGEM-3, AGEM-1 and AGEM-2 are shown in the following table:

Table 2: Nutrient removal efficiency for different sorption media

Sorption Media	Nutrient Removal Efficiency								
	PO_4^{-3}			NO_3^-			NH_3		
	C_1	C_2	C_3	C_1	C_2	C_3	C_1	C_2	C_3
Natural Soil	-	-	-	-	-	-	-	-	-
IFGEM-3	100%	98.32%	99.73%	44.39%	34.78%	37.85%	-	-	-
AGEM-1	95.82%	96.59%	99.84%	39.24%	29.76%	32.02%	-	-	-
AGEM-2	96.95%	99.37%	98.34%	85.43%	71.06%	73.16%	-	-	-

The performance efficiencies of Natural Soil, IFEGM, AGEM-1 and AGEM-2 for phosphate and nitrate removal and ammonia recovery in triplicates were investigated under varying influent conditions. Table 2 shows that while influent conditions have significantly impacted nitrate removal performance, they have not significantly impacted phosphate removal of IFGEM-3, AGEM-1 and AGEM-2 media. IFGEM-3 has the highest average phosphate removal efficiency (99.35%) under the studied influent concentrations (C_1, C_2, C_3) compared to that of 98.2% and 97.42% for AGEM-2, and AGEM-1, respectively. In contrast, AGEM-2 has the highest ranges of nitrate removal efficiency, which are between 71.06 % to 85.43 %, compared to that of IFGEM-3, which are between 34.78% to 44.39%, and for AGEM-1, between 29.76% to 39.24%. Nitrate removal can be attributed to the anticipation of both adsorption processes and nitrate reduction to ammonia and further to nitrogen gas (Equation 4-5). However, the increase in nitrate removal in AGEM-2 can be attributed to the presence of aluminum powder and to the increase in percentage by volume of iron filling compared to IFGEM-3 and AGEM-1.

However, none of the studied media demonstrated any removal efficiency for ammonia within the five-hour time interval. Instead, IFGEM-3, AGEM-1, and AGEM-2 were found to produce ammonia and the maximum ammonia production occurred after 5 hours of contact time. The reason for ammonia production was because of the reduction of nitrate to ammonia via iron that was among the constituents of these media (Huang et al. 2007). Also, the presence of aluminum flasks and powder in both AGEM media aided the reduction of nitrate to ammonia and thus, enhanced ammonia production (Murphy 1991). AGEM-2 has a 39.63% and a 30.82% higher ammonia production than IFGEM-3 and AGEM-1, respectively. Thus, AGEM-2 has nutrient recovery potential and its media can be reused and considered for agricultural crop production.

However, natural soil showed almost no nutrient removal efficiency and that could be due to its already high nutrient content, which prevents contaminated water from penetrating through its surface layers and, thus, weakening the soil's adsorption potential. Since there were insignificant differences in phosphate removal efficiencies among IFGEM-3, AGEM-1 and AGEM-2 media, and since AGEM-2 has the highest nitrate removal efficiency, AGEM-2 is considered the best candidate media. AGEM-2 is thus recommended for stormwater applications under varying nutrient influent conditions as this study has shown.

4.2 Physical Characteristics of the Studies Media

Table 3: **Material characteristics of Natural Soil and nutrient sorption media.**

Characteristics	Sorption Media			
	Natural Soil*	IFGEM-3	AGEM-1	AGEM-2
Surface Area (m^2 g^{-1})	9.37	0.7	1.274	1.714
Hydraulic Conductivity (cm s^{-1})	0.003(5.76)	0.0314(0.001)	0.030(0.0007)	0.027(0.00045)
Bulk Density (g cm^{-3})	2.36	1.37	1.42	1.52
Porosity (%)	40.43(2.86)	25.53(1.03)	30.54(1.72)	29.072(0.00045)

() Values in parenthesis signify standard deviation

With respect to physical characteristics, natural soil provided the lowest hydraulic conductivity of the media, while IFGEM-3 provided the highest. A high hydraulic conductivity (cm s^{-1}) reflects good permeability of a media, allowing contaminated water to pass through its layers, and thus, enhances the nutrient removal processes from water. Table 3 shows that natural soil has a large bulk density of 2.36g/cm^3 which is comparable to the bulk density of rocks, 2.65 g cm^{-3} (nrcs.usda.gov). This reflects the natural soil compaction and its poor water infiltration. The bulk density of IFGEM-3, AGEM-1, and AGEM-2 were 1.37, 1.42, and 1.714 g cm^{-3}, respectively, which is comparable to that of silt loam soil, 1.33 g cm^{-3} (nrcs.usda.gov). This indicates that the current sorption media were loose, well-aggregated, and have good nutrient adsorption potential.

Furthermore, the porosity of the natural soil is at the low range of that of the typical percentage of total porosity in a mineral soil that usually ranges between 40% to 60%. It indicates that natural soil was unlikely to remove nutrients from contaminated water. Porosity and bulk density have an inverse relationship, where an increase in bulk density reduces porous volume, porosity, and leads to a general reduction in water holding capacity. The Brunauer-Emmett-Teller (BET) surface area is a measurement of the required surface area of the monomolecular layer and the amount of adsorbate that can be held by such a surface area of the sorption media. For instance, Table 3 shows that the 9.37 m^2 monomolecular surface area of natural soil was necessary to absorb one gram of nutrient/nutrients, compared to that of only a 0.7 m^2 of IFGEM-3 media.

4.3 Chemical Characteristics of the Studies Media

pH, dissolved oxygen (DO), and oxidation reduction potential (ORP) were the chemical parameters measured during the isotherm tests. The pH of the effluent varied between 6.88 and 8.66 in the media columns and between 7.22 and 8.63 in the natural soil column at room temperature. The room temperature was between 21 and 23° C. The DO of the effluent varied between 5.68 and 9.18 and between 5.48 and 9.02 in the media and natural soil columns, respectively. Similarly, the ORP varied between 122.07 and 268.10 and between 141.90 and 268.10 in the media and natural soil columns, respectively. The DO, pH and ORP impact on the adsorption capacity of a filter media was determined in similar previous experiments but are beyond the scope of this study.

4.4 The Impact of the Contact Time on Nutrient Influent Concentrations of the Studied Media

Distilled water was spiked with three different influent concentrations of nitrate and phosphorus referred to as C_1 (0.9 mg/L NO_3^- and 0.3 mg/L PO_4^{-3}), C_2 (1.5 mg/L NO_3^- and 0.9 mg/L PO_4^{-3}) and C_3 (2 mg/L NO_3^- and 2 mg/L PO_4^{-3}). The alteration upon these influent concentrations (C_1, C_2, C_3) were investigated under various contact times between the spiked water and the studied sorption media.

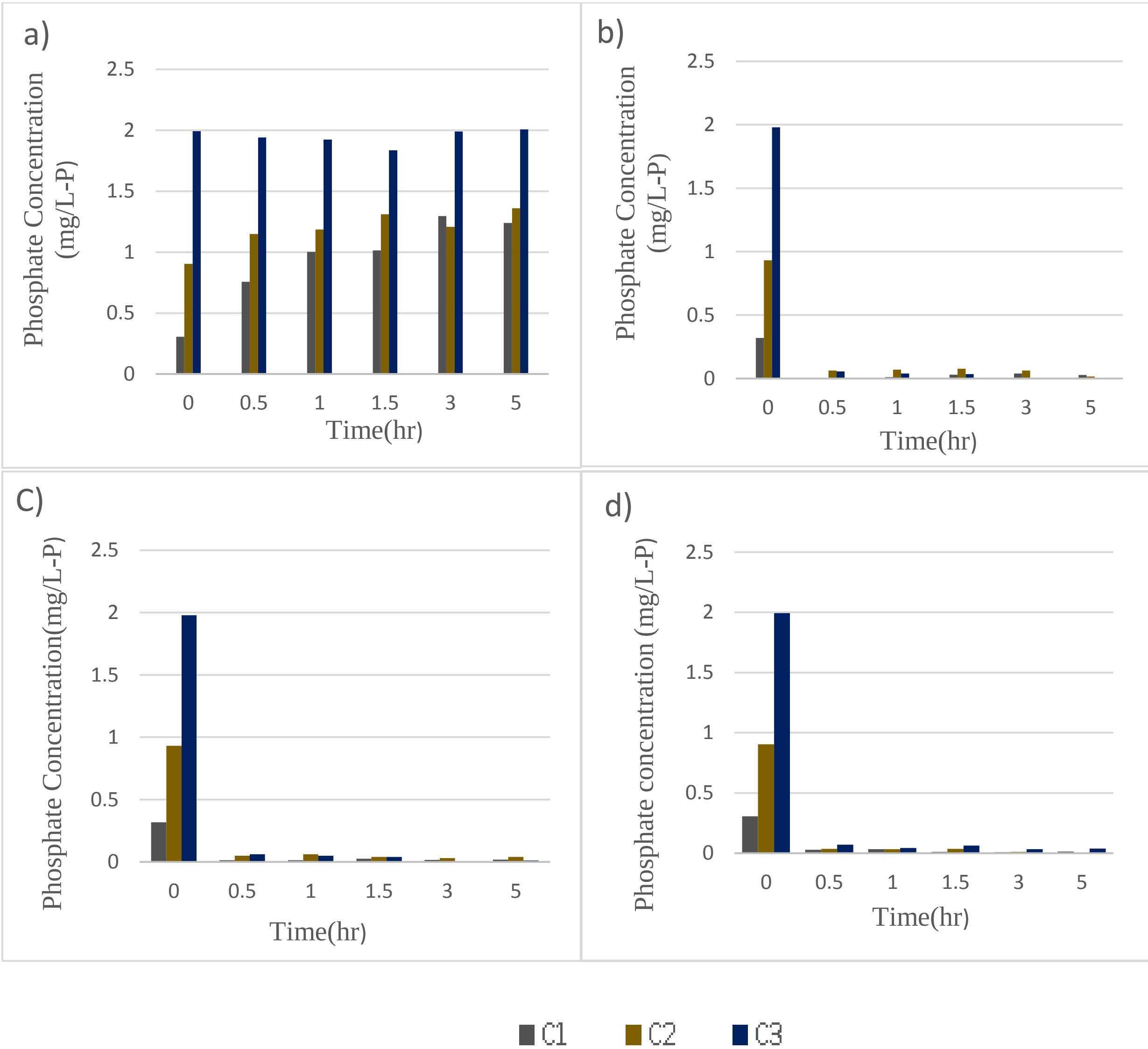


Figure 2 Influent phosphate concentration reduction with time for: a) natural soil, b) IFGEM-3, c) AGEM-1, and d) AGEM-2 at influent conditions C1, C2, and C3

Figure-2-a shows that influent phosphate concentrations (C1, C2, and C3) were not reduced when natural soil was utilized as the sorption media, meaning that it did not provide adsorption for phosphate species. Moreover, moderate phosphate concentrations, (C1 and C2) increased over the five hours of contact time with natural soil. However, for the high phosphate concentration (C3), natural soil provided some phosphate removal whereas the influent concentration was reduced from 2 mg/L-PO_4^{3-} to 1.94, 1.923, and 1.84 mg/L-PO_4^{3-} after a contact time of 30 minutes, 1 hour and 1.5 hours, respectively. However, 3 and 5 hours contact time caused the phosphate concentration to increase again to the starting influent concentration of 2.0mg/L-PO_4^{3-}. The reason for this could be related to the physical characteristics of the natural soil such as its low degree of porosity, which caused reduction in its interior surface area, onto which adsorption can occur. Also, natural soil could be saturated with nutrients such as phosphate, and when phosphate species leach out of the soil this causes an increase in phosphate concentrations which occurred in C1, C2 and eventually in C3.

However, and as Figures-2-b, 2c, and 2d show, IFGEM-3, AGEM-1 and AGEM-2 sorption media act similarly when the highest phosphate concentration reduction occurred immediately within the first 30 minutes of contact time. The highest phosphate reduction was achieved by IFGEM-3 media then followed by AGEM-2 and lastly by AGEM-1. But, since these green media did not reflect significant differences in their phosphate removals, phosphate cannot be the limiting nutrient in determining the best nutrient performance for these sorption media.

