

# REMOVAL OF NITRATES FROM STORMWATER USING NANOCCLAYS

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## ABSTRACT

### Removal of Nitrates from Stormwater Using Nanoclays Rubia Siddiqi

Creeks and rivers are often polluted as a result of stormwater runoff that carries various contaminants in to open water bodies, causing adverse environmental and health effects. Low impact development (LID) techniques are currently employed to treat this runoff prior to discharge. Nitrate, however, is not consistently removed by these LID techniques. This study analyzed the ability of several nanoclays to remove nitrate in runoff and determined the feasibility of using them as a soil supplement for LID implementation. Six different nanoclays and HCl-treated clays were compared (pre-modified trimethyl stearyl ammonium nanoclay, pre-modified dimethyl dialkyl amine nanoclay, unmodified hydrophilic bentonite, unmodified halloysite nanoclay, HCl modified hydrophilic bentonite and HCL modified kaolin) to the control clay, unmodified kaolin, for their ability to adsorb nitrate solution by batch adsorption experiments. The findings determined that the pre-modified trimethyl stearyl ammonium nanoclay was the most effective adsorbent, decreasing the nitrate concentration up to 86% for a nitrate to clay ratio of 6.25 mg: 1 g under normal pH (5-6) and temperature (25°C) conditions. The HCl acid modification did not prove to provide significant additional benefits to the clays. Column studies were also conducted on the most successful clay, pre-modified trimethyl stearyl ammonium nanoclay, to assess the breakthrough point when 0.1% w/w and 1% w/w of the nanoclay were added to Nevada Sand. The results showed a projected breakthrough pore volume of 17 when the larger fraction was added to the sand, and a corresponding hydraulic conductivity of 12.6 in/hr, which is 35% slower than the un-amended Nevada Sand. Such a high hydraulic conductivity indicated that future work can test larger fractions of clay to sand mixtures to achieve a higher number of pore volumes before the soil reaches its breakthrough point. Future studies can also further explore both batch and column experiments to assess the feasibility of implementing soil amendments to a filtration system by changing the experimental parameters, such as base soil material, types of nanoclays used, and the nanoclay to nitrate ratios. Additionally, synthetic stormwater from runoff should be used as the influent instead of a nitrate-only solution to reflect more realistic scenarios for a potential real-world application.

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## CHAPTER 1: INTRODUCTION

Throughout the country, stormwater runoff has caused flooding problems, mudslides, pollution of open water bodies, and other negative impacts to areas that are not prepared to manage this runoff. Both the incoming volume of water from rainfall events and the resulting constituents it carries in runoff need to be accounted for in the design of developed areas. This study focuses on the latter aspect of stormwater management and design: control of pollutants in runoff.

### 1.1 BACKGROUND

Stormwater runoff can carry constituents from parking lots, agricultural lands, and developed areas into open water bodies if proper stormwater management strategies are not in place. Receiving waters are subject to water quality degradation, harm to surrounding ecosystems, and potential human and ecological health problems from contact with that water. The identification of such urban water systems led to the development by the U.S. Environmental Protection Agency (EPA) of a list of impaired surface water bodies by each state, the 303(d) list. The waters on this list are threatened by specific identified contaminants, which are used to determine the Total Maximum Daily Load (TMDL) of those contaminants for each listed water body. The EPA and/or the Regional Water Quality Control Board (for California) determines the TMDL depending on the extent of the pollution and the potential uses of the water body<sup>1</sup>. Nutrients, such as phosphates and nitrates, are such contaminants that are included in the TMDL for water bodies on the 303(d) list. These nutrients are crucial for maintaining lakes and streams, as they provide support to aquatic organisms. However, an excess amount of nutrients can cause eutrophication, or excessive growth of algae and other

aquatic plants. This excessive plant growth can cause the death of aquatic organisms as the dissolved oxygen available reduces significantly with the degradation of the algae and plants. Eutrophication also increases the water's pH, which can be toxic and have a synergistic effect on other existing contaminants <sup>2</sup>.

Nitrates are the focus of this study because in addition to accelerating eutrophication, they can also cause harm to human health. Nitrates in drinking water are associated with gastric cancer, infectious diseases, Methemoglobinemia (commonly known as Blue Baby Syndrome), and diabetes <sup>3</sup>. Therefore, the concentration of nitrate from runoff needs to be controlled before it is discharged into surface water bodies that serve as a source of drinking water. Nutrients in receiving water bodies can originate from runoff that flows over agricultural fields or urban landscaping with fertilizers and animal feces, from point sources, and from developed areas with urban and septic discharges <sup>4</sup>.

Current efforts to remove pollutants from stormwater include low impact development (LID) best management practices (BMPs). These techniques are a supplement to conventional stormwater management systems, such as pipes, culverts, and storm drains. LID techniques can help improve water quality, and reduce runoff volume and peak flows entering the storm drainage system. LIDs accomplish these goals by facilitating natural processes, such as infiltration and evaporation, to occur in urban settings. They aim to route runoff away from streets and into bioswales, detention basins, and other LIDs prior to entering the storm drainage system. These techniques allow for pollutants to be filtered out before being routed to open water bodies.<sup>5</sup>

Sand filters are one example of an LID technique that is effective at removing dissolved nutrients which adsorb to the surface of the sand. However, they are not as commonly

used because they have high maintenance demands and can be expensive. They are also not recommended for areas that experience runoff with a large sediment content.<sup>6</sup>

Considering many sources of nitrates also release high sediments from agricultural runoff, a sand filter would not be the best option. Bioretention cells, however, are a better option. Bioretention cells are one of the most common LID techniques, combining biological and mechanical processes to control flows and remove pollutants. They are made up of a layer of vegetation, mulch, filter media, and sometimes an underdrain to route the incoming runoff into a storm drain after pollutants are filtered through the top layers<sup>6</sup>. Bioretention systems are effective at removing many types of pollutants through processes including filtration, adsorption, biodegradation, and plant uptake<sup>6</sup>. Although they are found to have high sediment, metal, and organic pollutant removal, their ability to remove nitrate has been found to vary between 1-80%<sup>6</sup>.

This variation is likely due to the variety of types of soil media that may be used in bioretention cells. Although sand is found to be effective at reducing total nitrogen levels, it is not supportive of plant life, likely due to the generally high hydraulic conductivity of sand which does not allow for water to remain in the system long enough to support growth for plant roots. As plant growth is a key aspect of effective bioretention cells, sand alone is not often used for bioretention cell media<sup>7</sup>. In addition, total nitrogen removal does not always indicate nitrate removal. Previous laboratory and pilot scale studies conducted on bioretention devices showed 50-75% removal of total Kjeldahl nitrogen and 60-80% removal of ammonium, but lower nitrate removal<sup>4</sup>. This inconsistency in nitrate reduction across bioretention cell applications has inspired the research and design of engineered bioretention media<sup>8</sup>. Bioretention cells are mainly

composed of sand mixed with small amounts of organic matter, silts, and clays<sup>6</sup>. The fine particles, specifically clays, not only allow for adsorption, but also reduce the naturally high hydraulic conductivity of sand itself to further facilitate water quality improvement.

## 1.2 NANOCLAYS

Physicochemical treatment of pollutants has been explored through a variety of technologies, with adsorption on solid adsorbents producing efficient and cost-effective results. For wastewater applications, activated carbon is the most widely used adsorbent but has decreased in popularity due to its high cost. Instead, clays have begun to gain popularity for not only their lower cost, but also for their high surface area available for adsorption as well as for their mechanical and chemical stability.<sup>9</sup>

Adsorption of various pollutants on clay minerals has been studied, showing the potential this material has for removing pollutants from water. One study showed that a clay's specific surface area and porosity largely affect the adsorption capacity of benzene, a volatile organic compound<sup>10</sup>. Clay has also been found to be an effective adsorbent for inorganics, including heavy metals and phosphate, which is a parallel to nitrate<sup>11,12</sup>. The removal of nitrate itself by clay has also been studied (Ouardi study), showing that an increase in pH decreases the adsorption capacity of the clay, and a higher clay to pollutant ratio increases adsorption of nitrate<sup>3</sup>. The clay used for the Ouardi study was composed of Kaolinite, Illite, Quartz and Calcite with a surface area of 53.47 m<sup>2</sup>/g, and has many porous and microporous particles that created cavities, providing binding sites for nitrate<sup>3</sup>. Another study by Bekele et al. conducted on Ethiopian bentonite clay also analyzed its ability to remove nitrate ions, finding that 80% removal was possible if the clay was subjected to HCl acid treatment and under optimal initial nitrate concentration,

clay dosage, contact time, temperature, and pH (250 mg/L, 2.0 g, 90 minutes, 30°C, 5, respectively) <sup>13</sup>.

Related to modifications of natural clay minerals, a study on nanoscale zero-valent iron particles supported by natural Hangjin clay was conducted to analyze their capacity to remove nitrobenzene from contaminated waters. The Hangjin clay supplemented with the nanomaterial was found to be 93% effective at removing nitrobenzene, while the clay alone and the nanomaterial alone resulted in 38% removal and 52% removal, respectively. The synergistic effect of combining the nanomaterial with the clay was attributed to an even distribution of the nanoscale zero-valent iron particles on the clay, making them more efficient and more capable of adsorption with the clay support.<sup>14</sup>

Nanotechnology is an emerging method to solve several issues in a variety of fields, from medicine to food preservation. Within this field, scientists have discovered that nanotechnology can also be applied to solve environmental problems, one of them being removing pollutants from water.<sup>15</sup> Combining the properties of nanomaterials and clay minerals is the focus of this study, building on findings from previous experiments.

These previous studies all show a similar trend that a high surface area has a significant effect on the ability of the material to adsorb pollutants. Because nanomaterials are known to have a high surface area, it is expected that they will also show high sorption characteristics. Their capacity to adsorb nitrates will be explored in batch adsorption and column breakthrough experiments. Although there have been studies that modify a clay with nanomaterials, adsorption on nanoclays themselves has not been explored widely. The hydraulic conductivity of soil amended with nanoclays will also be determined to assess the feasibility of implementing this material as a soil amendment for LIDs since

fine particles such as clays can reduce hydraulic conductivity, but a high hydraulic conductivity is important for infiltration in LID facilities. An effective nanoclay-based soil amendment would provide high nitrate sorption characteristics at a low enough loading that the effect on the hydraulic conductivity of the overall soil mixture is minimal.

## CHAPTER 2: MATERIALS AND METHODS

Batch adsorption studies and column breakthrough experiments were conducted on several different types of clays to analyze their ability to adsorb nitrate. The goal of the batch adsorption study was to determine the time required for each clay to reach its greatest potential of decreasing nitrate concentration. The column breakthrough experiments had a similar goal, but assessed through the number of pore volumes passed through a soil column before the clay-amended soil could not retain any more nitrate. The sections below describe the materials and methods used to accomplish these goals.

### 2.1 MATERIALS

The clays used in this study were four different nanoclays along with kaolin clay. The nanoclays used were two pre-modified montmorillonite clay bases, while the other two were unmodified halloysite nanoclay and unmodified hydrophilic bentonite. The clays were purchased from Sigma Aldrich, which provided basic product specifications for the unmodified halloysite nanoclay, and the sizes of the pre-modified nanoclays and the unmodified hydrophilic bentonite, as shown in Table 1 below.

