

**APPLICATION OF GRAPHENE-BASED MATERIALS FOR AMMONIUM REMOVAL
FROM AQUEOUS SOLUTION**

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To my Mom

who gave me wings and made me fly...

To my Dad

who stood by me and I stood tall...

To my aunt Shayesteh

who said no star was out of reach...

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Abstract

High levels of ammonium in water sources pose many environmental problems. Among current technologies used for ammonium removal, adsorption/ion-exchange is potentially a viable method. There is very limited information in the literature on application of graphene based materials as an adsorbent for ammonia. The main aim of this research was to investigate the application of graphene based material as an efficient adsorbent for ammonium removal from liquid phase, to optimize the ammonium uptake, and assess the feasibility of immobilizing the graphene on a solid surface.

In the first phase of this study, graphene oxide (GO) was synthesized according to an improved Hummer's method. The as-prepared material was treated by sodium hydroxide in order to create some sodium containing functional groups on the surface of adsorbent, which show high tendency to be exchanged with ammonium cations. The adsorbent was characterized by different characterization techniques such as Raman, FT-IR, XPS, and TEM in order to identify the properties of the material before and after adsorption process. These showed the typical peaks and morphology of graphene oxide material and adsorption of ammonium identified by reduction of sodium peaks and increase in nitrogen signal. Also, isotherms, kinetics, and thermodynamics studies were performed to investigate the adsorption behavior of sodium functionalized graphene oxide (GO-Na). The isotherm was best described by a Langmuir model with maximum capacity of 32 mg/g, which is higher than capacity for many common used adsorbents such as zeolites and resins reported in literature. Furthermore, the kinetic studies revealed that the process was very fast (reaching equilibrium within 5 minutes) and a pseudo-second order model was the best fit for this adsorption process. Thermodynamic data showed that the process was an exothermic and spontaneous reaction in the nature.

The second phase of this research was the investigation of the impacts of two critical factors (pH and temperature) on the adsorption of ammonium by GO-Na. Response surface methodology was utilized to assess the effect and optimize these two parameters on the solid phase concentration and the removal percentage of the adsorbent. The optimum pH and temperature to reach the maximum values for R% (58.23%) and q_e (27.45 mg/g) were predicted by the model at 8 and 45 °C, respectively. The results showed that temperature does not have a significant impact on the adsorption process, however, pH and the interaction of pH and temperature play a significant role in the adsorption process.

In the third phase of this study, the isothermic behavior of competitive ions including calcium, potassium, and sodium on GO-Na in a single-component and multi-component system was investigated. The Langmuir isotherm model was used to fit all the experimental results. The results showed that the maximum Langmuir adsorption capacities follow the order $K^+ \geq NH_4^+ > Ca^{2+}$ in single-component systems. In the multi-component system most of active sites were occupied by calcium cations, which limit the adsorption capacity of ammonium and potassium. A slight improvement in the contribution of ammonium removal from the multi-component system was detected by increasing the pH from 7 to 8.5, which can be explained by generation of additional favorable active sites for ammonium adsorption and formation of amide group on the surface of adsorbent in presence of OH^- ions. The regeneration studies of the used material obtained from multi-component system showed a constant adsorption capacity for both ammonium and potassium and a sudden reduction in calcium uptake from 1.5 to 0.7 meq/g in the first cycle, while it remained constant in the next cycles.

Finally, different kinds of sodium alginate-graphene oxide hydrogel beads were made in order to immobilize the GO powder. Results were not satisfactory for two main reasons. First, the

immobilization caused a reduction in the number of sites of GO available for adsorption. Second, calcium ions (necessary for bead formation) block ammonium adsorption.

Keywords: Graphene Oxide, Adsorption, TAN Removal, Isotherms, Kinetics, Thermodynamics, Optimization, pH, Temperature Competitive Adsorption, Ammonium, Sodium, Potassium, Calcium, Regeneration, Wastewater Treatment.

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List of Abbreviations

AA: Atomic Absorption

ANOVA: Analysis of Variance

BOD: Biochemical Oxygen Demand

CCD: Central Composite Design

COD: Chemical Oxygen Demand

C.V.%: Coefficient of Variance

CVD: Chemical Vapor Deposition

D-R: Dubinin-Radushkevich Equation

EIMWW: Explosive Impacted Mining Wastewater

FT-IR: Fourier Transform Infrared

F-value: Fisher Variation Ratio

GO: Graphene Oxide

GO-Na: Sodium Functionalized Graphene Oxide

GO-Na-N: Sodium Functionalized Graphene Oxide after Ammonium Adsorption

HOPG: Highly Ordered Pyrolytic Graphite

M: Molar

P-value: Probability Value

rGO: reduced Graphene Oxide

RSM: Response Surface Methodology

SD: Standard Deviation

SEM: Scanning Electron Microscopy

TAN: Total Ammonia Nitrogen

TEM: Transmission Electron Microscopy

w/w: Weight by weight

XPS: X-ray Photoelectron Spectroscopy

List of Nomenclatures

α : Elovich Constant related to Initial Adsorption Rate

β : Elovich Constant related to Adsorption Coefficient

β : Constant of the Adsorption Energy

ε : Polanyi Potential

a : Redlich-Peterson Constant

a_i^{Multi} : Equilibrium Ratio of Adsorbed Component i to all Adsorbed Components in Multi-Component System