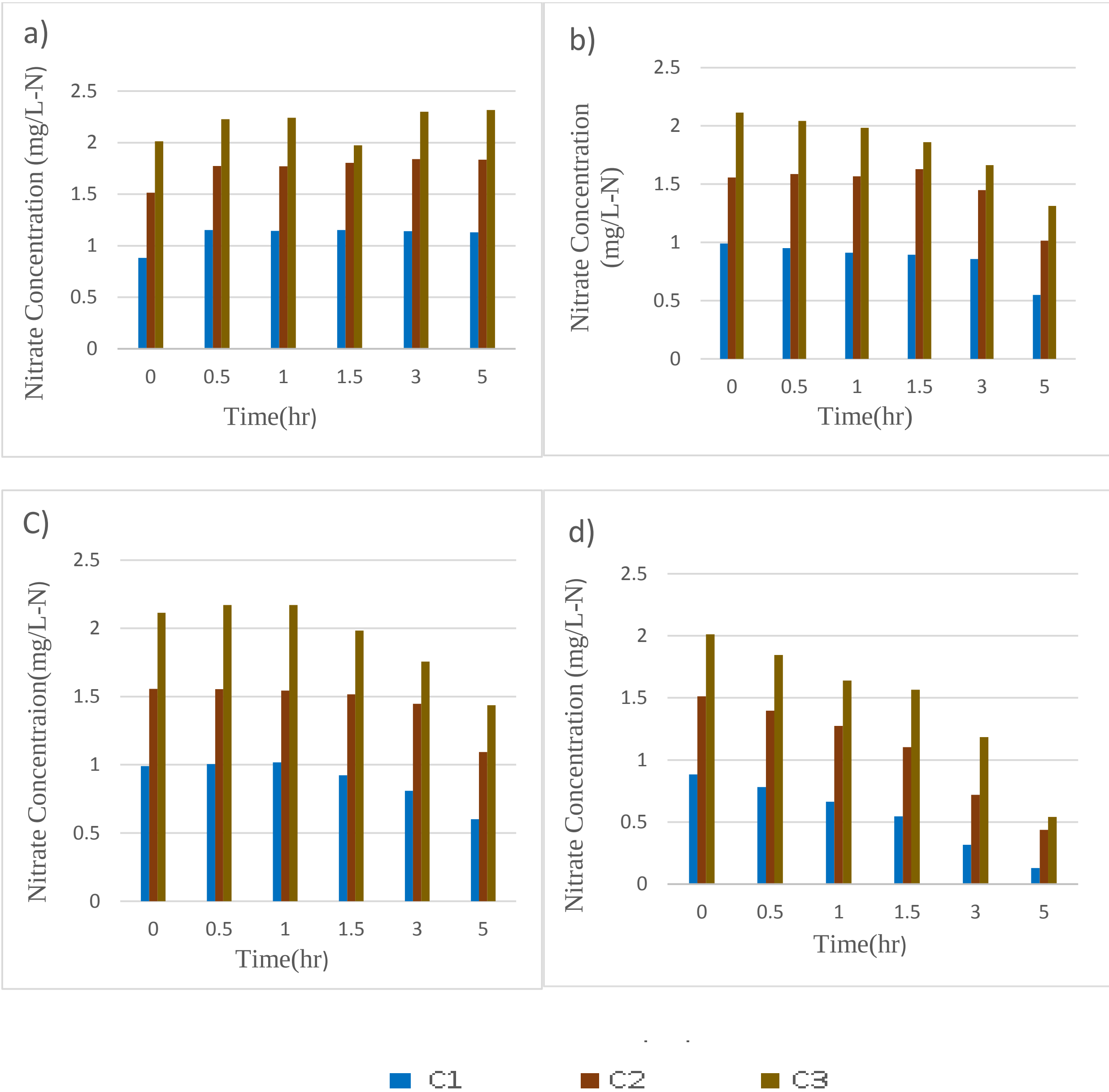


Figure 3 Influent nitrate concentration reduction with time for: a) natural soil, b) IFGEM-3, c) AGEM-1, and d) AGEM-2 at influent conditions C1,C2, and C3

Figure-3-a, for natural soil, shows that almost all nitrate influent concentrations (C1,C2,and C3) exhibit an increase in effluent concentration as contact time increases. As mentioned before, that could be due to nitrate leaking out of the saturated soil into the water samples; adding more nitrate species and increasing nitrate concentrations in the effluent samples. In contrast, and as Figures-3-b, 3c, and 3d show, all the studied green media attained a reduction in nitrate influent concentrations and this reduction was impacted by the influent concentrations. The contact time plays an essential role in which more nitrate concentration reductions can be achieved as more contact time is provided and, thus, this enhances the overall performance of the current green media.

The highest nitrate reduction under various influent concentrations and within the five-hour contact time was achieved by AGEM-2 (Figure-3-d). The second highest nitrate reduction was achieved by IFGEM-3, while AGEM-1 achieved the lowest. The remarkable performance of AGEM-2 in reducing nitrate species in effluent samples is linked to its media components and their optimized ratios that shape and impact AGEM-2's physical and chemical characteristics. For instance, the aluminum used in the form powder in AGEM-2 provides a vast number of tiny pores within its granular interior material resulting in an increase in porosity (ratio of pore volume to total volume) and, thus, increasing the amount of its interior surface area onto which adsorption can occur (Howe et al. 2012).

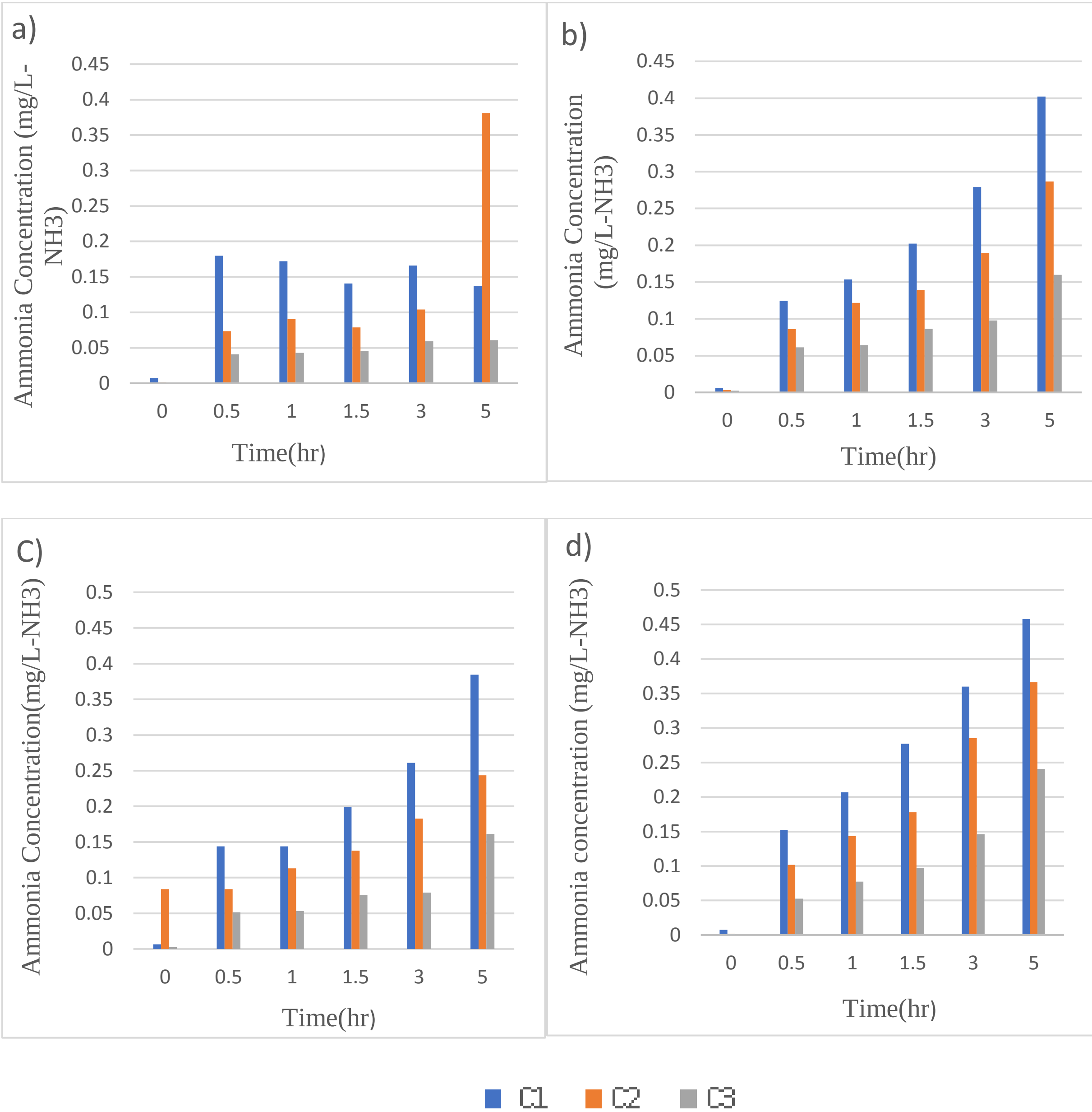


Figure 4 Ammonia generation with respect to time for: a) natural soil, b) IFGEM-3, c) AGEM-1, and d) AGEM-2 at influent conditions C1, C2, and C3

Figures 4-a through 4d show that all the analyzed effluent concentrations contain ammonia species, confirming that all the studied media have produced ammonia at different rates. It was observed that ammonia production increases as contact time increases. AGEM-2 has the highest ammonia production which consistently increased with contact time. The second highest ammonia production was accomplished by IFGEM-3 and the lowest ammonia production was accomplished by AGEM-1. The results indicate that AGEM-2 has a high ammonia recovery potential and that recovered nutrient can be utilized as an agricultural fertilizer. The ammonia production occurs as a by-product of redox reactions that reduce nitrate to ammonia, in the presence of iron and aluminum.

4.5 Isotherm Model Results

Several isotherm models were applied to the isotherm experimental data to predict the maximum adsorption capacities and obtain information on the adsorption processes. The best fit isotherm models were selected based on three main indexes. The first index is the coefficient of determination (R^2). The second index is the maximum adsorption capacities (q_{max}, mg/g) derived for phosphate, nitrate and ammonia. The third index is based on the model's ability to obtain consistent and logical results. The R^2 works as an indicator of how the theoretical data is related to the experimental data with a preferred R^2 value close to one. Also, the compatibility of the derived q_{max} compared to the experimental q_e for each tested nutrient is a good indicator of a strong relationship between the experimental and theoretical data. Finally, the stability of the model's performance in obtaining consistent and reliable results regarding the three influent conditions and the effluent triplicates for the columns for each media is a good indicator of a strong relationship between the experimental and theoretical data. Based on the above mentioned indexes, six models were chosen and ranked in descending order from the most to the least appropriate model as follows: Temkin> Langmuir > Harkin-Jura >Jovanovic> Freundlich & Halsey for phosphate and

Temkin> Langmuir > Jovanovic> Harkin-Jura > Freundlich & Halsey for nitrate and Langmuir > Temkin> Harkin-Jura for ammonia for the studied sorption media.

Applying the Langmuir isotherm model to Natural Soil resulted in high R^2 values for phosphate and nitrate removals, and ammonia production. Also, high R^2 values were attained from applying the model to IFGEM-3, AGEM-1 and AGEM-2 for phosphate and ammonia, but not for nitrate. In general, high R^2 values are used as indicators to the validation of the theoretical data obtained from a model with respect to the experimental data, and therefore, the Langmuir isotherm model is considered one of the 'best fit' model describing the current experimental data for all the current media for phosphate and ammonia.

Moreover, the Langmuir isotherm model was used to investigate the average maximum monolayer adsorption capacity (q_{max}) for Natural Soil, IFGEM-3, AGEM-1 and AGEM-2 for phosphate, nitrate and ammonia in triplicates under varying influent conditions. For phosphate under condition C3, (Tables 4-6) show that AGEM-1, AGEM-2 and IFGEM-3 have maximum average adsorption capacities of 12, 11.96, and 11.58 µg/g, respectively. Natural Soil has the least maximum average adsorption capacity of 0.027 µg/g. Moreover, AGEM-2 has the highest maximum average capacity for nitrate adsorption and ammonia production, while Natural Soil has the least among the studied sorption media. According to this model, considering the three influent conditions C1, C2, C3; IFGEM-3 and AGEM-1 have about a 2.54% better removal efficiency than AGEM-2 for phosphate while AGEM-2 has (99.7 %, 98.3%), (51.74 %, 39.63%) and (43.83%, 30.82%) better removal efficiency than Natural Soil, IFGEM-3 and AGEM-1 for nitrate removal and ammonia production, respectively. In general, according to the Langmuir model, AGEM-2 performs better than the rest of the studied sorption media with respect to nitrate and ammonia by having the highest average maximum adsorption capacity (q_{max}).