**Table 1 Properties of as-received nanoclays used in this study.**

<b>Name</b>	<b>Diam x Length</b>	<b>shape</b>	<b>pore size</b>	<b>surface area</b>
Unmodified Halloysite Nanoclay	30-70 nm x 1-3 $\mu$ m	nanotube	1.26-1.34 mL/g pore volume	64 m <sup>2</sup> /g
Unmodified Hydrophilic Bentonite	$\leq$ 25 $\mu$ m	-	-	-
Pre-modified trimethyl stearyl ammonium	$\leq$ 20 $\mu$ m	montmorillonite clay base	-	-
Pre-modified dimethyl dialkyl amine	$\leq$ 20 $\mu$ m	montmorillonite clay base	-	-

The pre-modified montmorillonite base nanoclays were subjected to treatment to have surface modifications that would change their properties. One was treated with 25-30% w/w trimethyl stearyl ammonium, while the other was treated with 35-45% w/w dimethyl dialkyl amine. The clays were purchased with the surface modifications already applied, which were expected to add a positive coating to the clays by the amine groups that are often associated with hydrogen atoms that would be able to attract anions like nitrate<sup>16</sup>. These clays are referred to as pre-modified trimethyl stearyl ammonium and pre-modified dimethyl dialkyl amine in this report.

Unmodified kaolin clay was used in this experiment as a control to observe the effects the nano-aspect of the nanoclays has on adsorption. A stock of unmodified kaolin was provided by the Cal Poly Civil and Environmental Engineering Department; consequently, specific clay characterization details are not available. The unmodified kaolin clay and the unmodified hydrophilic bentonite were tested in their as-received



form, but were also subjected to hydrochloric (HCl) acid modification (procedure discussed in Section 2.2.A) to observe any changes in their adsorption capacity. The reagent-grade HCl acid was purchased from Fisher Science.

To prepare the initial nitrate concentration introduced to the clays, both sodium nitrate and potassium nitrate were used. The sodium nitrate (CAS number 7631-99-4) was purchased from Fisher Science, while the potassium nitrate (CAS number 7757-79-1) was purchased from JT Baker Chemical Company (now available through Fisher Science).

The soil used as the base material for the column breakthrough experiment was Nevada Sand purchased from the Gordon Sand Company in 1997 by Cal Poly. It is a fine, uniform sand with a coefficient of uniformity of 1.06 and a mean grain diameter of 0.15 mm<sup>17</sup>. For further characterization of the sand, the specific gravity was determined through geotechnical analysis, as explained in Section 2.2.B.

## 2.2 TREATMENT AND CHARACTERIZATION METHODS

The ultimate goal of this research is to determine the feasibility of applying an effective clay material to an LID facility, which will likely involve infiltration through various soils. Therefore, several types of nanoclays were tested, of which some were treated to achieve surface modifications that may help with nitrate adsorption, to determine the best clay material. Geotechnical analysis was also conducted to characterize the clay and soil materials used in this experiment for implementation in practical applications. The surface modification and geotechnical analysis methods are explained in Section 2.2.A and Section 2.2.B, respectively.

### 2.2.1 SURFACE MODIFICATION

The unmodified kaolin and hydrophilic bentonite clays were surface modified with HCl acid to observe any changes in adsorption behavior, following a procedure developed by others<sup>13</sup>. Briefly, 5 grams of the as-received clay material was mixed with 25 mL of 2M HCl acid solution in a temperature controlled oil bath for 3 hours at 80°C. The treated clays were then cleaned using one of two different methods. For Method A, the HCl-clay mixture was filtered repeatedly in a vacuum filtration assembly with DI water until the pH of the rinse water reached 5-6. The treated clay was captured on a 0.2 µm nitrocellulose membrane. For Method B, the HCl-clay solution was split up into a few 50 mL falcon tubes, mixed with DI and sonicated with a probe sonicator (Bruker Nano Opt Interferometer, serial # NPF-11-209) to allow for adequate mixing, then centrifuged (Thermo Fisher Scientific, Sorvail Legend XTR, serial # 41291964) until the supernatant had separated from the clay. The supernatant was removed with a pipette, while the clay remained in the tube. Fresh DI water was then added to the tube and the procedure was repeated until the pH of the supernatant reached 5-6. After the clay was adequately rinsed, it was placed in glass petri dishes and oven dried at 105°C for approximately 24 hours.

### 2.2.2 GEOTECHNICAL TESTING

To characterize the base material used for the breakthrough experiment (discussed in Section 2.3.B), a specific gravity test was conducted on the Nevada Sand. The specific gravity test was conducted according to the ASTM D854 Test Method.

The hydraulic conductivity of the Nevada Sand, as well as that of the soil amendments (discussed in Section 2.3.B), was tested to assess the feasibility of implementing the nanoclay as a filtration device. The hydraulic conductivity was determined by the falling

head test, which has not been standardized by ASTM as of 1991, but can be referenced to the constant head test, ASTM D 2434-68 and AASHTO T 215-70.

## 2.3 EXPERIMENTAL PROCEDURES

The adsorption behavior of the different nanoclays was studied in both batch and column experiments, with the results of the batch experiment paving the testing parameters for the column experiment. Quality assurance and quality control (QA/QC) practices to ensure reliable data were utilized, as discussed in Section 2.4.

### 2.3.1 BATCH ADSORPTION

A batch adsorption experiment was conducted to determine the nitrate sorption capability of the four nanoclays compared to the unmodified kaolin clay, which served as a control. The batch adsorption study was conducted in two phases, with the second phase refined by the results of the first. In the first phase, a 50 mg/L  $\text{NO}_3\text{-N}$  solution was prepared using sodium nitrate. 35 mL of this nitrate solution were mixed with either 35 grams or 70 grams of clay (221:1 or 110:1 mg of nitrate to gram of clay, respectively), in a 50 mL falcon tube. Falcon tubes were shaken using a shaker table (Brunswick Incubator Shaker, model # 3530) for specific intervals ranging from 1 hour to 5 days.

In the second phase of the sorption study, a 1.42 mg/L nitrate solution ( $\text{NO}_3\text{-N}$ ) was prepared using potassium nitrate, and mixed with 35 mg of clay material to achieve a final ratio of 6.25 mg nitrate: 1 g of clay (and a 1:1 ratio of grams of clay to mL of solution). In the second phase, shorter time intervals were used for shaking the clay/nitrate mixtures, ranging from 1 to 120 minutes, based on the experiment conducted by Ouardi et al (2015) and findings from Phase 1.

For both phases, after the clay was mixed with the nitrate solution, the mixture was immediately sonicated using the probe sonicator for 10-20 seconds, or until no visible

clay particles remained in the solution. The content appeared milky in the falcon tube, which was assumed to mean the clay particles were dispersed in the solution in their nano form. This step was crucial to ensure that any aggregate clumps of the nanomaterials were broken up, allowing full benefit of the nanoscale size of the materials.

After shaking at about 325 rpm on the shaker table for the specific time intervals, sample tubes were put into the centrifuge for 1-5 minutes at a speed of 7,500-10,000 rpm, or until the clay had attached to the side of the tube and no particles were visible in the supernatant. The supernatant was then either immediately put into an ion chromatography system (IC) and IC autosampler system (Dionex, ICS-1600; AS-DV Serial # 15022516) for nitrate analysis, or they were sealed with the falcon tube cap and refrigerated for up to 2 days until IC analysis was conducted (discussed in Section 2.4).

### 2.3.2 COLUMN BREATHROUGH EXPERIMENTS

The column breakthrough experiments were conducted using a permeameter of height 2.98 inches and diameter of 2.43 inches, which was utilized as a small column. This column allowed for observation of the breakthrough concentration after various pore volumes of nitrate solution passed through the experimental soil mixture. The Nevada Sand served as the base material to which 0.1% w/w and 1% w/w of nanoclay or unmodified kaolin clay (which served as the baseline for comparison) was added. The cylinder in the permeameter held a mass of 346.5 grams of Nevada Sand, which had a dry weight of 344.19 grams. For the 0.1% w/w and 1% w/w soil amendments, tested clays were weighed to 0.34419 grams and 3.4419 grams, respectively, and sonicated with about 35 mL of DI water right before mixing with the Nevada Sand. A control of Nevada Sand with no clay amendment was tested as well.

The 0.1% w/w unmodified kaolin clay sonicated with DI water was added to 346.5 grams of Nevada Sand and mixed with a spoon, adding DI water as necessary to ensure the entire mass of clay was incorporated into the Nevada Sand. The consistency of the mixture was moist, but not pooling with water. This mixture was packed into the permeameter, and flushed with the top of the cylinder.

The burette attached to the permeameter apparatus was first filled with DI water, and the contents collected after 1 pore volume, 96.5 mL, and after 4 pore volumes to analyze background nitrate concentrations existing in the mixture. The burette was then filled with 1.7 mg/L  $\text{NO}_3\text{-N}$  solution and several pore volume samples were collected, ranging from 0.25-20 pore volumes, based on the porosity of pure Nevada Sand. This procedure was repeated for the 1% w/w unmodified kaolin clay sample and the 0.1% w/w and 1% w/w pre-modified trimethyl stearyl ammonium samples.

### 2.3.3 ANALYTICAL METHODS

To analyze the capacity of the various clays to adsorb nitrate, the nitrate concentration introduced initially to the system and the concentration at the end of the time interval or pore volume were compared using the IC, as specified in Section 2.3.A.

The IC analyzes samples by producing a curve with a specific area that corresponds to a concentration, which is determined by creating a calibration curve. The calibration curve was created by running known concentrations ranging from 0 mg/L  $\text{NO}_3\text{-N}$  to 100 mg/L  $\text{NO}_3\text{-N}$  through the IC, which resulted in corresponding curves and their areas. A graph of area vs. concentration was created to determine the best fit line and its equation (see Appendix). This equation was used to determine each unknown nitrate concentration from the known area resulting from the IC analysis.

## 2.4 QUALITY ASSURANCE AND QUALITY CONTROL

Both the batch experiment and the column experiment were tested with QA/QC parameters to serve as a check for any discrepancies, background behavior, and the accuracy and precision of the data collected.

Phase 1 of the batch experiment was conducted in triplicate for each time increment tested, which aimed to identify any outliers and observe the fluctuations in concentration that the clay may experience. Each time increment also included a single falcon tube that was filled with nitrate solution-only without any clay to observe any adsorption onto the falcon tubes. A split sample, or one identical sample to another, was tested through the IC to check the process and machine operations to ensure precise data was collected. A control verification standard (CVS) was also run through the machine for the same purpose. The CVS was prepared from a stock with a known concentration of 25 mg/L  $\text{NO}_3\text{-N}$ , and was analyzed towards the beginning, middle, and end of the run to check the entire IC run was operating correctly. If the CVS fell within  $\pm 10\%$  of the expected concentration, the data was assumed to be accurate.

Phase 2 of the batch experiment also included the CVS checks, splits, and nitrate-only samples. However, the nitrate-only samples were collected for the last time increment instead of every time increment tested. This was changed from Phase 1 because the last time increment would be indicative of the entire process's losses, deeming this control unnecessary to test for every time increment. Controls with clay-only mixed with DI water instead of nitrate solution, were also added to Phase 2 to determine if the tested clays leached any background nitrate concentrations. This background nitrate concentration would need to be subtracted from the IC nitrate concentration results, as

they would reflect nitrate concentrations from a source other than the nitrate solution as well as the nitrate concentration remaining after it had adsorbed onto the clays.

Phase 2 included a combination of duplicate runs and triplicate runs, limited by the time available for this study. Each run also included one sample tested in duplicate within the run as a control parameter to check the process in that particular test. Duplicates and triplicates were averaged and those values were used for analysis.

The column tests also included similar QA/QC processes, with duplicates for each trial and CVS's tested throughout the run. To test for background nitrate concentrations, the sand-clay mixtures were first flushed with DI water only, instead of the nitrate solution, and the effluent tested to observe if any nitrate leached. This analysis was conducted after one pore volume of DI and after four-five pore volumes of DI as a test to see if more nitrate leaching occurs as more water is flushed through the system. Another control, sand-only without any clay mixed in, was flushed with DI water only then nitrate solution to observe the capacity of the sand to retain any nitrate. This served as the control to which the clay amendments would be compared to observe any changes in adsorption.