a_i^{Single} : Equilibrium Ratio of Adsorbed Component i to all Adsorbed Components in Single-Component System

C : Intra Particle Constant

C_0 : Initial Concentration

C_e : Equilibrium Concentration

$^{\circ}\text{C}$: Degrees Celsius

E : Adsorption Energy

ΔG : Gibbs Free Energy Changes

ΔH : Enthalpy Changes

K : Kelvin

K_{ad} : Langmuir Adsorption Equilibrium Constant

K_d : Equilibrium Constant

K_F : Freundlich Adsorption Equilibrium Constant

K_{id} : Intra Particle Rate Constant

k_1 : Rate Constant for Pseudo-First Order Model

k_2 : Rate Constant for Pseudo-Second Order Model

n : Constant related to Surface Heterogeneity

q_e : Equilibrium Solid Phase Concentration

q_i^{Multi} : Sorption Capacity for Component i in Multi-Component System

q_i^{Single} : Sorption Capacity for Component i in Single-Component System

q_{Max} : Maximum Adsorption Capacity

q_{ref} : Solid Phase Concentration at time t_{ref}

q_t : Solid Phase Concentration at time t

R : Universal Gas Constant

$R\%$: Removal Percentage

R_L : Separation Factor

ΔS : Entropy Changes

T : Temperature

t : time

t_{ref} : Longest time in the Adsorption Process

V_0 : Initial Adsorption Rate for Pseudo-Second Order Model

ΔY : Adsorption Reduction Percentage

Chapter 1: Introduction

1.1. General background

In addition to the natural sources of ammonia, annually, over 2×10^{11} kilograms of ammonia are produced all around the world by the Haber-Bosch process, which combines molecular hydrogen and nitrogen to form ammonia to be used in many fields such as agriculture, mining industry, oil refining industry, and tannery [1]. The presence of excess ammonia in water bodies can cause many environmental problems such as eutrophication [2], depletion of dissolved oxygen in water resources [3], toxicity to aquatic animals and humans [4], and inhibition of microorganism in biological processes at high concentrations of ammonia [5]. The total ammonia nitrogen (TAN) toxicity is mainly related to ammonia [6].

When ammonia dissolves in water, ammonium ions are formed according to the reversible reaction shown as follow.



According to Equation 1.1, ammonia in water can be found in two forms: ammonium cation (NH_4^+) and ammonia (NH_3). In aquatic chemistry, usually the sum of these two forms is expressed as total ammonia nitrogen (TAN) [7]. The distribution of NH_4^+/NH_3 in water is a function of pH and temperature (Equation 1.2 to 1.5) [7, 8].



$$pH = pK_a + \log \left\{ \frac{[NH_3]}{[NH_4^+]} \right\} \quad (1.3)$$

$$pK_a = 0.09 + \frac{2729.92}{T} \quad (1.4)$$

$$f = \frac{[NH_3]}{[NH_3] + [NH_4^+]} = \frac{1}{[10^{(pK_a - pH)} + 1]} \quad (1.5)$$

In which, T is the temperature in Kelvins and f is the fraction of ammonia present in the unionized form [8].

As Figure 1.1 shows, by decreasing pH the concentration of H^+ increases and it makes the equilibrium shift to the right. Subsequently, more ammonium ions are formed. pK_a of 9.26 indicates that at this pH, both ammonia and ammonium ions have the same concentration, but at pH values less than neutral range, ammonium is the dominant form, while at a pH of more than 11 all cations are mostly converted to ammonia.