The average Langmuir isotherm constant (K_L), related to the energy of adsorption, was computed and the average separation factor (R_L) was calculated from Equation 7 for Natural Soil, IFGEM-3, AGEM-1 and AGEM-2 for phosphate, nitrate and ammonia, respectively. R_L values describe the nature of the adsorption, indicating that the equilibrium sorption is favorable for ammonia, Natural soil and AGEM-2 where $0<R_L<1$, and is unfavorable for Natural soil for phosphate and nitrate where $R_L>1$, and the equilibrium sorption is linear for IFGEM-3 for ammonia where $R_L=1$ (Webber and Chakkravorti 1974; Dada et al. 2012).

Table 4: Isotherm models' parameters for phosphate adsorption via varying sorption media

Isotherm Models	Natural Soil			IFGEM-3			AGEM-1			AGEM-2		
	PO_4^{-3}			PO_4^{-3}			PO_4^{-3}			PO_4^{-3}		
	C_1	C_2	C_3	C_1	C_2	C_3	C_1	C_2	C_3	C_1	C_2	C_3
Langmuir												
R^2	0.9944	0.9873	0.952	0.9011	0.9522	0.8944	0.9619	0.9879	0.6367	0.9571	0.8929	0.9682
q_{max}, ug g^{-1}	8.3401	0.7554	0.02737	1.648	5.09	11.582	-950.93	-473.89	-13475	1.597	1.6039	11.3629
K_L	-0.3269	-0.5801	-0.5602	-803.48	-859.87	1	1.6945	5.0543	11.596	-966.976	-1434.3	-854.43
Freundlich												
R^2	-	-	-	0.3021	0.9822	0.9555	0.9909	0.9879	0.8933	0.9909	0.9804	0.9924
n	-	-	-	58.1395	-24.390	-101.01	-16	-24.390	-104.17	-15.0376	-16.779	-0.6702
K,$(\mu g g^{-1})(L \mu g^{-1})^{1/n}$	-	-	-	1.8724	4.6377	11.2564	1.402	4.6377	11.256	1.30979	1.33475	10.7895
Temkin												
R^2	0.993	1	1	0.9727	0.9842	0.957	0.991	0.989	0.895	0.9919	0.9818	0.9928
B,(J/mole)	-0.006	-0.0075	-0.0115	-0.0001	0.0364	-0.0001	-0.001	-0.0003	-0.0001	-0.0001	-0.0001	-0.0003
A_T,(L/g)	2.048	1.055	0.503	2.3E-06	96.15	2.3E-49	0.2466	3.06E-07	2.3E-49	2.3E-06	2.3E-06	2.3E-16
Harkin-Jura												
R^2	0.9299	0.9553	0.9411	0.9549	0.9776	0.9526	0.9889	0.9855	0.8894	0.9888	0.9775	0.9917
A	70308	683625	9E+07	500266	45080	7868.8	463340	46832	7870.4	525669	513437	8500.1
B	-4.5553	-4E+06	-3E+08	107447	6659.7	333.02	89117	8433.2	322.09	104990	94035	866.71
Jovanovic												
R^2	-	-	-	0.987	0.986	0.958	1	1	1	1	1	1
q_{max}, µg g^{-1}	-	-	-	368.4	524.6	2542.0	1918	5595	12.0	1.84	1.84	11.96
K_J	-	-	-	3.34	1.127	0.513	3.355	1.14	0.512	3.5	1.13	0.514
Halsey												
R^2	-	-	-	0.9673	0.9822	0.9555	0.9909	0.9879	0.8933	0.9909	0.9804	0.9924
K_H	-	-	-	-0.073	-0.041	-0.010	-0.0625	-0.0515	-0.0096	-0.067	-0.060	-0.026
n_H	-	-	-	-6.618	-5.374	-4.487	-6.5697	-5.3979	-4.4867	-6.638	-6.619	-4.529

Table 5: Isotherm models' parameters for nitrate adsorption via varying sorption media

Isotherm Models	Natural Soil			IFGEM-3			AGEM-1			AGEM-2		
	NO_3			NO_3			NO_3			NO_3		
	C_1	C_2	C_3	C_1	C_2	C_3	C_1	C_2	C_3	C_1	C_2	C_3
Langmuir												
R^2	0.9995	0.998	0.9178	0.483	0.19	0.545	0.275	0.205	0.341	0.7242	0.6393	0.6372
q_{max}, ug g^{-1}	0.4551	-0.3314	0.03284	0.168	-0.051	0.227	-0.064	0.014	0.139	0.6177	2.6119	0.92387
K_L	-0.6769	-0.4652	-0.4493	-1.87	-0.939	-0.744	-1.43	-0.878	0.603	-4.54058	-0.3314	-1.3972
Freundlich												
R^2	-	-	-	0.8706	-	0.858	0.3372	0.6914	0.3979	0.7784	0.8368	0.8026
n	-	-	-	-0.2699	-	-0.19998	0.09767	-0.0940	0.07912	-1.04888	-0.5848	-39.216
$K,(\mu g g^{-1})(L \mu g^{-1})^{1/n}$	-	-	-	3.1601	-	23.917	78.23	9.678	7.9E-03	0.8149	2.0179	4.2482
Temkin												
R^2	0.629	1	0.999	0.9981	0.998	0.9964	0.995	0.999	0.997	0.9459	0.9789	0.9772
B,(J/mole)	0.037	-0.0108	-0.0128	-0.0043	-0.0077	-0.0099	-0.0047	-0.0078	-0.0107	-0.0021	-0.0049	-0.0062
A_T,(L/g)	0.8831	0.6532	0.499	0.98385	1	0.46409	1.01	0.638	0.473	0.78813	0.57636	0.42525
Harkin-Jura												
R^2	0.9985	0.9944	0.9411	-	0.0911	0.3259-	0.4098	0.0147	0.6713	0.3794	0.4071	0.3257
A	902811	3E+06	9E+07	-	1E+08	4E+06	7E+07	2E+07	-9E+06	2E+06	660255	173496
B	-8E+06	-1E+07	-3E+08	-	6E+07	8E+06	8E+08	9E+06	5E+07	2E+06	3E+06	1E+06
Jovanovic												
R^2	-	-	-	0.938	0.435	0.9284	0.394	0.714	0.446	0.924	0.920	0.901
q_{max}, μg g^{-1}	-	-	-	201.5	0.00	592.0	0.00	33770.0	0.00	7.77	20.0	24
K_J	-	-	-	5.23	-9.80	3.10	-13.98	8.31	-7.5	2.88	2.2	1.52
Halsey												
R^2	-	-	-	0.8706	0.4243	0.858	0.3372	0.6914	0.3979	0.7784	0.8368	0.8026
K_H	-	-	-	-3.704	12.057	-5.006	10.239	-10.636	12.639	-0.953	-1.710	-1.492
n_H	-	-	-	-8.060	-6.923	-3.733	-2.5481	-4.638	-11.75	-7.113	-6.205	-5.461

Table 6: Isotherm models' parameters for Ammonia adsorption via varying sorption media

Isotherm Models	Natural Soil			IFGEM-3			AGEM-1			AGEM-2		
	NH_3			NH_3			NH_3			NH_3		
	C_1	C_2	C_3	C_1	C_2	C_3	C_1	C_2	C_3	C_1	C_2	C_3
Langmuir												
R^2	1	1	1	0.9999	0.9999	0.9999	0.9999	0.9347	0.9999	0.9999	1	1
q_{max}, ug g^{-1}	18.012	104.809	-5.6792	37.086	34.023	20.553	0.00131	0.2973	16.3020	45.587	119.493	3.3E+11
K_L	-0.3023	-0.0561	1.18812	-0.1511	-0.1675	-0.2764	-4307.8	-3.4516	-0.3458	-0.12322	-0.0493	-1.8E-14
Freundlich												
R^2	-	-	-	-	-	-	-	-	-	-	-	-
n	-	-	-	-	-	-	-	-	-	-	-	-
K,$(\mu g g^{-1})(L \mu g^{-1})^{1/n}$	-	-	-	-	-	-	-	-	-	-	-	-
Temkin												
R^2	0.999	0.998	0.999	0.9726	0.9662	0.9799	0.980	0.975	0.975	0.9748	0.9715	0.9516
B,(J/mole)	0.0009	-0.0012	-0.0003	-0.0014	-0.001	-0.006	-0.0014	-0.0009	-0.0006	-0.0016	-0.0012	-0.0007
A_T,(L/g)	17.973	17.002	54.598	12.1825	18.1742	28.0316	12.182	11.524	28.032	11.444	15.643	111.529
Harkin-Jura												
R^2	0.9972	0.8844	0.9958	0.8958	0.8634	0.9203	0.9797	0.0147	0.8845	0.9056	0.8786	0.8279
A	-4E+06	-3E+06	-5E+07	-1E+06	-4E+06	-1E+07	-2E+06	2E+07	-2E+07	-82245	-2E+06	-9E+06
B	-6E+06	-6E+06	-4E+07	-3E+06	-7E+06	-2E+07	-4E+06	9E+06	-2E+07	-2E+06	-4E+06	-1E+07
Jovanovic												
R^2	-	-	-	-	-	-	-	-	-	-	-	-
q_{max}, μ g^{-1}	-	-	-	-	-	-	-	-	-	-	-	-
K_J	-	-	-		-	-	-	-	-	-	-	-
Halsey												
R^2	-	-	-	-	-	-	-	-	-	-	-	-
K_H	-	-	-	-	-	-	-	-	-	-	-	-
n_H	-	-	-	-	-	-		-	-	-	-	-

The Freundlich model describes the equilibrium for the sorption media having adsorption sites with different site energies. The average Freundlich adsorption capacity parameter K, the n values, and the average R^2 were calculated for Natural Soil, IFGEM-3, AGEM-1, and AGEM-2 for phosphate, nitrate and ammonia, respectively. The Freundlich adsorption capacity parameter K is related to the strength of the adsorptive bond while the n is related to the strength of the bond distribution or adsorption intensity, both were calculated and are provided in summary Tables 4 through 6. The adsorption intensity parameter, n, is less than 1 and this indicates that the bond energies increase with surface density (Reed and Matsumoto, 1993). By comparing the above values, IFGEM-3 is found to have the highest Freundlich adsorption capacity, K, followed by AGEM-1, while AGEM-2 has the lowest K. The n follows the same trend. For instance, for AGEM-2 for nitrate, the Freundlich adsorption capacity K and n values were found to be 2.360 μg $g^{-1}(L/\mu g)^{1/n}$ and -13.6164, respectively.

The Harkin-Jura and Halsey models explain multilayer adsorption processes in which a random distribution of the absorbent's sites are covered by more than one layer of the adsorbate and that a vertical interaction occurs between the molecules of these layers while the lateral interaction is ignored (Park and Seo 2011). The Halsey model exhibits relatively high coefficient of determination R^2 values for IFGEM-3 and AGEM-2 media for nitrate removal, indicating that the adsorption process is suitable to be defined by this model. The adsorption process of IFGEM-3 and AGEM-2 for ammonia were well defined by the Harkin-Jura model that reflects high R^2 values. In general, the fit of these two models for most of the experimental data suggests that both media, IFGEM-3 and AGEM-2, have multilayer adsorption processes for phosphate, nitrate and ammonia.

The Temkin model was chosen to give a better understanding of the nature of the adsorption process for the studied media. Summary Tables 4 through 6 display high R^2 values obtained from the applications of the Temkin model, indicating that the experimental data for Natural Soil, IFGEM-3, AGEM-1 and AGEM-2 for phosphate, nitrate, and ammonia are well described by this model. The Temkin isotherm model explains whether the adsorption process is physical, or chemical based on the amount of heat released or gained per mole of an absorbate (Dada et al., 2012). The parameter *B* is related to the heat of the sorption while A_T is the Temkin isotherm equilibrium binding constant. *B* and A_T values are calculated from the slope and intercept, respectively, by fitting the experimental data into the linear form of the equation and plotting q_e verses Ln C_e. The *B* numerical value indicates the amount of energy used per mole while the negative sign preceding the *B* value indicates the release of energy upon the attachment of the absorbate (pollutant) to the interface of the green sorption media. For example, for AGEM-2, the *B* values reflect the physical adsorption processes where $B < 20$ KJ/mole and the R^2 values are 0.9459, 0.9789, 0.9772 for the nitrate removal for the triplicates, respectively. In general, the Temkin model exhibits high R^2 values for both media, IFGEM-3 and AGEM-2, for phosphate, nitrate and ammonia in triplicates, and the *B* values are low, which suggests physical adsorption processes occur.