## CHAPTER 3: RESULTS AND DISCUSSION

### 3.1 BACKGROUND NITRATE CONCENTRATION

As explained in Section 2.3.A, the batch adsorption study was conducted in two phases, the second phase modified by findings from the first. The batch studies were followed by the column studies that served as a bench-scale experiment for future implementation. During the batch adsorption experiment, all seven of the clay materials displayed background nitrate concentrations when exposed to the control DI. Table 2 below displays the averaged values of background concentrations resulting from IC analysis on each of the clays.

**Table 2 Background concentrations resulting from batch experiments.**

Type of Clay	Background Nitrate Concentration (mg/L NO <sub>3</sub> -N)	IC Experimental Reported Values (mg/L NO <sub>3</sub> -N)	% of IC-Reported Values
Unmodified Kaolin	0.51	1.69-1.83	<b>28-30</b>
Pre-modified Trimethyl Stearyl Ammonium	0.48	0.72-0.80	<b>60-67</b>
Pre-modified Dimethyl Dialkyl Amine	0.48	1.11-1.43	<b>34-44</b>
Unmodified Halloysite	0.49	1.65-1.69	<b>29-30</b>
Unmodified Bentonite	0.53	1.66-1.71	<b>31-32</b>
HCl Modified Kaolin	0.51	1.64-1.70	<b>30-31</b>
HCl Modified Bentonite	0.48	1.66-1.75	<b>27-29</b>



This table is indicative of the amount of nitrate inherent to the samples by sources other than the introduced nitrate solution, both in terms of concentration and its relativity to the total value reported by the IC. The last column in Table 2, “% of IC-Reported Values”, shows that all seven clays have a background concentration of greater than 25% of the total concentration reported by the IC for the samples taken at each time increment in question. However, each clay’s IC analysis resulted in a value of about 0.50 mg/L NO<sub>3</sub>-N, which is not expected as each clay has various chemical compositions, and therefore this concentration may not be leaching from the clays themselves. The source of the background nitrate concentration is unclear, as the DI blanks that were run through the IC did not produce any detectable NO<sub>3</sub>-N concentrations, so the DI is likely not the source. The surrounding air may be a factor that contributed to the total nitrate concentration, but this was not confirmed in this experiment. If the clays are in fact the source of the background nitrate concentration, this indicates that nitrates are inherent to the clay materials tested and may be released in aqueous environments. Although the source was not identified in this experiment, a background nitrate concentration was still reported by the IC and therefore needed to be subtracted from the total reported IC values for both Phase 1 and Phase 2 of the study. This showed a more accurate representation of the clays’ ability to reduce external nitrate concentrations introduced via the nitrate solution influent. The smaller of the range of percentages was used as a conservative estimate for adsorption, subtracting less background nitrate concentration and therefore leaving a larger portion of the IC result as the indication of the remaining nitrate concentration in solution (see Appendix for example calculations).

The column experiments were also tested for background nitrate concentrations released by the sand and clay mixtures by running DI water through the column prior to introducing the nitrate solution. The results showed that the sand and clay mixtures also contributed more than 25% of the initial NO<sub>3</sub>-N solution introduced, as shown in Table 3 below.

**Table 3 Background concentrations resulting from column experiments.**

<b>Description of Soil</b>	<b>Background Nitrate Concentration (mg/L NO<sub>3</sub>-N)</b>	<b>Initial Nitrate Solution Introduced (mg/L NO<sub>3</sub>-N)</b>	<b>% of Initial Nitrate Solution Introduced</b>
Nevada Sand Only	0.51	1.69	<b>30</b>
0.1% Trimethyl Stearyl Ammonium	0.47	1.69	<b>28</b>
1% Trimethyl Stearyl Ammonium	0.56	1.69	<b>33</b>
0.1% Kaolin	0.67	1.68	<b>40</b>
1% Kaolin	0.58	1.68	<b>34</b>

For this set of data, however, the background nitrate concentrations were not subtracted during analysis of the number of pore volumes reached at breakthrough. Because the column experiments were aimed at reflecting a real-world scenario in which these soil amendments would be applied to a filter media, the background nitrate concentrations (if leached by the clays) would also be released and would therefore reach breakthrough sooner than if these concentrations were taken out for this analysis. Therefore, for the goals of this aspect of the study, the background concentrations remained intact.

### 3.2 PRELIMINARY SORPTION STUDIES

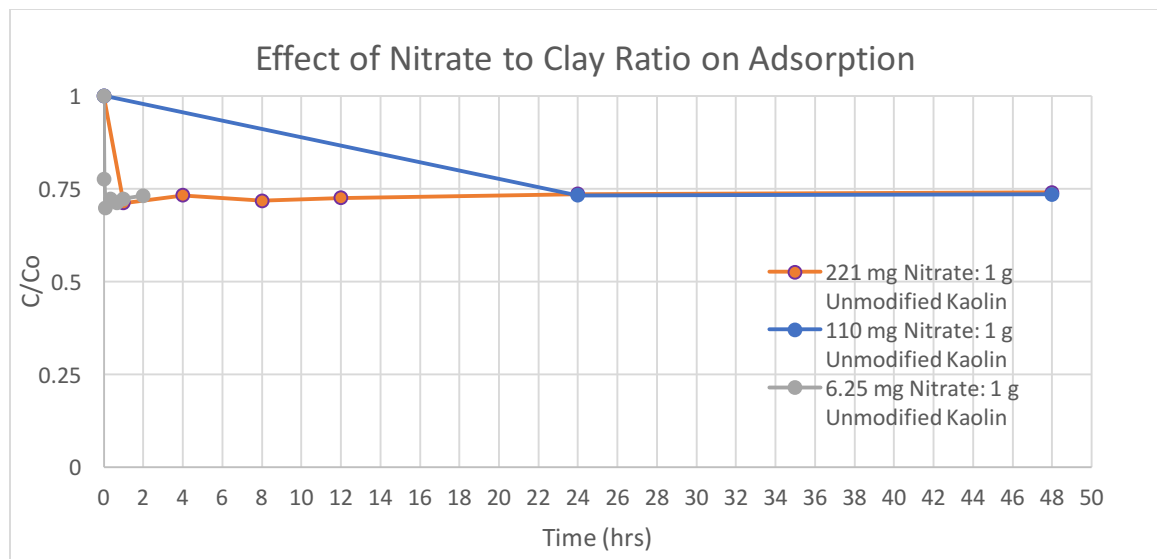
Phase 1 served as the preliminary study that was refined in Phase 2 (discussed in Section 3.3) to obtain more conclusive findings. Phase 1 conducted studies on unmodified kaolin as a control and unmodified halloysite as a representative nanoclay, to learn about the general time needed to decrease nitrate concentration and reach equilibrium.

The unmodified kaolin clay study used a starting concentration of 50 mg/L  $\text{NO}_3\text{-N}$ , in contact with either 35 mg or 70 mg of unmodified kaolin. The effect of clay dosage was tested to observe any differences in adsorption behavior. First, 35 mg of unmodified kaolin, then 70 mg of unmodified kaolin were exposed to 50 mg/L  $\text{NO}_3\text{-N}$  for 4-5 days (96-120 hours) of contact time, resulting in a ratio of 221 mg of nitrate: 1 g of clay (221:1) and 110 mg of nitrate: 1 g of clay (110:1), respectively. This nitrate concentration is significantly higher than environmentally relevant nitrate concentrations in stormwater runoff.

Note that Phase 2 was adjusted to reflect typical nitrate concentrations in surface waters, which range from about 0.1 mg/L to 2.10 mg/L<sup>18,19</sup>. Therefore, an initial nitrate concentration of 1.42 mg/L  $\text{NO}_3\text{-N}$  was prepared and shaken with 35 mg of unmodified kaolin (resulting in the ratio 6.25 mg nitrate: 1 g clay or 6.25:1). The expectation was that a lower nitrate loading rate that is more reflective of real world scenarios would result in more adsorption, due to the fewer number of nitrate molecules competing for adsorption sites on the clay. The Phase 2 ratio results are included in Figure 1 for comparison.

Figure 1 compares these three ratios, normalized for initial concentration. After being shaken with nitrate solution for 1, 4, 8, 12, 24, 48, 72, 96, and 120 hours, the unmodified kaolin showed a maximum concentration decrease of 29% under the 221 mg nitrate: 1 g clay ratio, followed by a 27% maximum decrease during the 110:1 ratio, and 30% for the

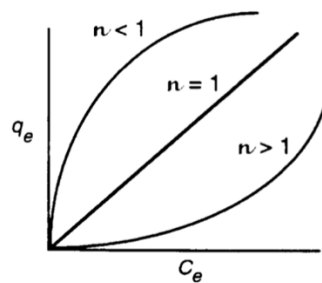
6.25:1 ratio. The minor fluctuation of 1-2% can be ignored and assumed that all three ratios have similar adsorption capacities. These results show that various nitrate to clay loading ratios used in this study did not make a significant impact on unmodified kaolin clay's adsorption capacity. This may imply that unmodified kaolin is capable of adsorbing about 30% of nitrate in runoff that flows through it, irrespective of the initial concentration.



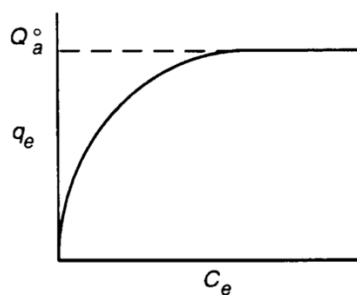
**Figure 1 Comparison of unmodified kaolin adsorption at different nitrate to clay ratios.**

Intuitively, it may be expected that a lower nitrate to clay ratio will result in more adsorption. However, the observed behavior actually follows expected sorption isotherm models. Two isotherm models, Freundlich and Langmuir, are used to characterize adsorption behavior and are shown in Figure 2. Both have a linear trend at low equilibrium concentrations, which the data from this study also follows, as shown in Figure 3. It cannot be concluded which isotherm model the results from this study follows, as additional data points are needed to observe behavior in larger concentrations.

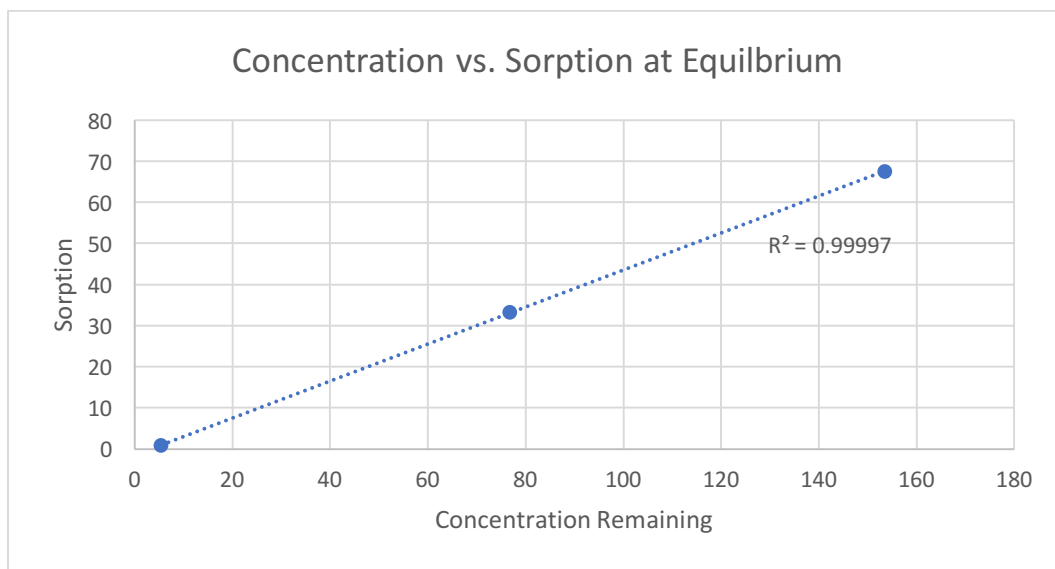
Freundlich:  $q = k_f c^n$



Langmuir:  $q = q_{\max} \frac{K_L c}{1 + K_L c}$



**Figure 2** General sorption models of Freundlich and Langmuir isotherms used to characterize adsorption behavior.<sup>20</sup>



**Figure 3** Concentration vs. Sorption at equilibrium for 221:1, 110:1, and 6.25:1 mg of nitrate to g of kaolin clay ratios.