4.6 Sorption Media Characterizations Based on Varying Isotherm Models' Assumptions

Table 7 shows high R^2 values and the consistency of the model to obtain reasonable and compatible results with the current experimental data for the three influent conditions. Natural Soil, IFGEM-3, AGEM-1 and AGEM-2 demonstrated that the heat released or gained during the adsorption process is a function of temperature and linearly decreases with coverage. The sorption media's layers have molecules with binding energies that are uniformly distributed, resulting in a well distributed absorbate layer on the interface of the media. Natural Soil and AGEM-2 for phosphate, nitrate and ammonia removal, and IFGEM-3, and AGEM-1 for phosphate and ammonia can be characterized by having a homogenous sorption surface where a certain number of the absorbent's sites demonstrate the same free energy changes. Equilibrium adsorption distribution of the pollutants between liquid and solid phases were well defined by these sorption media.

IFGEM-3, AGEM-1, AGEM-2 for phosphate and ammonia, and Natural Soil for phosphate, nitrate and ammonia, can be characterized by having a heterogeneous pore distribution that may lead to an uneven amount of absorbate within the same layer of media. IFGEM-3, AGEM-1 and AGEM-2 media demonstrate both monolayer and multilayer adsorption behaviors that make them more efficient in absorbing phosphate than absorbing nitrate (Table 21). Furthermore, IFGEM-3 and AGEM-2 for phosphate and nitrate removal demonstrate mechanical contact between these nutrients and the media, permitting the calculation of the maximum adsorption capacities by describing these homogenous media with respect to their nutrient concentrations. Finally, the multilayer adsorption behavior allows more pollutants (nutrients) to be absorbed by the media where multilayers; a layer above the layer of absorbate, can be formed, and thus, causing an increase in sorption surface area of a media, resulting in an overall better removal performance.

Table 7: Suggested characterizations for the sorption media based on the assumptions of the applied isotherm models

Isotherm Models	Natural Soil			IFGEM-3			AGEM-1			AGEM-2		
	PO4-3	NO_3	NH_3	PO4-3	NO_3	NH_3	PO4-3	NO_3	NH_3	PO4-3	NO_3	NH_3
Langmuir												
Monolayer Adsorption	x	x	x	x		x	x		x	x	x	x
Validates Absorbate Equilibrium Distribution Between the Liquid and solid Phases	x	x	x	x		x	x		x	x	x	x
Homogeneous Surface(Fixed identical adsorbent's sites; sites have the same free-energy change)	x	x	x	x		x	x		x	x	x	x
Freundlich												
Multi-Layer Adsorption				x	x		x			x	x	
Reversible Adsorption				x	x		x	x		x	x	
Uniform Energy Distribution				x	x		x	x		x	x	
Temkin												
The adsorption heat of an adsorbent's layer is a function of temperature	x	x	x	x	x	x	x	x	x	x	x	x
Adsorption heat is linearly decreasing with coverage	x	x	x	x	x	x	x	x	x	x	x	x
Binding energies are uniformly distributed	x	x	x	x	x	x	x	x	x	x	x	x
Harkin-Jura												
Multilayer adsorption	x	x	x	x		x	x		x	x		x
Heterogeneous pore distribution	x	x	x	x		x	x		x	x		x

Isotherm Model	Natural Soil			IFGEM-3			AGEM-1			AGEM-2		
	PO4-3	**NO_3**	**NH_3**	**PO4-3**	**NO_3**	**NH_3**	**PO4-3**	**NO_3**	**NH_3**	**PO4-3**	**NO_3**	**NH_3**
Jovanovic Model												
Mechanical contact between adsorbate and adsorbent				x	x	x	x			x	x	
Permitting the calculation of the maximum adsorption of the sorption media				x	x		x			x	x	
Elovich Model												
Multilayer adsorption				x	x		x			x	x	
The adsorption sites are exponentially increase with adsorption				x	x		x			x	x	
Permitting the calculation of the maximum adsorption of the sorption media				x	x		x	x		x	x	
Redlich-Peterson												
Multilayer adsorption				x	x		x			x	x	
Henry's Equation when β=1												
Describes adsorbate concentrations in homogenous and heterogenous sorption media				x	x		x			x	x	
Halsey Model												
Multilayer adsorption				x	x		x			x	x	
Heterosporous Nature				x	x		x	x		x	x	

CHAPTER FIVE: COLUMN STUDY RESULTS AND DISCUSSION

5.1 Column Study

The purpose of column study was focused on testing nitrate adsorption capacity and life expectancy for IFGEM-3 and AGEM-2 media. The isotherm study conducted indicated that all tested sorption media, except natural soil, had high phosphate removal, and the difference between their removal efficiencies were insignificant. Also, the study showed that AGEM-2 had the best nitrate removal efficiency followed by IFGEM-3 and that the difference between their adsorption efficiencies were significant. Furthermore, since the AGEM-2 media was demonstrated to have the highest ammonia recovery for reuse potential, followed by IFGEM-3 media, nitrate is considered the decisive nutrient in determining the best media in terms of adsorption performance and life expectancy for future stormwater runoff nutrient control applications.

Thus, phosphate, nitrate and ammonia removals for IFGEM-3 and AGEM-2 media were further tested via the adsorption study (Figure 1) where each media utilized three columns that were exposed to the same influent condition of 2mg/L -PO_4^{3-} and 2mg/L -NO_3^- in distilled water and a flow rate of 3mL/min. Unfiltered effluents were collected from each media at the same contact times and analyzed for phosphate, nitrate and ammonia in triplicates using the analyzed methods and measuring range presented in Table 1.

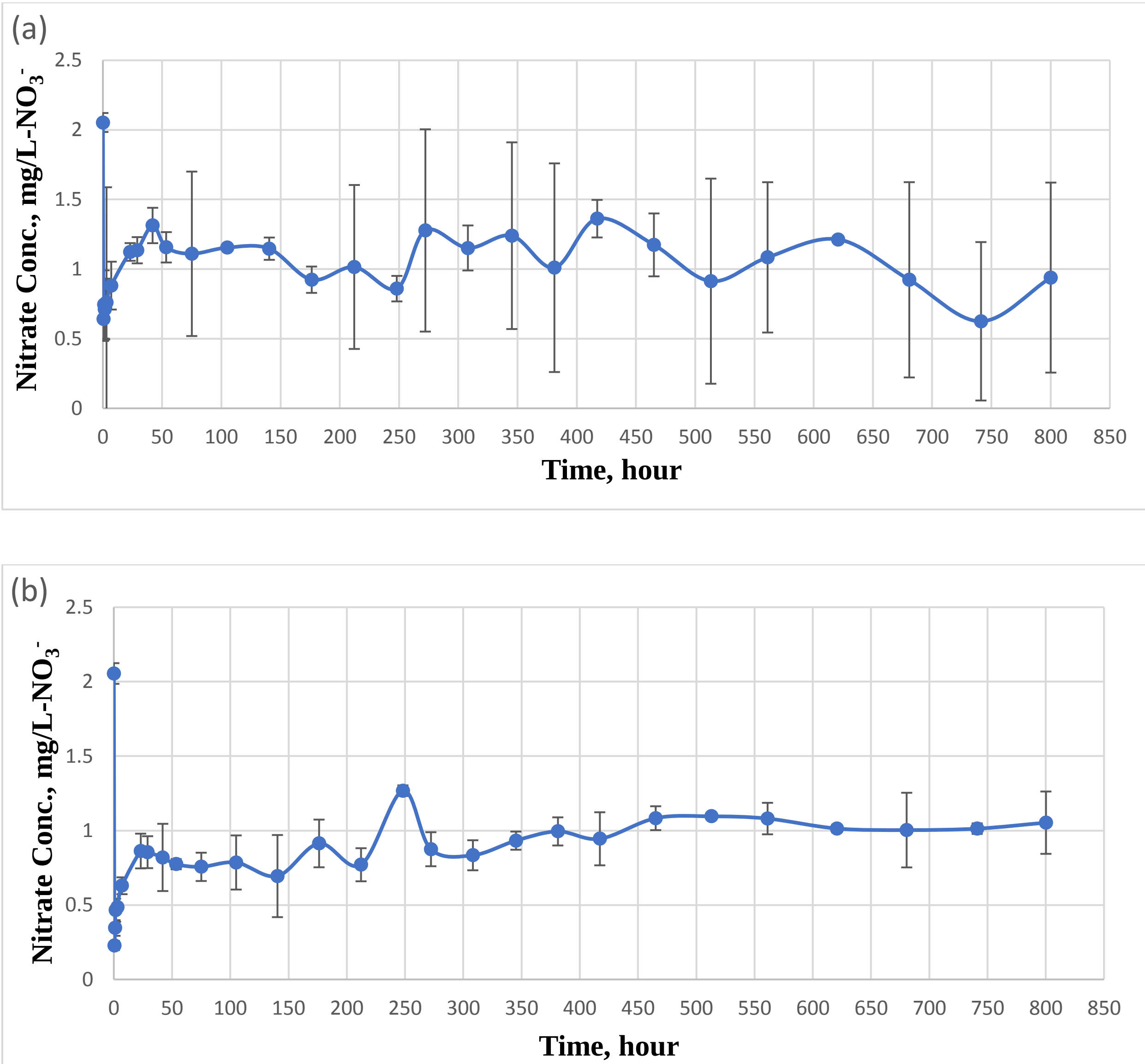


Figure 5 Effluent nitrate concentrations versus time with influent concentration of 2.0 mg/L-NO_3^- and a flow rate of 3 mL min^{-1} for (a) IFGEM-3, (b) AGEM-2 sorption media . Triplicate column concentrations were averaged.

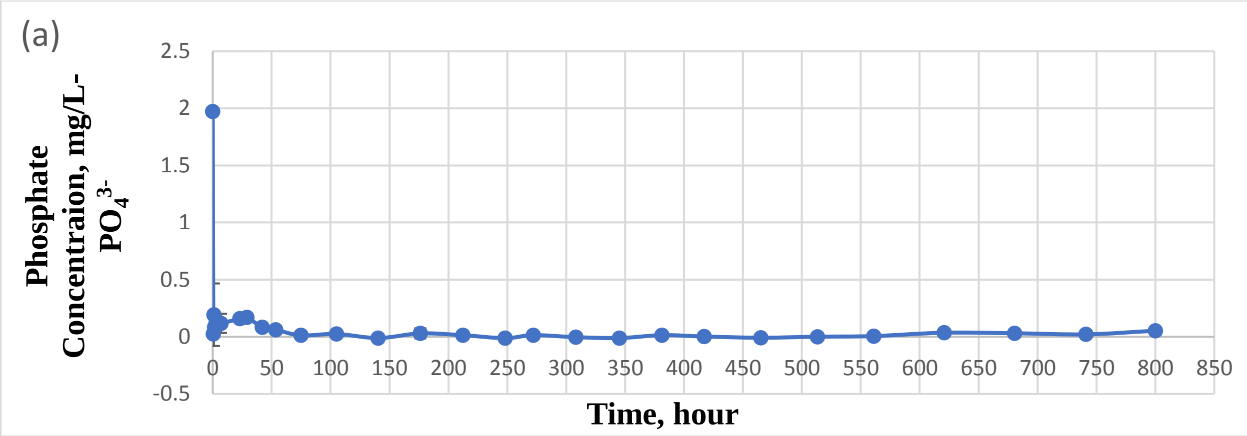
The effluent nitrate concentrations versus time graphs (Figure-5) demonstrated that both IFGEM-3 and AGEM-2 immediately started to absorb nitrate at different rates. The nitrate adsorption rate for IFGEM-3 was fluctuated at a larger scale compared to the fluctuation in nitrate adsorption rate for AGEM-2. It is hypothesized that the discrepancy in nitrate adsorption rates between IFGEM-3 and AGEM-2 were due to the differences in their recipe components that resulted in a decrease in the surface area in IFGEM-3 ($0.7 m^2/g$) compared to that of more than the double surface area in AGEM-2 ($1.714\ m^2/g$). Also, the inclusion of aluminum powder within AGEM-2 media recipe improved its media homogeneity and its particle size distribution compared to the opposite of that as a result of having large particles of tire crumb within the IFGEM-3 recipe components. The larger surface area and the well particle size distribution for AGEM-2 enhanced its nitrate adsorption removal efficiency, with time, resulting in a more consistent adsorption rate behavior with respect to nitrate removal as it is depicted in Figure 5-b.

On the other hand, the inclusion of aluminum powder along with the iron fillings within AGEM-2 media matrix, decreased the fluctuation in its nitrate adsorption rate by doubling the chances of removing nitrate in a more consistent fashion compared to only the inclusion of iron fillings as in IFGEM-3 media matrix. The chemical interaction of iron filling, aluminum particles, and nitrate species within AGEM-2 media matrix increased nitrate removals and resulted in ammonium/ammonia production or nitrogen gas as it depicted in the following equations:

$$NO_3^- + 10H^- + 4Fe \rightarrow NH_4^+ + 3H_2O + 4Fe^{2+} \quad (25)$$

$$3NO_3^- + 4Al + 8H_2O \rightarrow NH_3 + 4Al(OH)_3 + OH^- + 2NO_2^- \quad (26)$$

$$3NO_3^- + 4Al + 7H_2O \rightarrow N_{2\,(g)} + 4Al(OH)_3 + 2OH^- + NO_2^- \quad (27)$$



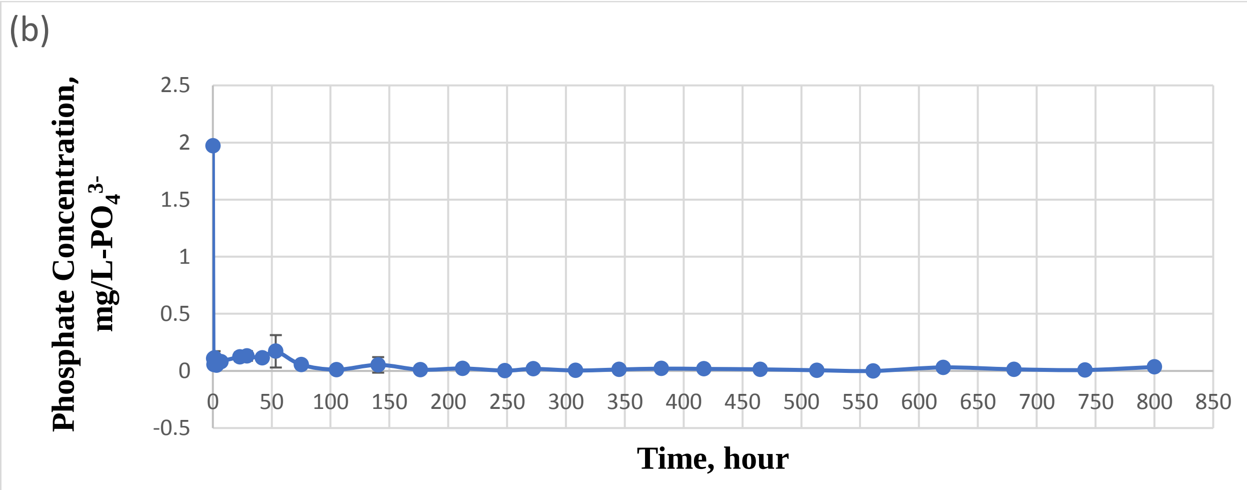


Figure 6 Effluent phosphate concentrations versus time with influent concentration of 2.0 mg/L-PO_4^{3-} and a flow rate of 3 mL min^{-1} for (a) IFGEM-3, (b) AGEM-2 sorption media . Triplicate column concentrations were averaged

The effluent phosphate concentrations versus time graphs (Figure 6) show that IFGEM-3 and AGEM-2 sorption media were very effective in removing phosphate species from the spiked water solution and that their adsorption processes followed a similar adsorption trend. Both media immediately started to absorb phosphate species where they approached their maximum removal efficiencies within the first 30 minutes of contact time. Moreover, IFGEM-3 and AGEM-2 continued to remove phosphate at constant adsorption rates with respect to contact time. Figure 6 shows that the effluent phosphate concentrations did not increase or reach symmetric values with the initial phosphate concentrations and thus, the driving force of the adsorption processes was powering phosphate removals. Therefore, both media did not reach the breakthrough where the media stop the treatment objective and needed to be replaced. The breakthrough point is important in calculating the life expectancy of a sorption media, and therefore, the life expectancies for IFGEM-3 and AGEM-2 with respect to phosphate were neither considered nor calculated in this study.

It is hypothesized that IFGEM-3 and AGEM-2 effectiveness in removing phosphate was related to three factors. Frist factor was to the interaction between the phosphate, iron and aluminum ions where the last two acted as electron donors resulted in phosphate removal in the form of solid precipitates [$Fe_3(PO_4)_2*8H_2O$] and an insoluble salt [$AlPO_4$] as it depicted via the following equations:

$$3Fe^{2+} + 2HPO_4^{2-} + 8H_2O \rightarrow Fe_3(PO_4)_2 * 8H_2O + 2H^+ \quad (28)$$

$$Al^{3+} + H_3PO_4^{-} \rightarrow AlPO_4 + 2H^+ \quad (29)$$

The second factor contributed to the effective removal of phosphate in both media was related to the presence of ammonia species in the water solution as a byproduct component due to the reduction of nitrate via iron and aluminum ions. Therefore, Ammonia can aid the removal of phosphate when it interacts with phosphate species producing triammonium phosphate; a colorless crystalline solid, as is shown in the following equation:

$$H_3PO4 + 3\ NH_3 \rightarrow (NH_4)_3PO_4 \quad (30)$$

The third factor is hypothesized to the media characteristics that was suggested by the isotherm study, where the sorption media tended to develop both monolayer and multilayer adsorption behaviors with respect to phosphate, resulted in more phosphate removals than in nitrate.

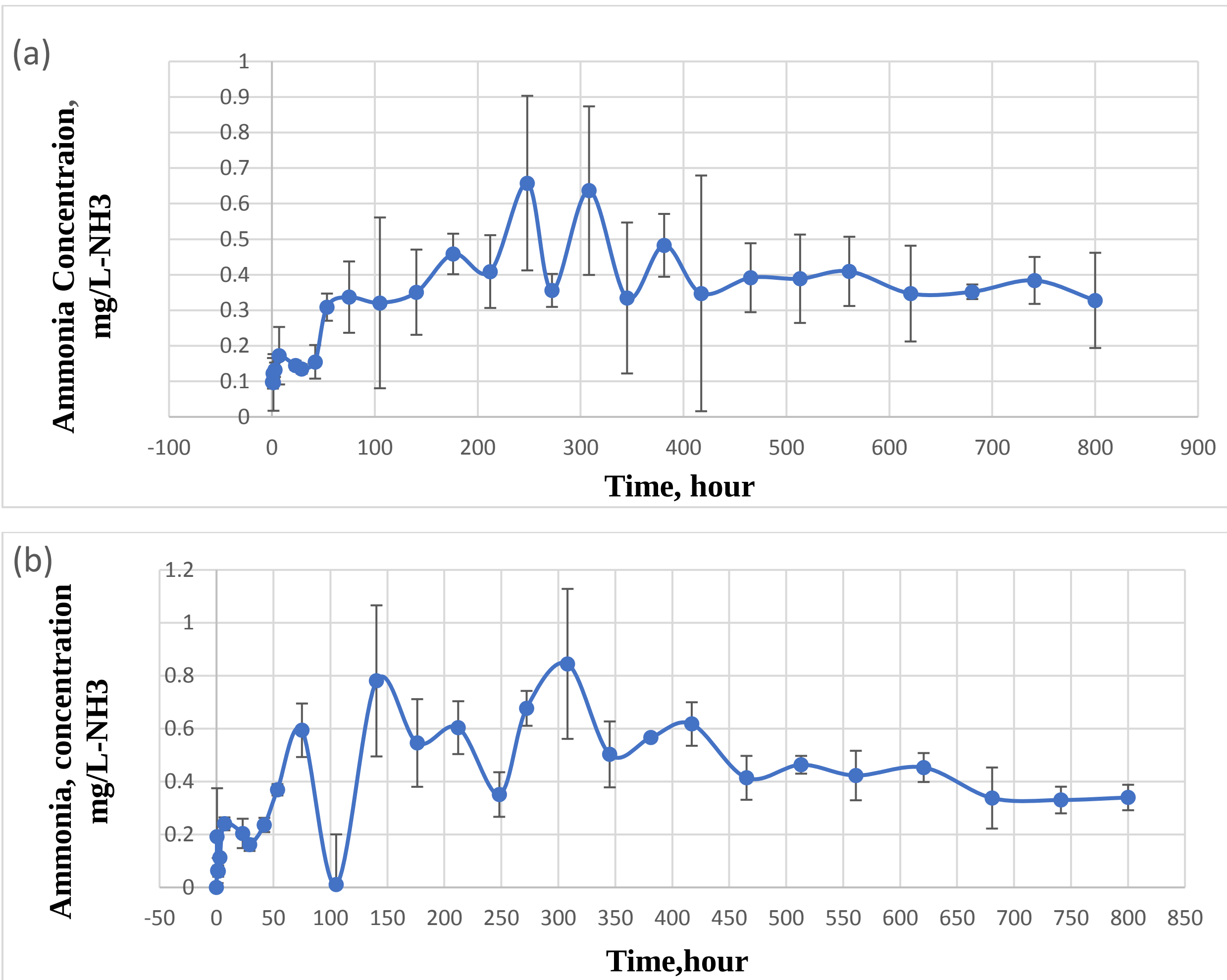


Figure 7 Effluent ammonia concentrations versus time with influent concentration of 2.0 mg/L-$PO_4^{3-}$and 2.0mg/L-NO_3^- with a flow rate of 3 mL min^{-1} for (a) IFGEM-3, (b) AGEM-2 sorption media . Triplicate column concentrations were averaged

Effluent ammonia concentrations versus time graphs (Figure 7) show that IFGEM-3 and AGEM-2 were both produced ammonia as a byproduct component due to the chemical interactions between nitrate, iron and aluminum where the last two acted as electron donors resulting in reducing nitrate to ammonia as it was shown in Equations 1 through 3. AGEM-2 recovery potential curve fluctuated at a larger scale within the first 350 hours of experimental time compared to that of IFGEM-3. Moreover, Figure 7 shows that AGEM-2 had produced more ammonia than IFGEM-3 which is consistent with the isotherm results with respect to ammonia production. Within the range of 450 and 800 hours of experimental time, both media seemed to experience a reduction in ammonia species and their ammonia recovery curves adopted a semi steady production trend. This reduction in ammonia production could be due to an increase in nitrate removals resulted in less ammonia and/or could be due to the ammonia that has been utilized to remove phosphate species into a solid component as it was mentioned before. It also could be due to a much higher conversion rate of ammonia to nitrogen gas, compared to that of ammonia production.

5. 2 Simulation of Breakthrough Processes

The column adsorption nitrate data for IFGEM-3 and AGEM-2 were fit into a Bohart-Adams (B-A) model and Modified Dose-Response (MDR) model to evaluate which one best defines the adsorption process (Table 8). The results indicated that the nitrate adsorption data was best described by the MDR model where higher R^2 values obtained than that of B-A model. The differences between the two model predictions could be due to the symmetrical breakthrough curves assumed by the B-A model that were not displayed by IFGEM-3 and AGEM-2. Also, the B-A model assumes that the adsorption data for a media follows a pseudo-first order model. The kinetics of the current sorption media; IFGEM-3 and AGEM-2, revealed that the media were poorly related to the pseudo-first order model.

Table 8: Bohart-Adams (B-A) and Modified Dose-Response (MDR) model parameters for nitrate obtained from the dynamic adsorption study

Sorption Media	BTC Model	BTC Equation	R^2
IFGEM-3	B-A	$Y = -7E - 05x + 0.029$	0.002
	MDR	$Y = 0.148x - 0.4559$	0.228
AGEM-2	B-A	$Y = -0.0014x + 0.7574$	0.394
	MDR	$Y = 0.2368x - 1.2598$	0.826

MDR→ $Y = \ln[C_0/(C_0\text{-}C_e)]$, X→ = $\ln(Q.C_0.t)$

(B-A)→ $Y = \ln[C_0/(C_e\text{-}1)]$, X = time, hours

The column study tests did not reach the point of exhaustion, where the effluent concentration becomes equal the influent concentration (C_0=C_e), as they reached asymptotic removal rates over time (Figure-8). It is hypothesized that the breakthrough was not completely reached due to the multilayer adsorption capabilities that were suggested earlier by the isotherm models. The isotherm models showed that the studied media provided much more surface area and higher-energy adsorption sites. Also, it is hypothesized that the adsorptive capacity for the media was reached within the column tests' experimental contact time, but the media continued to remove nitrate by iron and aluminum that are within their media matrices. The chemical interactions between nitrate, iron and aluminum resulted in the conversion of nitrate to ammonia which, eventually, started to appear and gradually increased in the effluent solution and causing the pH to decrease. In addition, nitrate could also be removed by iron and aluminum, and lost to the atmosphere in the form of nitrogen gas.