Phase 1 also compared unmodified kaolin clay to unmodified halloysite nanoclay under the same contact time (4 days), initial nitrate concentration (50 mg/L NO<sub>3</sub>-N) and clay mass (35 mg), resulting in a 221:1 ratio. The higher of the two ratios used in this phase was chosen assuming that the perceived advantages of a nanoclay would allow for more or equal adsorption to take place with a lower amount of adsorbent necessary.

Unmodified halloysite was arbitrarily chosen as the first nanoclay to compare adsorption capacities, with the results displayed in Table 4.

**Table 4 Adsorption capacity of unmodified halloysite as compared to unmodified kaolin.**

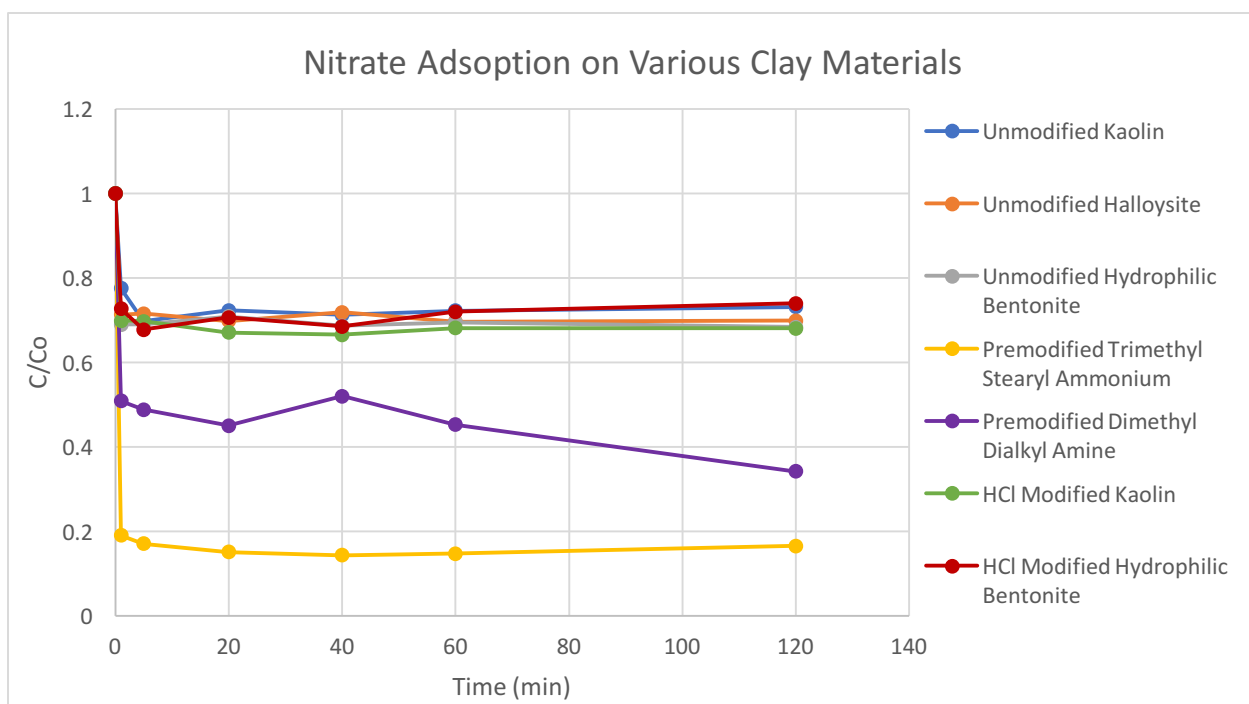
<b>Time (hr)</b>	<b>C/C<sub>0</sub> (unmodified halloysite)</b>	<b>C/C<sub>0</sub> (unmodified kaolin)</b>
0	1.00	1.00
96	0.68	0.75

Unmodified halloysite was only sampled after the total duration of 4 days (96 hours), which showed a total nitrate concentration decrease of 32%. Although the unmodified kaolin had a maximum decrease of 29% for the 221:1 ratio, it had decreased the nitrate by 25% after 4 days, which is a notable difference as compared to the unmodified halloysite that had adsorbed 7% more nitrate after the same time period. The properties associated with nanomaterials, such as high surface areas, were likely somewhat beneficial for this high ratio of 221 mg of nitrate: 1 g of clay. This finding supported cause to further investigate the behavior of different types of nanoclays in regards to their ability to adsorb nitrate, which was carried out in Phase 2. A comparison between a nitrate to clay ratio of 221:1 and 6.25:1 for the unmodified halloysite was also conducted.

The lower ratio resulted in a maximum concentration decrease of 30%, as compared to the 32% decrease observed with the higher ratio. This finding supports that changing nitrate to clay ratios does not significantly affect the adsorption capacity of unmodified halloysite for nitrate, in agreement with the findings for unmodified kaolin in this study. Phase 1 also identified that 1 hour is sufficient time to reach the equilibrium point for adsorption. Figure 1 shows that the nitrate concentration remains fairly constant after the 1-hour sample, with minor fluctuations occurring for the remainder of the time increments. This was further explored in Phase 2, during which shorter time increments were tested to identify more specifically the time at which the nitrate concentration decreases.

### 3.3 SORPTION EFFECTS OF VARIOUS CLAY MATERIALS

For Phase 2 of the batch adsorption study, nitrate adsorption was tested on seven different clay surfaces. The surfaces chosen were the four as-received nanoclays (pre-modified trimethyl stearyl ammonium, pre-modified dimethyl dialkyl amine, unmodified halloysite, and unmodified hydrophilic bentonite), the two HCl acid modified clays (HCl modified hydrophilic bentonite nanoclay and HCl modified kaolin clay), and unmodified kaolin clay as a control. The seven clays were shaken for a maximum of 120 minutes, with samples collected intermittently to observe the effects of contact time on adsorption, as shown in Figure 4. For this phase, the nitrate to clay ratio was 6.25:1, while the clay mass to solution volume ratio was 1 mg: 1 mL.



**Figure 4 Average nitrate adsorption capacity of clay materials during Phase 2. Background nitrate concentration has been removed (See Appendix).**

The initial  $\text{NO}_3\text{-N}$  concentration was to be 1.42 mg/L of  $\text{NO}_3\text{-N}$ , but due to standard laboratory limitations, the nitrate solution prepared was between 1.6 -1.9 mg/L  $\text{NO}_3\text{-N}$  according to IC analysis, which still falls within the range of typical concentrations found in stormwater. This results in a ratio of about 7.09-8.41 mg of nitrate: 1 g of clay, which is slightly higher than that which was originally expected (6.25 mg of nitrate: 1 g of clay). Figure 4 presents normalized concentration over time to account for these slight variations in initial concentration.

Despite the slight variation in starting concentration, analysis can still be conducted on the various clays as the trend is still a reflection of clay behavior. The seven clays were all shaken for 1, 5, 20, 40, 60, and 120-minute time intervals to observe the range of adsorption behaviors with changing contact times. Phase 1 showed that equilibrium was



reached by the first time increment tested at 60 minutes; Phase 2 tested shorter time intervals to observe whether equilibrium was reached prior to the 60-minute mark found in Phase 1. All seven clays displayed the steepest decline after immediate contact of 1-5 minutes, indicating that the main adsorption occurs fairly quickly after contact with the clay. The clays then reach equilibrium by the 20-minute sample, after which the concentration remains fairly constant for the remainder of the time sampled.

Achieving equilibrium by 20 minutes was not expected, as two previous studies found that equilibrium was reached at approximately 180 minutes<sup>3</sup> or after 90 minutes<sup>13</sup>. These two previous studies had similar environmental parameters as were used in this study with a temperature of 20-30°C and a pH of about 5, but different clay types were used. The Bekele study used an Ethiopian bentonite clay<sup>13</sup>, while the Ouadi study used a Moroccan clay mineral that is made up of Kaolinite, Illite, Quartz and Calcite<sup>3</sup>. The clays used in this study were similar species, but not the identical sources, potentially affecting both sorption behavior and other characteristics. The clays tested in this study have different surface properties and characteristics arising from their nano-size that may have prompted them to fill up their sites available for adsorption more quickly than those clays used in the previous studies.

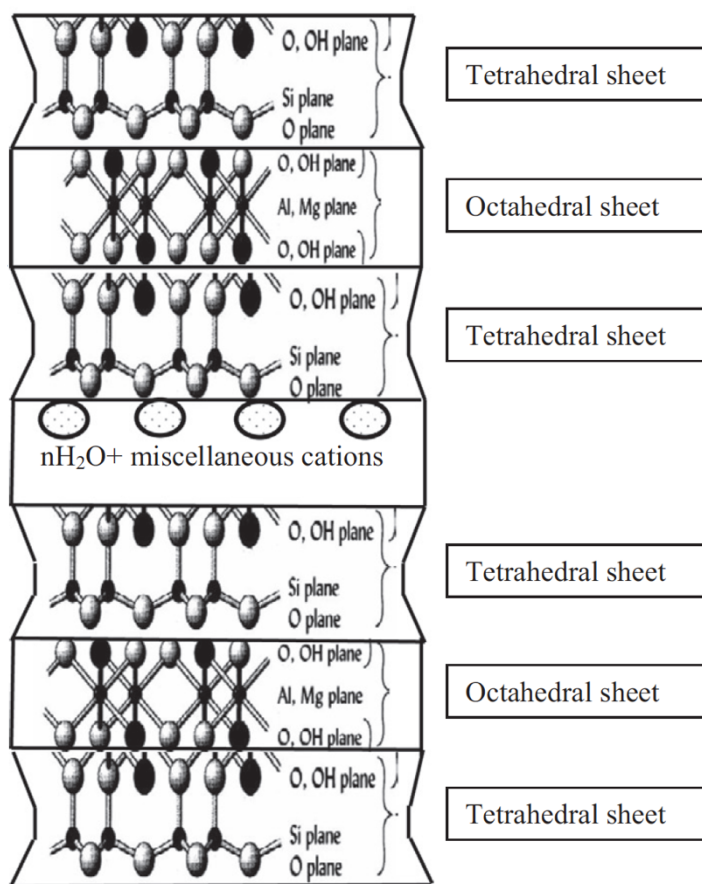
Additionally, this study found more nitrate reduction could be achieved by one of the pre-modified nanoclays tested (86%), compared to the 80% decrease achieved by the Bekele study and the 72% decrease by the Ouadi study. As shown in Figure 3, none of the seven clays completely removed nitrate. Although the starting concentration and the nitrate to clay ratio was fairly low, the clays were not able to treat it completely. This implies that

these particular clays may not have the capacity to retain all of the nitrate they are exposed to on their surfaces.