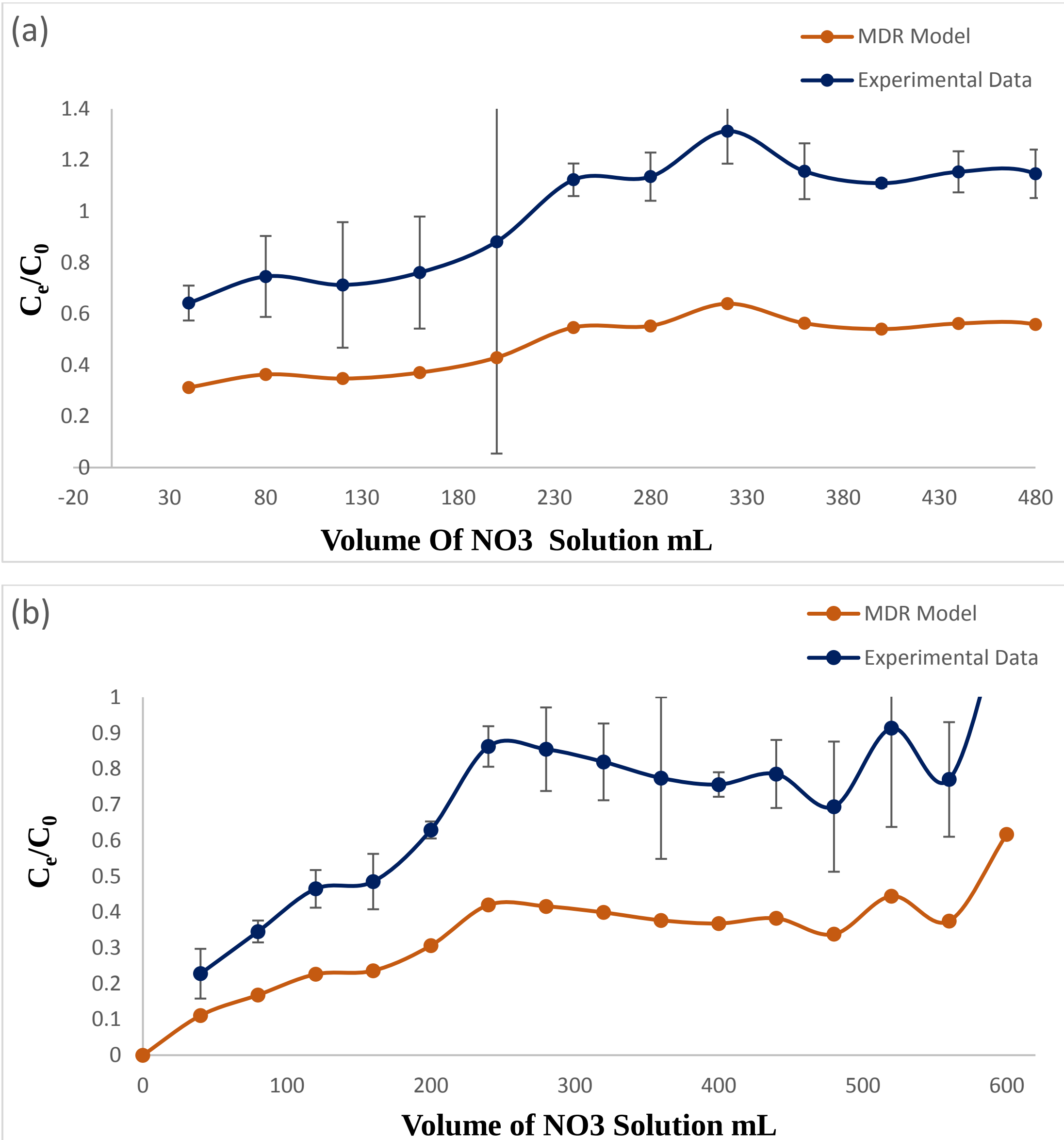


Figure 8 Experimental and MDR breakthrough curves for adsorption of nitrate with C_0 = 2.0mg/L for (a).IFGEM-3 and, (b) AGEM-2 with a horizontal scale adjusted based on the volume of nitrate solution mL

The results obtained from the MDR model showed that AGEM-2 has a much greater maximum adsorption capacity (q_{max}) for nitrate than the maximum adsorption capacity of IFGEM-3, which is consistent with the results obtained from the isotherm study. AGEM-2 exhibited a maximum nitrate adsorption capacity (q_{max}) of 408.8 μg/g at an 88.9% removal efficiency, while IFGEM-3 exhibited a maximum nitrate adsorption capacity of 43.53 μg/g at a 68.72% removal efficiency.

The maximum adsorption capacities (q_{max}) derived from the isothermal test in condition 3 (C3), 2mg/L phosphate and 2mg/L nitrate, were found to be less than the q_{max} obtained from the column test for IFGEM-3 and AGEM-2 with respect to nitrate. The discrepancy in q_{max} could be due to the longer experimental contact time (HRT) of the column test (800 hours) compared to the experimental contact time of the isotherm test (5 hours). The 800 hours of contact time extended the physical removal time and the chemical reaction time for nutrient precipitation, allowing more nitrate species to be removed and captured by the media and thus, increasing its adsorption capacity. Unlike the isotherm test, the column test represents more of the adsorption process in full-scale applications where a continuous contaminated waterflow enters and exits the media retrieving more nitrate species that need to be removed, forcing the media to work at its maximum removal capacity. Furthermore, a continuous nitrate load might lead to a multilayer adsorption behavior, in which a layer above the nutrient layer becomes accumulated on the immediate exterior surface of the media resulting in an increase of adsorption capacity. Also, as the inflow drips into the column and approaches the bottom, more nutrient species can adhere to the media surface or near the inner porous surface as a result of enlarging the surface area upon which the adsorption process can occur.

5.3 Life Expectancy of the Sorption Media

The life expectancy of the sorption media was determined with respect to nitrate in this study (Figure-9). The life expectancy of the filter media depends on the amount of media used and the maximum adsorption capacity of nitrate for that media. The usage rate measures the amount of media needed to treat 1 L of contaminated water. This can be calculated by subtracting the effluent concentration at various percentage removals from the influent concentration and that value is then divided by the maximum adsorption capacity (q_{max}) for that media. The actual flow rate (Q) that needs to be treated is calculated for a known amount of media and contact time using the density and the porosity of that media (Hossain et al. 2010).

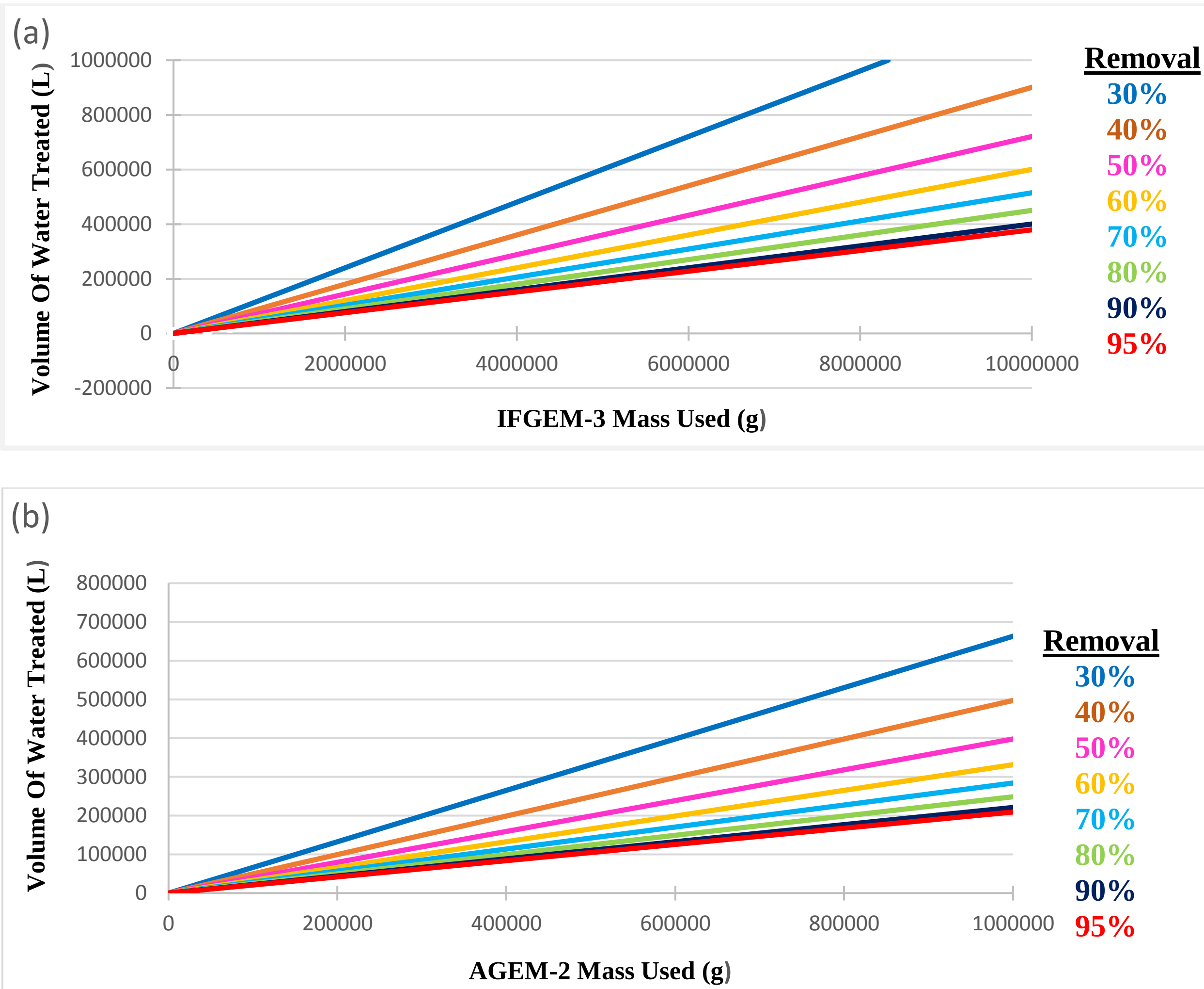


Figure 9 Volume of water to be treated using varying masses of (a) IFGEM-3, (b) AGEM-2 to multiple removal efficiencies with an initial nitrate concentration of 2.0 mg/L and 1 hour of contact time

The life expectancy with respect to nitrate for both IFGEM-3 and AGEM-2 at 80% removal was calculated using the life expectancy curves for both media (Figure-9). An average amount, 105772.5g of each media with an influent concentration of 2.0 mg/L-NO_3^- and a 2.0 mg/L-PO_4^{3-} was used. The total amount of actual water volume that needed to be treated was 19.71L and 19.23L [i.e., (105772g of IFGEM-3)*(1cm^3/1.37g)*(1m^3/10^{6}cm^3)*(0.2553)*(1000L/m^3)] for IFGEM-3 and AGEM-2, respectively. For instance, when allowing 1 hour of contact time, flow rates would be 19.71L/hr. and 19.23L/hr. for IFGEM-3 and AGEM-2, respectively. The volumetric water that could be treated by the amount of media utilized were found to be 5000L and 25000L (Figure-9) for IFGEM-3 and AGEM-2 respectively. Thus, the life expectancies with respect to nitrate, are 10.57 and 54.2 days [i.e. (5000L)/(1hr/19.71L)*(1day/24hr)] for IFGEM-3 and AGEM-2, respectively. Therefore, AGEM-2 has a longer life expectancy and a higher adsorption capacity than IFGEM-3, which is consistent with the isotherm results.

5.4 Comparative Analysis of the Studied Green Sorption Media

Comprehensive comparison of the removal efficiency of IFGEM-3, AGEM-1 and AGEM-2 with respect to phosphate and nitrate is summarized in Table 9. Phosphate removal for IFGEM-3, AGEM-1 and AGEM-2 are reasonable and competitive. AGEM-2 nitrate removal efficiency is adequate and within the range of nitrate removal efficiencies in other studies. Therefore, based on AGEM-2’s superior adsorption performance and recovery potential, AGEM-2 is recommended for phosphate and nitrate removals, and for ammonia recovery in future stormwater-runoff treatments.

Table 9 Comparison of the studied green media's nutrient removal performances

Sorption Media	Components	Total Nitrate Removal	Total Phosphate Removal	References
IFGEM-3	Sand (83.0% volume), tire crumb(10.0% volume), clay (2.0% volume), iron filling (5.0% volume)	(34.78- 44.39%)	(98.32-100%)	This study
AGEM-1	Sand (78.0% volume), tire crumb(10.0% volume), clay (2.0% volume), iron filling (5.0% volume), aluminum flasks (5.0% by volume)	(29.76-39.24%)	(95.82- 99.84%)	This study
AGEM-2	Sand (85.0% volume), clay (3.0% volume), iron filling (7.5% volume), aluminum powder (4.5% by volume)	(71.06-85.43%)	(96.95-98.37%)	This study

CHAPTER SIX: CONCLUSION

6.1 Final Remarks

The nutrient removal efficiencies and the maximum adsorption capacities for IFGEM-3, AGEM-1 and AGEM-2 against natural soil were explored for phosphate and nitrate removal, and ammonia recovery under various influent conditions at room temperature. While IFGEM-3 media contained iron, AGEM media contained iron and aluminum in the form of powder and flasks. The isotherm test results showed that, within similar contact time, all the tested media (except natural soil) behaved similarly in removing phosphate, the differences in their phosphate removal efficiencies were insignificant and, therefore, phosphate was not considered the limiting nutrient in selecting a media with the best adsorption performance. Also, compared to the rest of the media, it was found that AGEM-2 performed the best at removing nitrate and this result was supported by the dynamic column tests conducted later on in the second part of the study. Ammonia was generated as a result of the nitrate reduction via iron filling and aluminum in the media matrix. The study showed that the AGEM-2 media had the highest ammonia recovery amongst the other media indicating it could potentially be reused as a fertilizer for urban agriculture planting applications. Furthermore, the isotherm modeling results showed that AGEM-2 had the highest average maximum adsorption capacity (q_{max}) and the highest ammonia recovery followed by IFGEM-3, and then AGEM-1, while the natural soil had the lowest.

The isotherm models that best fit the isotherm experimental data were selected and ranked based on three indices: the corresponding coefficient of determination R^2, the equilibrium maximum adsorption capacities (q_{max}) obtained from the isotherm models, and the consistency of the model's performance in attaining reliable and reasonable results for the triplicate samples under various influent concentrations. According to these criteria, the utilized models were ranked per nutrient species based on their ‘best fit’ as follows; Temkin> Langmuir > Harkin-Jura >Jovanovic> Freundlich & Halsey for phosphate, Temkin> Langmuir > Jovanovic> Harkin-Jura > Freundlich & Halsey for nitrate and Langmuir > Temkin> Harkin-Jura for ammonia for the studied sorption media.

The current sorption media and the nature of the adsorption processes of these media were further described and understood based on the applied isotherm models’ assumptions derived from their equations. For example, for all the studied sorption media, the heat released or gained during the adsorption process was a function of temperature and decreased linearly with coverage. Also, well distributed adsorption coverage was expected along the interface layers of the sorption media due to their molecules’ binding energies that were uniformly distributed. Furthermore, the equilibrium adsorption distribution of the nutrients between liquid and solid phases can be well identified by the utilized sorption media. Also, a multilayer adsorption process was suggested by the adsorption behavior of phosphate and nitrate where multilayer adsorption caused an increase in the media’s surface area. This resulted in the formation of an inaccessible equilibrium maximum adsorption capacity within the experimental contact time between the media and the nutrients. Finally, both monolayer and multilayer phosphate adsorption processes were suggested based on the IFGEM-3, AGEM-1 and AGEM-2 media’s performances that made them more efficient in absorbing phosphate than absorbing nitrate. In contrast, Natural soil, IFGEM-3, and AGEMs for phosphate removal, and ammonia recovery can be characterized as having heterogeneous pore distribution and homogenous sorption coverage where its interface surface sites demonstrated the same free energy changes. Also, IFGEM-3 and AGEM-2 for phosphate and nitrate removal demonstrated a mechanical contact between the nutrients and the media, permitting the calculation of the maximum adsorption capacities by describing these homogenous media with respect to their nutrient concentrations.

It was found that physical and chemical characteristics, various influent concentrations, and the contact times between the media and the nutrients all impacted the performance of studied adsorption media. The inclusion of aluminum powder in AGEM-2 had increased the tiny pore volume within the total volume of the sorption media. This resulted in a general increase in the interior surface area onto which the adsorption processes had occurred and, thus, enhancing the nutrient removal of AGEM-2. Moreover, unlike the aluminum flasks, aluminum in its powder form was easier to chemically react with other nutrient species, such as phosphate, forming solid and salt components that were precipitated. Also, it was found that higher influent concentrations resulted in higher removal performances where more nutrients species are available for removal, enabling the sorption media to work at their highest efficiency. Moreover, the study showed that increasing the contact time between the studied sorption media and the nutrients resulted in better removal performances.

The results of the dynamic column tests conducted for IFGEM-3 and AGEM-2, showed that AGEM-2 had a maximum nitrate adsorption capacity of 0.4088 mg/g at 88.9 % removal while IFGEM-3 had a maximum nitrate adsorption capacity of 0.0739 mg/g at 69.55 % removal. The life expectancy curves were constructed with respect to nitrate using the maximum adsorption capacities obtained from applying the breakthrough Modified Dose Response Model (MDR) for both IFGEM-3 and AGEM-2. With a known influent concentration, the usage rates can be calculated at various effluent percentage removals. The corresponding volumetric water that can to be treated by a specific amount of sorption media can be found. Therefore, the life expectancy of the tested sorption media can be calculated by finding the amount of water treated by a specific amount of media utilizing the curves in Figure-9. For instance, at 80 % removal with an influent nitrate concentrations of 2.0 mg/L and a flow rate of approximately 20 L/hour, life expectancies of 10.57 and 54.2 days were expected for IFGEM-3 and AGEM-2, respectively. Both isotherm and column studies suggested that AGEM-2 had the best adsorption performance and is recommended for future stormwater runoff and wastewater phosphate and nitrate removal applications.

6.2 Future Work

- Conducting further studies to test IFGEM-3 and AGEM-2 media by allowing both physio-chemical and biological nutrient removals to cover all aspects of their removal efficiencies and adsorption capacities
- Enhance sorption media removal efficiency and nutrient adsorption capacity for nitrate, phosphate and ammonia recovery by considering a different ratio of iron filling, aluminum powder and clay for future studies
- Investigate more physical and chemical properties that impact a media's adsorption strength or magnitude such as the solubility of a nutrient in a solvent
- Incorporate the non-linear method as well as the third and the fourth variable equilibrium isotherm models and demonstrate whether or not there are new information on a media's adsorption performance

- Conducting further studies on IFGEM-3 and AGEM-2 using stormwater runoff instead of distilled water and demonstrate whether or not this substitution will change the initial amount adsorption and the adsorption rate in the columns
- Allowing more contact time between the sorption media and nutrient species to reach the point of exhaustion where the media reaches its maximum adsorption capacity
- Utilizing a constant experiment contact time (HRT) for both isotherm and column tests and demonstrate whether or not this equivalency of contact time will result on obtaining a similar q_{max}.

APPENDIX A:
LANGMUIR AND FREUNDLICH MODEL TABLES

Table 10 Langmuir isotherm parameters for Natural Soil media at varying influent concentrations

Chemical Species	Influent Conc (mg/L)	Isotherm equations	R^2 value	$q_{max}K_L$	K_L	q_{max} (mg g^{-1-})
Phosphate	0.306	$Y = -366.71x + 119.89$	0.9944	-0.00272695	-0.32693409	0.008340979
Phosphate	0.9047	$Y = -2281.9x + 1323.8$	0.9873	-0.00043823	-0.58013059	0.000755401
Phosphate	1.9933	$Y = -65222x + 36537$	0.952	-0.000015332	-0.56019441	0.0000273695
Nitrate	0.88333	$Y = -3246x + 2197.5$	0.9995	-0.000308071	-0.67698706	0.000455063
Nitrate	1.51333	$Y = -6487.4x + 3017.8$	0.998	-0.00015414	-0.46517865	-0.000331367
Nitrate	2.01333	$Y = 67790x - 30455$	0.9178	0.0000147514	-0.44925505	0.0000328353
Ammonia	0.00733	$Y = -183.66x + 55.518$	1	-0.00544484	-0.30228683	0.018012176
Ammonia	0.001333	$Y = -170.21x + 9.5411$	1	-0.0058751	-0.05605487	0.104809718
Ammonia	0.003	$-Y = -148.2x - 176.08$	1	-0.00674764	1.188124157	-0.005679237

Table 11 Langmuir isotherm data for IFGEM-3 media at varying influent concentrations

Chemical Species	Influent Conc (mg/L)	Isotherm equations	R^2 value	$q_{max}K_L$	K_L	q_{max} (mg g^{-1-})
Phosphate	0.319	$Y = -0.7551x + 606.71$	0.9011	-1.32433	-803.483	0.001648
Phosphate	0.9313	$Y = -0.2285x + 196.48$	0.9522	-4.37637	-859.869	0.00509

Chemical Species	Influent Conc (mg/L)	Isotherm equations	R^2 value	$q_{max}K_L$	K_L	q_{max} (mg g^{-1-})
Phosphate	1.98	$Y = -0.0109x + 86.341$	0.8944	0.011582	1	0.011582
Ammonia	0.0063	$Y = -178.42x + 26.964$	0.9999	-0.00560	-0.15113	0.037086
Ammonia	0.00333	$Y = -175.49x + 29.392$	0.9999	-0.0057	-0.16749	0.034023
Ammonia	0.00233	$Y = -176x + 48.654$	0.9999	-0.00568	-0.2764	0.020553

Table 12 Langmuir isotherm parameters for AGEM-1 media at varying influent concentrations

Chemical Species	Influent Conc (mg/L)	Isotherm equations	R^2 value	$q_{max}K_L$	K_L	q_{max} (mg g^{-1-})
Phosphate	0.319	$Y = -0.6206x + 590.15$	0.9619	-1.611344	-950.9346	0.0016945
Phosphate	0.9313	$Y = -0.0515x - 2.3443$	0.9879	-2.39521	-473.89	0.0050543
Phosphate	1.98	$Y = -0.0064x + 86.238$	0.6367	-156.25	-13475	0.011596
Ammonia	0.0063	$Y = -177.65x + 24.249$	0.9999	-0.005629	-4307.8	0.0000013067
Ammonia	0.00333	$Y = -974.48x + 3363.5$	0.9347	-0.001026	-3.4516	0.000297309
Ammonia	0.00233	$Y = -177.4x + 61.342$	0.9999	-0.005637	-0.34578	0.016302044

Table 13 Langmuir isotherm parameters for AGEM-2 media at varying influent concentrations

Chemical Species	Influent Conc (mg/L)	Isotherm equations	R^2 value	$q_{max}K_L$	K_L	q_{max} (mg g^{-1-})
Phosphate	0.8833	$Y = -0.6474x + 626.02$	0.9571	-1.54464	-966.9756	0.001597
Phosphate	0.90467	$Y = -0.4347x + 623.47$	0.8929	-2.300437	-1434.254	0.0016039
Phosphate	1.9933	$Y = -0.103x + 88.006$	0.9682	-9.7087378	-854.42719	0.01136286
Ammonia	0.00733	$Y = -178.02x + 21.936$	0.9999	-0.005617	-0.12322	0.045587
Ammonia	0.00133	$Y = -169.89x + 8.3687$	1	-0.0058862	-0.0492595	0.1194929
Ammonia	0	$Y = -166.61x + 3E - 12$	1	-0.00599988	-1.79996E-14	3.3333E+11

Table 14 Freundlich isotherm data for IFGEM-3 media at varying influent concentrations

Chemical Species	Influent Concentration (mg/L)	Isotherm equations	R^2 value	n	K (mg g^{-1})$(L/mg)^{1/n}$	K (µg g^{-1}) $(L/µg)^{1/n}$
Phosphate	0.319	$Y = 0.0172x - 2.7276$	0.3021	58.1395	0.0018724	1.8724
Phosphate	0.9313	$Y = -0.041x - 2.3337$	0.9822	-24.390	0.0046377	4.6377
Phosphate	1.98	$Y = -0.0099x - 1.9486$	0.9555	-101.010	0.0112564	11.2564