The pre-modified trimethyl stearyl ammonium showed the greatest nitrate adsorption capacity out of the seven clays tested, reaching a maximum of 86% decrease in  $\text{NO}_3\text{-N}$  concentration. The maximum removal was achieved after 40 minutes of contact time, but remained above 80% removal throughout the 120-minute span of the experiment. Such a high nitrate removal can be attributed in part to this nanoclay's surface properties brought about from the trimethyl stearyl ammonium modification. This modification is associated with producing cations on the surface of the material and adding a positive surface charge by way of the plentiful hydrogen atoms linked with its methyl ( $\text{CH}_3$ )<sup>21</sup>, stearyl ( $\text{C}_x\text{H}_x$ )<sup>22</sup>, and ammonium ( $\text{NH}_4$ ) groups<sup>23</sup>. The overall positive charge resulting from this modification likely facilitated adsorption of the negatively-charged nitrate ions.

The other pre-modified nanoclay, dimethyl dialkyl amine, was the second-most effective adsorbent, decreasing the nitrate concentration by a maximum of 66%. This result can also be attributed in part to its modified surface properties. The surface modification added an overall positive charge to the nanoclay<sup>23</sup>, allowing for the nitrate to bind more effectively to it. However, it was less effective than the trimethyl stearyl ammonium modification, possibly because there may have been less hydrogen atoms applied in this modification. The fewer number of hydrogen atoms on the surface of the pre-modified dimethyl dialkyl amine nanoclay may explain why fewer nitrates were able to bind to it. In addition to the surface treatment design that increases anionic sorption, both of these nanoclays have a montmorillonite clay base, which also has properties that favor nitrate adsorption. Montmorillonite is composed of silica tetrahedral sheets surrounding an

alumina octahedral sheet, with exchangeable cations in the interlayer space <sup>10</sup>. The presence of the cations in the montmorillonite, likely resulting from the weakly bound silica sheets that leave room for ions and water to infiltrate <sup>11</sup>, may explain the high adsorption capacity of the pre-modified nanoclays for nitrate, which is an anion and can readily attach to cations. Figure 5 is a representation of the physical and chemical structure of montmorillonite.

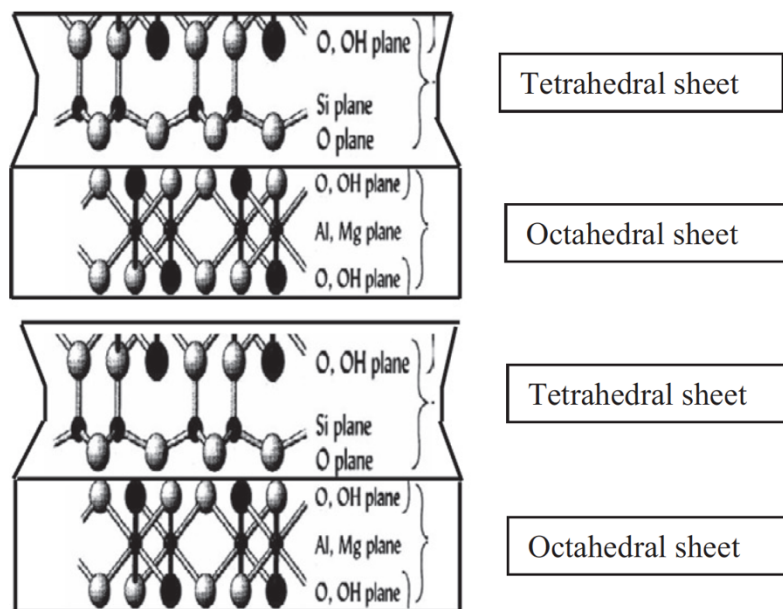


**Figure 5 Structural diagram of montmorillonite clay<sup>11</sup>.**

Both of the pre-modified nanoclays performed significantly better than the unmodified kaolin control. The unmodified kaolin reached a maximum concentration decrease of 30% after 5 minutes of contact, then reached equilibrium with a concentration decrease of

27-29%. This result shows that not only are there fewer sites available for adsorption on the unmodified kaolin, but they are also taken up fairly quickly. Because kaolin has a much lower cation exchange capacity compared to montmorillonite<sup>24</sup>, this behavior was expected.

Unmodified kaolin showed slightly less nitrate reduction than the other nanoclays as well, with the exception of unmodified halloysite, which also had a maximum nitrate reduction of approximately 30%. This result was different from the findings in Phase 1, which showed that unmodified halloysite had decreased nitrate concentration by 7% more than the unmodified kaolin. The difference between these two phases in regards to unmodified halloysite and unmodified kaolin were the time periods tested and the nitrate to clay ratios. Phase 1 determined that the tested nitrate to clay ratios were not a significant factor affecting unmodified halloysite or kaolin adsorption, so the longer time period of 4 days in Phase 1 versus the shorter time in Phase 2 may have affected their adsorption behavior. The similar response by the two clays may be attributed to the unmodified halloysite's structural similarity to unmodified kaolin, as halloysite belongs to the kaolin group<sup>10</sup>. Kaolin is primarily composed of kaolinite<sup>24</sup>, which has repeating layers of a silica tetrahedral sheet bound to an alumina octahedral sheet by oxygen atoms, while the layers are connected to each other through hydrogen bonds, as shown in Figure 6<sup>10</sup>. Because physical adsorption operates on the surface of the clay minerals through weak Van der Waal forces, the strong hydrogen bonds may not leave room for other molecules to intrude the clay, thereby making it difficult for nitrate anions to adsorb on the surface.



**Figure 6 Structural diagram of Kaolinite<sup>11</sup>.**

The other nanoclay, unmodified hydrophilic bentonite, performed slightly better than the unmodified kaolin clay and the unmodified halloysite, but not as well as the pre-modified nanoclays. Unmodified hydrophilic bentonite reached a maximum nitrate concentration decrease of 32% which does not meet the expectations for this clay. Bentonite is mainly composed of montmorillonite<sup>11</sup>, the same base material of the pre-modified nanoclays, giving it a similar structure and therefore behavioral characteristics of the high performing pre-modified nanoclays. The hydrophilic nature of this nanoclay led to the expectation that it would have an even higher swelling capacity than regular montmorillonite, and therefore more room for ion exchange. However, this result was not seen in this study. Because adsorption takes place on the surface of molecules, the surface properties of the nanoclays likely have more of an impact on sorption than their inner structure. The pre-modified nanoclays had surface modifications while the unmodified

bentonite did not, which may explain why the two pre-modified nanoclays performed better than their unmodified counterpart.

To explore the effects surface modifications have on nanoclays, an HCl acid treatment was applied to the unmodified kaolin control as well as the unmodified hydrophilic bentonite. The surface treatment was modeled after a previous study that found an optimal 80% nitrate reduction using surface-treated bentonite clay<sup>13</sup>. The unmodified hydrophilic bentonite was chosen because the reference study also used a type of bentonite clay. Furthermore, as discussed above, bentonite is similar structurally to montmorillonite clays which had previously shown successful sorption characteristics after surface modification.

The HCl acid treatment was expected to enhance adsorption by increasing the number of active sites on the clay through the addition of hydrogen ions, or a positive charge, by way of the dissociation of hydrogen and chloride ions<sup>13</sup>. However, the surface treatment did not seem to provide improved adsorption capabilities to the unmodified hydrophilic bentonite or to the unmodified kaolin. The nitrate concentration decreased by approximately 32% for both unmodified and HCl modified hydrophilic bentonite. Similarly, the HCl modified kaolin showed only a 3% improvement compared to the unmodified kaolin. These results were considered insignificant, as slight fluctuations in adsorption are expected between sample analyses.

These results were unexpected, as a previous study found that the HCl acid treatment was effective, showing an 80% decrease on the Ethiopian bentonite clay that the example study examined as opposed to the 32% decrease found in this study<sup>13</sup>. However, the chemical composition of bentonite clay found in various locations differs, making the

adsorption capacity for nitrate differ between bentonite clay types <sup>13</sup>. The Ethiopian bentonite used in the Bekele study was composed of 61% SiO<sub>2</sub>, 11.5% Al<sub>2</sub>O<sub>3</sub>, 6.9% Fe<sub>2</sub>O<sub>3</sub>, and less than 5% of several other oxides by weight <sup>13</sup>. The specific chemical constituents and the geographical origin of the unmodified hydrophilic bentonite used in this study were not provided by Sigma Aldrich, but assuming it is primarily composed of montmorillonite, it could have had 57.41% SiO<sub>2</sub>, 15.66% Al<sub>2</sub>O<sub>3</sub>, 4.93% Fe<sub>2</sub>O<sub>3</sub>, and less than 5% of other oxides <sup>10</sup> or 65.34% SiO<sub>2</sub>, 12.89% Al<sub>2</sub>O<sub>3</sub>, 2.38% Fe<sub>2</sub>O<sub>3</sub>, and less than 5% of other oxides <sup>11</sup> or numerous other variations of these chemicals. Characteristics of clay materials differs from location to location, which is why these montmorillonite clays have various compositions, and each will affect its properties and behavior towards other constituents, including nitrate.

The procedure for this treatment was also slightly amended from the example study, as the same resources and materials were not available. Specifically, the temperature controller on the oil bath available had a temperature fluctuation of  $\pm 20^{\circ}\text{C}$ , never remaining at the target temperature of  $80^{\circ}\text{C}$ , which was used in the reference study. This may have also made a difference to the HCl acid treatment by not allowing for the consistent temperature conditions for acid activation to take place on the nanoclay's surface.

This specific surface modification did not have the same effects as the surface modifications that the pre-modified trimethyl stearyl ammonium and pre-modified dimethyl dialkyl amine nanoclays had. The pre-modified nanoclays were subjected to several constituents (methane, amine, alkyl groups) that likely had synergistic effects on the montmorillonite nanoclay base and had several sources of hydrogen atoms, whereas

the HCl acid did not. The stronger proton treatment on the pre-modified nanoclays gave them an adsorption advantage over the HCl treated clays, which should have still performed better than shown in these results.

Overall, the nanoclays resulted in a higher adsorption capacity as compared to the unmodified kaolin control, which can be attributed to the nanoclays' large surface areas. Nanomaterials are emerging in industry because of their advantageous properties and behaviors that arise with their increased surface area. The pre-modified nanoclays tested in this study are especially indicative of the advantages of nano-sized particles for adsorption.