Table 15 Freundlich isotherm data for phosphate for AGEM-1 sorption media at varying influent concentrations

Chemical Species	Influent Concentrations (mg/L)	Isotherm equations	R^2 value	n	K (mg g^{-1})(L/mg)$^{1/n}$	K (µg g^{-1}) (L/µg)$^{1/n}$
Phosphate	0.319	$Y = -0.0625x - 2.8532$	0.9909	-16	0.001402	1.402
Phosphate	0.9313	$Y = -0.0515x - 2.3443$	0.9879	-24.390	0.004638	4.6377
Phosphate	1.98	$Y = -0.0096x - 1.9486$	0.8933	-104.167	0.0112564	11.256

Table 16 Freundlich isotherm data for phosphate for AGEM-2 sorption media at varying influent concentrations

Chemical Species	Influent Concentration (mg/L)	Isotherm equations	R^2 value	n	K (mg g^{-1})(L/mg)$^{1/n}$	K (µg g^{-1}) (L/µg)$^{1/n}$
Phosphate	0.306	$Y = -0.0665x - 2.8828$	0.9909	-15.037594	0.00130979	1.309785
Phosphate	0.905	$Y = -0.0596x - 2.8746$	0.9804	-16.778524	0.00133475	1.33475
Phosphate	1.993	$Y = -0.0255x - 1.9670$	0.9924	-0.6701964	0.01078947	10.789467

APPENDIX B:
ELOVICH & JOVANOVIC MODEL TABLES

Table 17 Elovich Isotherm for sorption media at varying influent concentrations

Media	Chemical Species	Elovich Isotherm			
		Isotherm Equations	R^2	q_{max} (mg/g)	K_e
IFGEM-3	Phosphate	$Y = 9906.7x - 19.96$	0.987	9906.7	-19.96
		$Y = 4695.1x - 26.882$	0.9855	4695.1	-26.882
		$Y = 8311x - 97.802$	0.9578	8311	-97.802
AGEM-1	Phosphate	$Y = 9378.2x - 19.209$	0.9929	9378.2	-19.209
		$Y = 3806.7x - 22.353$	0.9901	3806.7	-22.353
		$Y = 8073.4x - 94.906$	0.8973	8073.4	-94.906
AGEM-2	Phosphate	$Y = 9306.8x - 18.286$	0.9929	9306.8	-18.286
		$Y = 10224x - 19.716$	0.9839	10224	-19.716
		$Y = 3421.6x - 41.309$	0.9931	3421.6	-41.309
IFGEM-3	Nitrate	$Y = 1103x - 8.1512$	0.9376	1103	-8.1512
		$Y = -1638.6x - 1.6428$	0.4347	-1638.6	-1.6428
		$Y = 617.8x - 8.3579$	0.9284	617.8	-8.3579
AGEM-1	Nitrate	$Y = -0.002x + 6E - 05$	0.3486	-0.002	6E-05
		$Y = 0.0005x + 0.0051$	0.7502	0.0005	0.0051
		$Y = -0.0003x - 6E - 05$	0.4292	-0.0003	6E-05
AGEM-2	Nitrate	$Y = 929.6x - 7.5785$	0.9931	929.6	-7.5785
		$Y = 558.64x - 7.712$	0.9782	558.64	-7.712
		$Y = 412.26x - 7.6418$	0.9767	412.26	-7.6418

Table 18 Jovanovic Isotherm for sorption media at varying influent concentrations

Media	Chemical Species	Jovanovic Isotherm			
		Isotherm Equations	R^2	q_{max} (mg/g)	K_j
IFGEM-3	Phosphate	$Y = -59.44x - 0.9986$	0.987	-0.9986	-59.44
		$Y = -28.171x - 0.6452$	0.9855	-0.6452	-28.17
		$Y = -49.866x + 0.9329$	0.9578	0.9329	-49.866
AGEM-1	Phosphate	$Y = -3.3387x - 6.2567$	1	-6.2567	-3.3387
		$Y = -1.1316x - 5.1858$	1	-5.1858	-1.1316
		$Y = -0.5132x - 4.4328$	1	-4.4328	-0.5132
AGEM-2	Phosphate	$Y = -3.5115x - 6.2982$	1	-6.2982	-3.5115
		$Y = -3.5112x - 6.2986$	1	-6.2986	-3.5112
		$Y = -0.5151x - 4.4259$	1	-4.4259	-0.5151
IFGEM-3	Nitrate	$Y = -6.6177x - 1.6018$	0.9376	-1.6018	-6.6177
		$Y = 9.8316x - 16.947$	0.4347	-16.947	9.8316
		$Y = -3.7068 - 0.5242$	0.9284	-0.5242	-3.7068
AGEM-1	Nitrate	$Y = 13.98x - 16.321$	0.3943	-16.321	13.98
		$Y = -8.3032\,x + 3.5198$	0.7141	3.5198	-8.3032
		$Y = 7.4728x - 17.985$	0.4461	-17.985	7.4728
AGEM-2	Nitrate	$Y = -2.8809x - 4.858$	0.9244	-4.858	-2.8809
		$Y = -2.16x - 3.9111$	0.9201	-3.9111	-2.16
		$Y = -1.5218x - 3.7297$	0.9007	-3.7297	-1.5218

APPENDIX C:
HARKIN-JURA, HALSEY & TEMKIN MODEL TABLES FOR IFGEM-3 & AGEM-2

Table 19 Harkin-Jura and Halsey Isotherm model tables for IFGEM-3 and AGEM-2 sorption media

Sorption Media	Chemical Species	Halsey Isotherm				Harkin-Jura Isotherm			
		Isotherm Equation	R^2	K_H	n	Isotherm Equation	R^2	A	B
IFGEM-3	Phosphate	$Y = -0.0728x - 6.6179$	0.9673	-0.073	-6.618	$Y = 107447x + 500266$	0.9549	500266	107447
		$Y = -0.041x - 5.3736$	0.9822	-0.041	-5.374	$Y = 6659.7x + 45080$	0.9776	45080	6659.7
		$Y = -0.0099x - 4.4868$	0.9555	-0.010	-4.487	$Y = 333.02x + 7868.8$	0.9526	7868.8	333.02
	Nitrate	$Y = -3.7039x - 8.0598$	0.8706	-3.704	-8.060	-	-	-	-
		$Y = 12.057x - 6.9234$	0.4243	12.057	-6.923	$Y = 6E + 07x + 1E + 08$	0.0911	1E+08	6E+07
		$Y = -5.0006x - 3.7331$	0.858	-5.006	-3.733	$Y = 8E + 06x + 4E + 06$	0.3259	4E+06	8E+06
	Ammonia	-	-	-	-	$Y = -3E + 06x - 1E + 06$	0.8958	-1E+06	-3E+06
		-	-	-	-	$Y = -7E + 06x - 4E + 06$	0.8634	-4E+06	-7E+06
		-	-	-	-	$Y = -2E + 07$ −1E+07	0.9203	-1E+07	-2E+07
AGEM-2	Phosphate	$Y = -0.0665x - 6.638$	0.9909	-0.067	-6.638	$Y = 104990x + 525669$	0.9888	525669	104990
		$Y = -0.0596x - 6.6191$	0.9804	-0.060	-6.619	$Y = 94035x + 513437$	0.9775	513437	94035
		$Y = -0.0255x - 4.5292$	0.9924	-0.026	-4.529	$Y = 866.71x + 8500.1$	0.9917	8500.1	866.71
	Nitrate	$Y = -0.9534x - 7.1125$	0.7784	-0.953	-7.113	$Y = 2E + 06x + 2E + 06$	0.3794	2E+06	2E+06
		$Y = -1.7101x - 6.205$	0.8368	-1.710	-6.205	$Y = 3E + 06x + 660255$	0.4071	660255	3E+06
		$Y = -1.4921x - 5.4612$	0.8026	-1.492	-5.461	$Y = 1E + 06 + 173496$	0.3257	173496	1E+06
	Ammonia	-	-	-	-	$Y = -2E + 06x - 822447$	0.9056	-82245	-2E+06
		-	-	-	-	$Y = -4E + 06x - 2E + 06$	0.8786	-2E+06	-4E+06
		-	-	-	-	$Y = -1E + 07x - 9E + 06$	0.8279	-9E+06	-1E+07

Table 20 Temkin Isotherm Model for IFGEM-3 and AGEM-2 sorption media

Sorption Media	Chemical Species	Temkin Isotherm			
		Isotherm Equation	R^2	B(J/mole)	A_T (L/g)
IFGEM-3	Phosphate	$Y = -0.0001 + 0.0013$	0.9727	-0.0001	2.26033E-06
		$Y = 0.0364x + 0.1662$	0.9842	0.0364	96.15233647
		$Y = -0.0001x + 0.0112$	0.957	-0.0001	2.28569E-49
	Nitrate	$Y = -0.0043x + 7E - 05$	0.9981	-0.0043	0.9838527
		$Y = -0.0077x + 0.0034$	0.998	-0.0077	1
		$Y = -0.0099x + 0.0076$	0.9964	-0.0099	0.46409
	Ammonia	$Y = -0.0014x - 0.0035$	0.9726	-0.0014	12.18249
		$Y = -0.001x - 0.0029$	0.9662	-0.001	18.17415
		$Y = -0.0006x - 0.002$	0.9799	-0.0006	28.03162
AGEM-2	Phosphate	$Y = -0.0001x + 0.0013$	0.9919	-0.0001	2.26033E-06
		$Y = -0.0001x + 0.0013$	0.9818	-0.0001	2.26033E-06
		$Y = -0.0003x + 0.0108$	0.9928	-0.0003	2.31952E-16
	Nitrate	$Y = -0.0021 + 0.0005$	0.9459	-0.0021	0.788127
		$Y = -0.0049x + 0.0027$	0.9789	-0.0049	0.576361
		$Y = -0.0062x + 0.0053$	0.9772	-0.0062	0.425352
	Ammonia	$Y = -0.0016x$-0.0039	0.9748	-0.0016	11.4439396
		$Y = -0.0012x - 0.0033$	0.9715	-0.0012	15.642632
		$Y = -0.0007x - 0.0024$	0.9516	-0.0007	111.529119

APPENDIX D:
MONOLAYER & MULTILAYER ADSORPTION SUMMERY TABLE FOR SORPTION MEDIA

Table 21 Monolayer and multilayer adsorption for sorption media

Isotherm Models	Natural Soil			IFGEM-3			AGEM-1			AGEM-2		
	$PO4^{-3}$	NO_3	NH_3	$PO4^{-3}$	NO_3	NH_3	$PO4^{-3}$	NO_3	NH_3	$PO4^{-3}$	NO_3	NH_3
Average Maximum Adsorption Capacity,(mg/g)	0.00003	0.0002	0.0390	0.0116	0.00019	0.0306	0.012	0.0002	0.0055	0.01196	0.01726	0.0825
q_e ($_{experiment}$)	0.00094	0.00024	0.0003	0.0119	0.0048	0.0094	0.0119	0.0041	0.0003	0.01176	0.00884	0.00031
Langmuir												
Monolayer Adsorption	X	X	X	X		X	X		X	X	X	X
R^2	0.978	0.972	1	0.916	0.41	0.9999	0.862	0.274	0.978	0.939	0.667	0.9999
q_{max}, mg/g	0.00304	0.00024	0.039	0.00611	0.00020	0.0306	-	0.000077	0.0055	0.00485	0.00138	0.0825
Freundlich												
Multi-Layer Adsorption				X	X		X			X	X	
R^2	-	-	-	0.747	0.8643	-	0.9574	0.573	-	0.988	0.8059	-
K,$(mg^{-1})(Lmg^{-1})^{1/n}$	-	-	-	-0.0224	0.01353	-	-0.0482	0.0293	-	-0.0108	0.00236	-
Harkin-Jura												
Multilayer adsorption	X	X	X	X		X	X		X	X		X
R^2	0.9421	0.978	0.959	0.9617	0.2085	0.8932	0.9546	0.4653	0.626	0.986	0.3707	0.8707
Halsey Model												
Multilayer adsorption				X	X		X			X	X	
R^2	-	-	-	0.9683	0.7176	-	0.9574	0.4755	-	0.9879	0.8060	-
K_H	-	-	-	-0.0413	1.116	-	-0.0412	4.0807	-	-0.051	-1.385	-

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