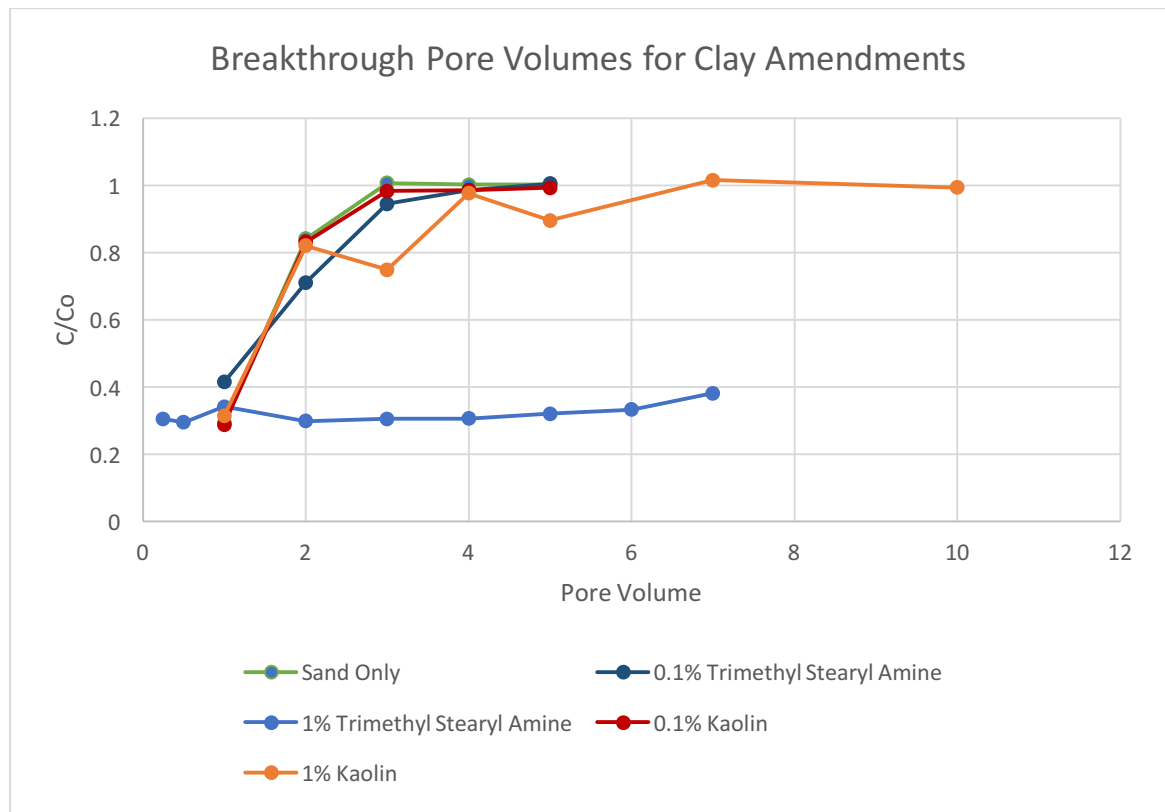
### 3.4 BREAKTHROUGH EXPERIMENTS AND HYDRAULIC CONDUCTIVITY

Hydraulic conductivity determines the feasibility of implementing a soil amendment for a bioretention mechanism, as too low of a hydraulic conductivity will prevent adequate infiltration needed to prevent flooding. As a comparison to Nevada Sand, Concrete Sand, which is another media tested for use in biofiltration units, was found to have a hydraulic conductivity of 42.2 in/hr. This is more than double that of Nevada Sand alone, and is a very high infiltration rate for adequate water quality improvement. The Concrete Sand was also not able to retain the clay in its mixture well, but instead washed out the clay through its pores. Therefore, Concrete Sand was not used for the soil amendment. The Nevada Sand, on the other hand, had a slower hydraulic conductivity as it is made up of finer, more uniform particles. It was also able to trap the added clay minerals in its pores, which was necessary for the column tests to determine its adsorption capability.

The Nevada Sand, which was found to have a specific gravity of 1.8 from the geotechnical test conducted, was treated with 0.1% and 1% w/w of unmodified kaolin clay and pre-modified trimethyl stearyl ammonium nanoclay to compare breakthrough



pore volumes. This test was conducted using an initial concentration of about 1.7 mg/L  $\text{NO}_3\text{-N}$ , and determined the number of pore volumes this solution could pass through the different soil amendments before the same or higher concentration “broke through”. The number of pore volumes reached at breakthrough indicate what this soil would be able to handle during storm events. The larger number of pore volumes the soil is able to flush the solution through before reaching breakthrough, the better the adsorption capacity of the soil. Figure 7 shows the breakthrough curves for the four experimental conditions compared to the sand-only control.



**Figure 7 Breakthrough curves for clay amended Nevada Sand.**

The pre-modified trimethyl stearyl ammonium was chosen as the nanoclay to compare with baseline conditions after determining in the batch study that this clay had the

greatest potential to adsorb nitrate. The HCl modified nanoclays were not chosen to be tested in this experiment because they resulted in similar adsorption capabilities as the unmodified kaolin clay, which was included as a control in this experiment. Low clay fractions were added to the sand as a precaution to prevent excessively lowering the hydraulic conductivity of the Nevada Sand and to minimize potential costs of nanoclay materials for the practical implementation of this soil as a filtration device. The curves show that both the 0.1% w/w unmodified kaolin clay amendment and the 0.1% w/w pre-modified nanoclay amendment behave almost identically to Nevada Sand only, reaching breakthrough within 3 or 4 pore volumes. This was expected, as there was not enough clay in the mixture to adsorb much more nitrate than the sand alone.

The 1% w/w clay amendments both performed better than the smaller fraction of clay amended soil, with the unmodified kaolin-amended soil reaching breakthrough after 7 pore volumes, and the nanoclay-amended soil reaching 38% of the initial concentration after 7 pore volumes. The nanoclay shows a slight, but steady inclination after 2 pore volumes, with a projected breakthrough at 17 pore volumes, assuming a polynomial behavior trend. This is much higher than the other clay amended soils, showing great potential for this type of nanoclay to be effective at removing nitrate in a filtration unit. The 1% addition of clay, however, did reduce the hydraulic conductivity of the sand by 46% (pre-modified trimethyl stearyl ammonium) and by 36% (unmodified kaolin clay). This is a significant reduction considering the minimal amount of clay added, though the overall hydraulic conductivity is still quite high, as shown in Table 3. The hydraulic conductivity of all four clay amendments ranges from 10-13 in/hr, while the recommended infiltration rate to achieve greater nitrate removal in a biofiltration device

is 1-2 in/hr <sup>6</sup>. This recommendation is one order of magnitude lower than the hydraulic conductivities of the clay-amended soil. This indicates that the soil mixture can afford to have a larger clay fraction added to it if the other components in bioretention soil media that may lower hydraulic conductivity, such as silt and organic matter, are accounted for as well to avoid compromising the soil's filtration ability.

**Table 5 Hydraulic Conductivities of Soils Tested**

<b>Soil Description</b>	<b>Hydraulic Conductivity (in/hr)</b>
Nevada Sand	19.3
0.1% Trimethyl Stearyl Ammonium Nanoclay	10.5
1% Trimethyl Stearyl Ammonium Nanoclay	12.6
0.1% Unmodified Kaolin	12.4
1% Unmodified Kaolin	12.4

As seen in the table above, the hydraulic conductivity did not change with the larger fraction of unmodified kaolin clay added, while the pre-modified nanoclay had an increase of about 20% after the 1% w/w was added. This increase in hydraulic conductivity was not expected, as more clay in soil tends to decrease infiltration rates. However, the procedure for mixing the amendments may have resulted in the formation of preferential flow pathways which would affect hydraulic conductivity calculations.

### 3.5 QUALITY ASSURANCE AND QUALITY CONTROL RESULTS

The QA/QC parameters tested all indicated that the experiment was conducted with proper techniques and the data is usable for discussion. The triplicate samples tested during Phase 1 of the batch experiment all had standard deviations that fell within 4% of

the average, implying that the experimental process was executed precisely. The samples that were filled with nitrate solution only, without any clay adsorbents, did not display any adsorption losses to the falcon tube walls. The concentration in these tubes remained within 10% of the initial concentration added, thus deeming the losses negligible for analysis of the results. There was one outlier in this phase: one of the 3-day nitrate-only samples, which resulted in a concentration that was 96% lower than the initial concentration. The 2-day and 4-day nitrate only samples in that same run resulted in a 0.04% and 1% difference from the initial concentration, and the other 3-day nitrate only sample resulted in a 2% difference, all of which indicate that this was not a natural phenomenon that occurred, but was instead an outlier as no other results follow this drastic change. This outlying point was not included in subsequent analysis.

Phase 2 had two outliers for the entirety of the experiment: one occurred during the pre-modified trimethyl stearyl ammonium run at the first 1-minute test, which showed a concentration of 1.25 mg/L  $\text{NO}_3\text{-N}$ , as opposed to the other two runs which resulted in concentrations of 0.8 and 0.81 mg/L  $\text{NO}_3\text{-N}$  for the 1-minute test (before subtracting out the background nitrate concentration). The other outlier occurred at the first hydrophilic bentonite 40-minute run, resulting in a concentration of 0.90 mg/L  $\text{NO}_3\text{-N}$ , while the remainder of the time intervals all had concentrations between 1.64 and 1.72 mg/L  $\text{NO}_3\text{-N}$  for both trials, also before subtracting out the background nitrate concentration. The background nitrate concentrations did not need to be subtracted to identify outliers, as all of the data points would be reduced by the same proportional amount. These outliers were not included in the analysis of the results, and were omitted from the calculation of averages that determined overall adsorption capacity of the various nanoclays.

The batch experiments using unmodified kaolin and the two pre-modified nanoclays were conducted in triplicates, while the remaining 4 clays (unmodified halloysite, unmodified hydrophilic bentonite, HCl modified bentonite, and HCl modified kaolin) were all conducted in duplicate due to time constraints. All multiples of the samples fell within a 10% standard deviation of each other, except for the pre-modified dimethyl dialkyl amine tests. The multiple samples that were run for this nanoclay allowed for a representative range of the capacity for it to reduce nitrate, and averages were taken to compare adsorption. The duplicates in the batch experiments showed a relative percent difference that also fell within 10% for each sample taken. The controls to test for adsorption losses to the falcon tubes at the 120-minute time increment for each run also showed that there were negligible losses, as most samples fell within 4% of the initial concentration added, with one within 6% of the initial concentration. These minimal losses were not taken into account when determining the adsorption capability of the nanoclays. Aside from overall duplicate and triplicates, each run included one sample that was conducted identically to another (the 60-minute time interval) to ensure that the process of the experiment was carried out consistently from sample to sample. These types of duplicates also showed that they all fell within 5% of each other, implying that the process was carried out reliably.

Both Phase 1 and Phase 2 included CVS's and splits as machine checks. The CVS's tested during these runs fell within 10% of the expected 25 mg/L  $\text{NO}_3\text{-N}$ , indicating correct representations of the unknown nitrate concentration samples by the IC. Those that showed greater than a 10% discrepancy from the expected concentration indicated the data collected before it to be unreliable, and this data was therefore omitted from

analysis. There were only two CVS's that led to omitting data, one that resulted in no data and the other that resulted in a 19% difference from the expected  $\text{NO}_3\text{-N}$  concentration. The data points that were taken out of consideration due to the 19% discrepancy were one of the 60-minute duplicates for pre-modified dimethyl dialkyl amine and the following 120-minute sample. The CVS that had an output of no data caused 12 data points to be excluded from analysis: one of the unmodified kaolin clay runs for the entire duration of 1-120 minutes, including the sample taken for background nitrate concentration, and the 40, 60, and 120-minute pre-modified dimethyl dialkyl amine nanoclay samples for that specific run, also including the background nitrate sample. Although this was a significant amount of data taken out, there were enough data points from other replicates of the run to have information for each clay's behavior at those specific time intervals.

In addition to the CVS's, a split of one sample during each IC run was also included as a secondary check. The results displayed nearly identical values for each split sample, with most splits showing a 1% difference between each other, but overall reaching a maximum 6% discrepancy between splits. This indicated that the machine was operating correctly as they all fell within 10% of each other.

The column test also included both CVS's and duplicates for each sample, and those results confirmed that the data was reliable for this phase as well. The CVS's all fell within 10% of the expected 25 mg/L  $\text{NO}_3\text{-N}$  concentration, so the IC results were all included in analysis. The duplicates allowed for averages to be taken for a better representation of the resulting concentrations instead of using just one single sample.

## CHAPTER 4: CONCLUSIONS AND RECOMMENDATIONS

The findings from this study suggest that certain nanoclays can successfully adsorb nitrate, but further experimentation is needed before they can be applied to real-world LIDs.

The batch adsorption experiment indicated that the pre-modified montmorillonite-based nanoclays are the most effective at adsorbing nitrate, as compared to kaolin, bentonite, and halloysite species. Surface modifications that apply a positive coating to the nanoclay, like the trimethyl stearyl ammonium and the dimethyl dialkyl amine modifications applied to montmorillonite, have very high adsorption capacities for typical nitrate loadings from runoff, reaching 86% and 66% under normal pH and temperature conditions (5-6, 25°C), with a nitrate to clay ratio of 6.25 mg: 1 g.

The properties associated with nanomaterials such as different behaviors with larger surface areas were not shown to have significant advantages over the unmodified control clay, kaolin, unless a surface modification was used. This may be a result of possible aggregation of the nanoclays, which would prevent them from exhibiting their true nano-size and the corresponding characteristics. For this specific experiment, the characteristics of the surface of the material are vital, as adsorption is a surface-based process. The HCl acid modification that was aimed at changing the surface of the clays did not prove to have a beneficial impact on the adsorption capacity, unlike previous studies<sup>13</sup>. The small impact the modification had during this experiment is not reflective of its expected advantages, and must therefore be explored in more detail in future research. Perhaps a system able to more reliably maintain a constant temperature during treatment would create the desired environmental conditions for the HCl acid

modification to be successful. Additionally, different surface modifications should also be explored to identify the optimal conditions for nitrate adsorption.

The column breakthrough experiments were indicative of the feasibility of using nanoclays as a soil amendment for treatment of stormwater such as in a bioretention cell installation. Under the tested parameters (pre-modified trimethyl stearyl ammonium surface modified nanoclay added to Nevada Sand, exposed to 1.7 mg/L NO<sub>3</sub>-N solution), the 1% w/w nanoclay amendment resulted in the best outcome out of the 4 conditions, reaching a projected nitrate breakthrough at 17 pore volumes. However, future experimentation should run the experiment until breakthrough is reached for a more accurate breakthrough pore volume result. The hydraulic conductivity of this best-case scenario was 12.6 in/hr, while a bioretention cell is recommended to have an infiltration rate of 1-2 in/hr for nitrate removal. Therefore, a larger clay fraction could be added to the Nevada Sand and possibly extend the useful life, but would need to account for additional materials that go into a bioretention cell that reduce hydraulic conductivity (e.g. silt and organic matter).

Further column studies with different base materials could also be conducted, perhaps with a soil mixture that is recommended for use in industry. This would allow for a comparison with an in-use soil and possible alterations that would enhance bioretention cell performance. For a more in-depth look at the adsorption capacity of such an amendment, a batch study could also be conducted to compare the nanoclay's ability to adsorb nitrate compared to that of the industry-approved soil.

For future work, the batch adsorption studies should also be tested under different environmental conditions. For example, changing the nitrate to clay ratios for the



nanoclays and not just the unmodified kaolin to observe any changes in adsorption.

Testing more variations of nanoclays, either purchased from a manufacturer or amended with different surface modification methods, would also provide a greater understanding of nanomaterial behavior in this context. In the future, it is recommended that instead of a nitrate-only solution, synthetic stormwater is used as the influent. Synthetic stormwater, or solution made in lab that mimics real stormwater with known concentrations of typical constituents in stormwater, would give a more realistic representation of the behavior of nanoclays in a real-world application where they would be exposed to not only nitrate, but other constituents in runoff as well. This may change their adsorption capacity, as other pollutants may compete for the same adsorption sites on the nanoclays. If repeated studies show feasible application of nanoclays in a bioretention soil media, an extensive health and environmental risk assessment would need to be conducted prior to adoption of the new media. For example, the health effects pertaining to ingestion, inhalation, or skin exposure to nanoclays should be studied, in the chance that they are released into open water bodies in which both humans and aquatic life come in contact with.

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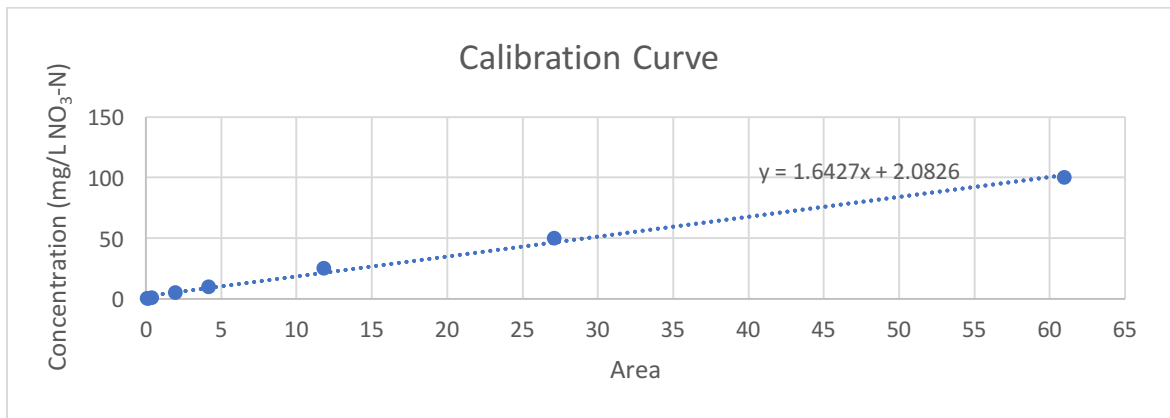
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## APPENDICES

## APPENDIX A: CALIBRATION CURVES

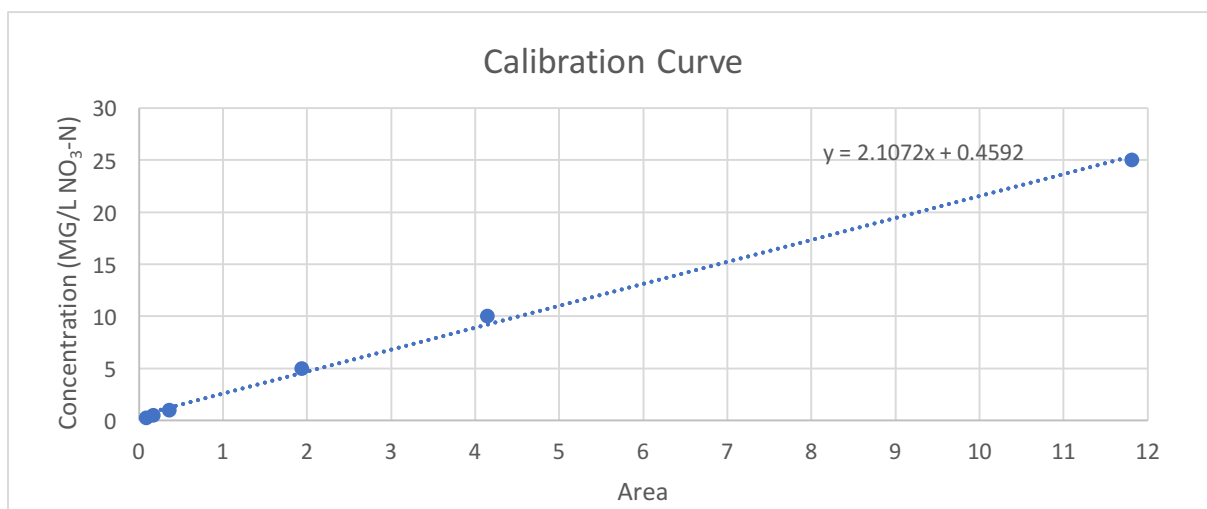
1. Calibration data and curve for Phase 1 starting concentration 50 mg/L NO<sub>3</sub>-N

Calibration Curve		
Sample Name	Area	Concentration (mg/L NO <sub>3</sub> -N)
0 nitrate 0 nitrite	n.a.	-
0.25 nitrate 0.125 nitrite	0.0861	0.25
0.5 nitrate 0.25 nitrite	0.1694	0.5
1 Nitrate 0.5 Nitrite	0.3587	1
5 Nitrate 2.5 Nitrite	1.9376	5
10 Nitrate 5 Nitrite	4.1438	10
25 Nitrate 12.5 Nitrite	11.8101	25
50 Nitrate 25 Nitrite	27.1125	50
100 Nitrate 50 Nitrite	60.9656	100



2. Calibration data and curve for Phase 2 starting concentration 1.42 mg/L NO<sub>3</sub>-N

Calibration Curve		
Sample Name	IC Area	Concentration (mg/L NO <sub>3</sub> -N)
0 nitrate 0 nitrite	n.a.	-
0.25 nitrate 0.125 nitrite	0.0861	0.25
0.5 nitrate 0.25 nitrite	0.1694	0.5
1 Nitrate 0.5 Nitrite	0.3587	1
5 Nitrate 2.5 Nitrite	1.9376	5
10 Nitrate 5 Nitrite	4.1438	10
25 Nitrate 12.5 Nitrite	11.8101	25





## APPENDIX B: SPECIFIC GRAVITY TEST

Initial Moisture Content (Moist Method)	
Tare I.D.	ST-40
Tare Mass, g	100.27
Wet Mass + Tare, g	163.56
Dry Mass + Tare, g	163.03
% Moisture	0.8%

Soil Type	Moist Mass, g with 250ml Pycnometer	Moist Mass, g, with 500 ml Pycnometer
SP, SP-SM	60.5	100.8
SP-SC, SM, SC	45.4	75.6
Silt or Clay	35.3	50.4

Note: Values in above table are generated from the reported %M and guidance from Table 2 of ASTM D854-06

Pycnomter and Test Data	
Pycnometer I.D.	4
Calibrated Volume of Pycnometer, ml	499.14
Average Calibrated Mass of Dry Pycnomter, g	185.61
Mass of Pycnometer+Soil+Water, g	711.37
Test Temperature, C	23.8
Density of Water at Test Temp, g/ml	0.99764
Temperature Coefficient, K	0.99943

After Test Data	
Tare I.D.	11
Tare Mass, g	723.06
Dry Mass + Tare, g	785.76
Mass of Oven Dry Solids, g	62.70

Calculations	
Mass of Pycnomter and Water at Test Temperature, g	683.57
Specific Gravity at Test Temperature	1.80
Specific Gravity at 20 Degrees C	1.80

## APPENDIX C: RAW DATA

1. Phase 1 Batch Adsorption-Results from IC Analysis, after applying equation from calibration curve for Phase 1. The values shown are without any QA/QC applied and background concentrations are not subtracted.

Data Results: Run 1- Kaolin Only 35 mg clay per 35 mL of 50 mg/L NO <sub>3</sub> -N			
Sample Description	Sample Name	Area	Concentration (mg/L NO <sub>3</sub> -N)
Control Verification Standard 25 ppm	cvs	13.2085	23.77
1 hour Kaolin Sample A	1ka	25.8904	44.59
1 hour Kaolin Sample B	1kb	27.5796	47.37
1 hour Kaolin Sample C	1kc	27.872	47.85
1 Hour NO3 only, no Kaolin	1k0	28.6509	49.13
4 hour Kaolin Sample A	4ka	28.5877	49.02
4 hour Kaolin Sample B	4kb	27.5331	47.29
4 hour Kaolin Sample C	4kc	27.6746	47.52
4 Hour NO3 only, no Kaolin	4k0	30.7372	52.55
8 hour Kaolin Sample A	8ka	27.2444	46.82
8 hour Kaolin Sample B	8kb	27.4775	47.20
8 hour Kaolin Sample C	8kc	27.3426	46.98
8 Hour NO3 only, no Kaolin	8k0	29.316	50.219472
Deionized Water	DI	n.a.	#VALUE!
Control Verification Standard 25 ppm	cvs	15.2475	27.12
12 hour Kaolin Sample A	12ka	27.3922	47.06
12 hour Kaolin Sample B	12kb	27.6455	47.48
12 hour Kaolin Sample C	12kc	27.9631	48.00
12 Hour NO3 only, no Kaolin	12k0	29.0926	49.8526492
24 hour Kaolin Sample A	24ka	28.4801	48.85
24 hour Kaolin Sample B	24kb	27.6941	47.56
24 hour Kaolin Sample C	24kc	28.4224	48.75
24 Hour NO3 only, no Kaolin	24k0	29.1337	49.9201354
48 hour Kaolin Sample A	48ka	28.3309	48.60
48 hour Kaolin Sample B	48kb	28.7579	49.30
48 hour Kaolin Sample C	48kc	27.7685	47.68
48 Hour NO3 only, no Kaolin	48k0	29.1801	49.9963242
48 hour Kaolin Sample C Split	split 48kc	27.7199	47.60
Initial Conc, with Kaolin Sample A	0ka	28.3072	48.56
Initial Conc, with Kaolin Sample B	0kb	28.2289	48.43
Initial Conc, with Kaolin Sample C	0kc	27.554	47.33
Initial Conc of Solution Added to Samples	0k0	31.0464	53.06
Deionized Water	di	n.a.	#VALUE!

Control Verification Standard 25 ppm	cvs	13.3941	24.08
Deionized Water	di	0.0073	2.09
Deionized Water	DI Shutdown	n.a.	#VALUE!

Data Results: Run 2- Kaolin Only 35 mg clay per 35 mL of 50 mg/L NO <sub>3</sub> -N			
Sample Description	Sample Name	Area	Concentration (mg/L NO <sub>3</sub> -N)
Deionized Water	DI	n.a.	#VALUE!
Control Verification Standard 25 ppm	CVS	15.0678	26.82
0 hour Kaolin Sample A (no shaking)	0ka	27.5046	47.25
0 hour Kaolin Sample B (no shaking)	0kb	27.5949	47.39
0 hour Kaolin Sample C (no shaking)	0kc	27.5167	47.27
0 Day NO3 only, no Kaolin	0k0	27.592	47.388664
24 hour Kaolin Sample A	24ka	27.8031	47.74
24 hour Kaolin Sample B	24kb	27.8448	47.80
24 hour Kaolin Sample C	24kc	28.3537	48.64
1 Day NO3 only, no Kaolin	24k0	27.7488	47.6461296
Deionized Water	DI	0.0107	2.10
Control Verification Standard 25 ppm	CVS	14.1632	25.34
48 hour Kaolin Sample A	48ka	27.8846	47.87
48 hour Kaolin Sample B	48kb	28.5058	48.89
48 hour Kaolin Sample C	48kc	28.2182	48.42
2 Day NO3 only, no Kaolin	48k0	27.6044	47.4090248
3 Day Kaolin Sample A	3ka	28.1018	48.23
3 Day Kaolin Sample B	3kb	28.6176	49.07
3 Day Kaolin Sample C	3kc	28.5799	49.01
3 Day NO3, no kaolin	3k0	0.0213	2.1175746
Deionized Water	DI	0.0051	2.09
4 Day kaolin Sample A	4ka	28.4923	48.87
4 Day kaolin Sample B	4kb	28.8129	49.39
4 Day kaolin Sample C	4kc	28.9969	49.70
4 Day NO3, no Kaolin	4k0	27.9645	48.000309
5 Day Kaolin Sample A	5ka	28.2556	48.48
5 Day Kaolin Sample B	5kb	28.8408	49.44
5 Day Kaolin Sample C	5kc	28.8864	49.51
5 Day NO3, no Kaolin	5k0	28.0033	48.06
5 Day Kaolin Sample B (split)	split 5kb	28.8811	49.51
Deionized Water	DI	0.0083	2.10
Control Verification Standard 25 ppm	cvs	15.0596	26.81
Deionized Water	DI	0.0075	2.09
Deionized Water	DI Shutdown	n.a.	#VALUE!

Data Results: Run 3- Kaolin and Nanoclay (Halloysite) 70 mg clay per 35 mL of 50 mg/L NO <sub>3</sub> -N and 35 mg of halloysite per 35 ml			
Sample Description	Sample Name	Area	Concentration (mg/L NO <sub>3</sub> -N)
Deionized Water	DI	n.a.	#VALUE!
Control Verification Standard 25 ppm	CVS	13.1694	23.71
0 hour Kaolin Sample A (no shaking)	0ka	26.7734	46.04
0 hour Kaolin Sample B (no shaking)	0kb	26.8955	46.25
0 hour Kaolin Sample C (no shaking)	0kc	26.9209	46.29
0 Day NO3 only, no Kaolin	0k0	27.3892	47.06
1 Day Kaolin Sample A	Mka	27.5069	47.25
1 Day Kaolin Sample B	Mkb	27.2783	46.87
1 Day Kaolin Sample C	Mkc	27.0784	46.55
1 Day NO3 only, no Kaolin	Mk0	27.5404	47.30
Deionized Water	DI	0.0045	2.09
Control Verification Standard 25 ppm	CVS	13.3089	23.94
2 Day Kaolin Sample A	Tka	27.6427	47.47
2 Day Kaolin Sample B	Tkb	27.3483	46.99
2 Day Kaolin Sample C	Tkc	27.1877	46.72
2 Day NO3 only, no Kaolin	Tk0	27.6986	47.56
3 Day Kaolin Sample A	Wka	27.3205	46.94
3 Day Kaolin Sample B	Wkb	27.5736	47.36
3 Day Kaolin Sample C	Wkc	27.7049	47.57
3 Day NO3, no kaolin	Wk0	27.8384	47.79
Deionized Water	DI	n.a.	#VALUE!
4 Day kaolin Sample A	Rka	27.6896	47.55
4 Day kaolin Sample B	Rkb	27.7811	47.70
4 Day kaolin Sample C	Rkc	27.7307	47.62
4 Day NO3, no Kaolin	Rk0	27.8917	47.88
4 Day Nanoclay (Halloysite) Sample A	Rna	26.4364	45.49
4 Day Nanoclay (Halloysite) Sample A Split	Split Rna	26.4002	45.43
4 Day Nanoclay (Halloysite) Sample B	Rnb	25.9057	44.62
4 Day Nanoclay (Halloysite) Sample C	Rnc	26.5869	45.74
4 Day NO3 only , no Nanoclay (Halloysite)	Rn0	28.1454	48.30
Deionized Water	DI	0.0026	2.09
Control Verification Standard 25 ppm	cvs	15.3553	27.30
Deionized Water	DI	0.0091	2.10
Deionized Water	DI Shutdown	n.a.	#VALUE!

2. Phase 2 Batch Adsorption-Results from IC Analysis, after applying equation from calibration curve for Phase 2. The values shown are without any QA/QC applied and background concentrations are not subtracted. Raw data is presented differently from Phase 1 because Phase 2 was conducted in several runs with various nanoclays tested, so the data was compiled into more concise tables for better readability.

<b>Unmodified Kaolin</b>		
Time (min)	Concentration (mg/L NO <sub>3</sub> -N)	Average Concentration
0	1.631	1.697
	1.708	
	1.753	
1	1.719	1.282
	1.716	
	1.932	
5	1.675	1.202
	1.738	
	1.714	
20	1.635	1.192
	1.626	
	1.838	
40	1.635	1.209
	1.709	
	1.804	
60	1.674	1.216
	-	
	1.748	
	1.702	
	1.672	
	1.820	
120	1.727	1.244
	1.752	
	1.775	

<b>Premodified Trimethyl Stearyl Ammonium</b>		
Time (min)	Concentration (mg/L NO <sub>3</sub> -N)	Average Concentration
0	1.631	1.697

	1.708	
	1.753	
1	1.252	0.322
	0.798	
	0.811	
5	0.800	0.289
	0.695	
	0.819	
20	0.749	0.255
	0.714	
	0.749	
40	0.734	0.243
	0.716	
	0.725	
60	0.772	0.249
	0.699	
	0.727	
	0.745	
	0.729	
	0.715	
120	0.733	0.280
	0.738	
	0.814	

Premodified Dimethyl Dialkyl Amine		
Time (min)	Concentration (mg/L NO3-N)	Average Concentration
0	2.024	1.828
	1.708	
	1.753	
1	1.854	0.933
	1.108	
	1.278	
5	1.733	0.897
	1.079	
	1.318	
20	1.753	0.828
	1.068	
	1.102	

40	1.720	0.838
	1.085	
	1.149	
60	1.698	0.838
	1.147	
	1.122	
	1.711	
	1.113	
	1.112	

Unmodified Halloysite		
Time (min)	Concentration (mg/L NO <sub>3</sub> -N)	Average Concentration
0	1.631	1.669
	1.706	
	-	
1	1.685	1.190
	1.669	
	-	
5	1.682	1.193
	1.680	
	-	
20	1.670	1.164
	1.633	
	-	
40	1.714	1.198
	1.658	
	-	
60	1.690	1.161
	1.641	
	-	
	1.616	
	1.646	
	-	
120	1.651	1.165
	1.655	
	-	

Unmodified Hydrophilic Bentonite
----------------------------------

Time (min)	Concentration (mg/L NO3-N)	Average Concentration
0	1.631	1.663
	1.694	
	-	
1	1.684	1.146
	1.665	
	-	
5	1.692	1.147
	1.658	
	-	
20	1.717	1.177
	1.693	
	-	
40	0.899	1.141
	1.669	
	-	
60	1.722	1.154
	1.635	
	-	
	1.697	
	1.675	
	-	
120	1.670	1.136
	1.657	
	-	

HCl modified Bentonite		
Time (min)	Concentration (mg/L NO3-N)	Average Concentration
0	1.727	1.727
	1.727	
	-	
1	1.750	1.254
	1.711	
	-	
5	1.650	1.169
	1.640	
	-	



20	1.674	1.219
	1.717	
	-	
40	1.670	1.182
	1.647	
	-	
60	1.732	1.242
	1.733	
	-	
	1.691	
	-	
	-	
120	1.698	1.276
	1.806	
	-	

HCl modified Kaolin		
Time (min)	Concentration (mg/L NO3-N)	Average Concentration
0	1.694	1.694
	1.694	
	-	
1	1.705	1.183
	1.690	
	-	
5	1.708	1.180
	1.682	
	-	
20	1.677	1.136
	1.625	
	-	
40	1.655	1.127
	1.629	
	-	
60	1.681	1.153
	1.675	
	-	
	1.705	
	1.611	

	-	
120	1.677	1.152
	1.657	
	-	

# APPENDIX D: SAMPLE CALCULATIONS

BACKGROUND NITRATE CONCENTRATIONS: UNMOD KAOLIN

PHASE 2 RESULTS { IC Reported value:  $1.69 \frac{\text{mg}}{\text{L}} \text{NO}_3\text{-N} - 1.83 \frac{\text{mg}}{\text{L}} \text{NO}_3\text{-N}$

BKGD CONC:  $0.51 \frac{\text{mg}}{\text{L}} \text{NO}_3\text{-N}$

(BKGD) % of IC value: 28-30%.

For conserv. estimate: use 28%.

ex: for phase 2, UNMOD KAOLIN, Time 1 min:

IC Reported: 1.72; 1.93

Average =  $\left( \frac{1.72 + 1.93}{2} \right) = 1.825$

AVG CONC DECREASE =  $1.825 - 0.51 = 1.315 \frac{\text{mg}}{\text{L}} \text{NO}_3\text{-N}$   
(SUBTRACT BKGD)

ex: for phase 1, UNMOD KAOLIN, Time 1 hr

IC Reported AVG VALUE:  $46.60 \frac{\text{mg}}{\text{L}} \text{NO}_3\text{-N}$

ACCOUNT FOR BKGD

TO GET DECREASE IN CONC:  $46.60 - (46.60 \times 0.28)$

$= 33.56 \frac{\text{mg}}{\text{L}} \text{NO}_3\text{-N}$

INITIAL CONC:  $47.22 \frac{\text{mg}}{\text{L}} \text{NO}_3\text{-N}$  conservative

% decrease:  $\frac{47.22 - 33.56}{47.22} \times 100\% = 28.9\%$

→ if we had used 30% BKGD VALUE:

$46.60 - (46.60 \times 0.3) = 32.62 \frac{\text{mg}}{\text{L}} \text{NO}_3\text{-N}$  (remaining in tube)

% dec =  $\frac{47.22 - 32.62}{47.22} = 30.9\%$  shows greater decrease