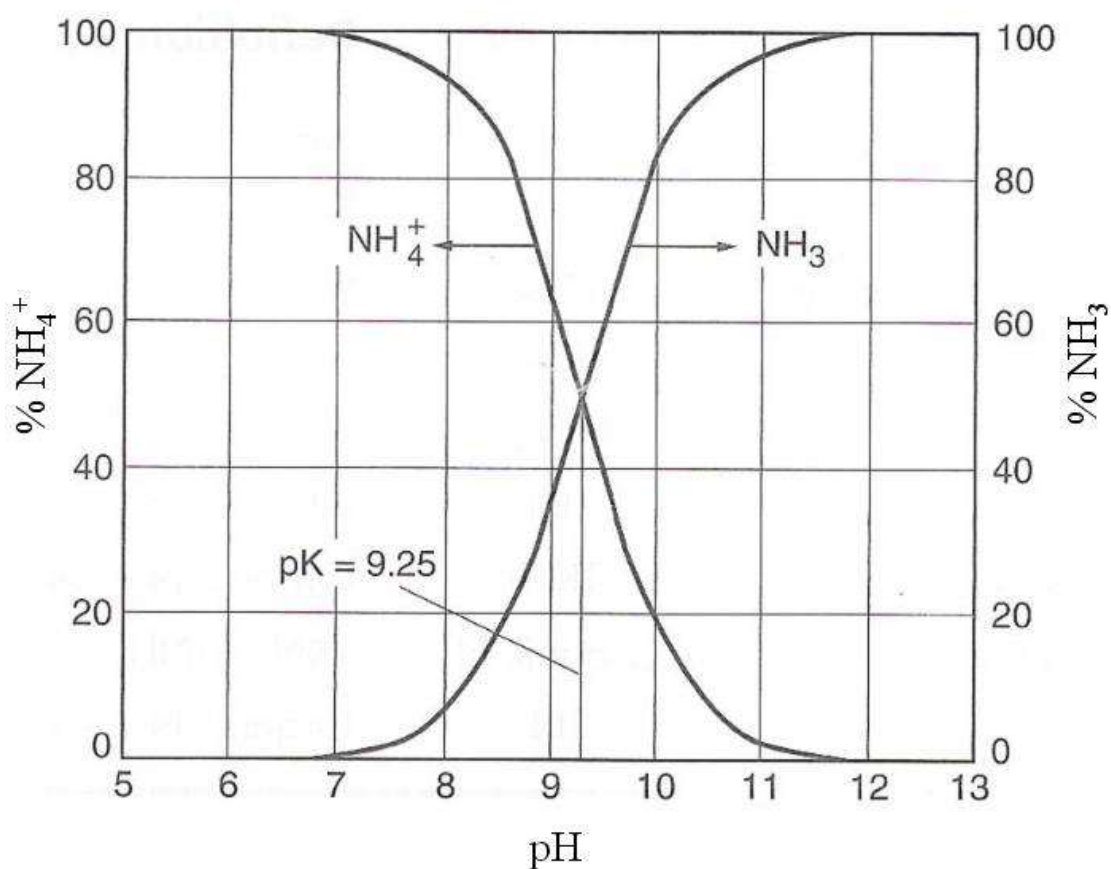


Figure 1.1. Ammonium and ammonia distribution as a function of pH [9]

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To meet the ammonia discharge regulations several methods have been proposed to remove TAN from the liquid phase, they can be placed in three categories: biological, physical, and chemical techniques. The direct removal of ammonia gas from aqueous solutions (air stripping) have some disadvantages because they are high energy demanding, and time consuming, require high costs of aeration, and produce air pollution due to release of ammonia gas. The biological treatment method is widely used, however, it is susceptible toxicity at high concentrations of ammonia. One effective way for ammonia removal is converting ammonia to ammonium cation by adjusting the pH of aqueous solution and then removing it from liquid phase. Adsorption/ion exchange has attracted much interest as one of the most efficient method for ammonium cation removal due to its simple and economical operation, fast kinetics, better recovery of ammonium cations, less sludge production and less disposal problems [10, 11]. The most common adsorbents are zeolites and resins. In literature, various adsorbents have been applied for ammonium removal so far, but the adsorption capacity of most of them is rather low. Therefore, there is a need to find more effective adsorbents for ammonium removal from liquid phase. Assessment of new and more effective adsorbents for ammonium removal from liquid phase has been of interest to researchers.

1.2. Research objectives

With the rapid growth of environmental awareness over the past decades, many environmental standard limits were set to control the release of ammonia into the environment. Total Ammonia Nitrogen (TAN) toxicity is mainly related to dissolved ammonia in water bodies and the distribution of dissolved ammonia to ammonium cation is a function of two important factors; pH and temperature. US EPA has set two standard limits as acute and chronic limits to protect the aquatic life based on pH and temperature. At pH of 7 and temperature of 20°C, the US EPA

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acute criterion and the chronic levels are 17 mg TAN/L and 1.9 mg TAN/L, respectively [12]. It is necessary to find an efficient way to decrease the concentration of TAN to meet the standard criteria.

In this study, the application of graphene based materials for ammonium cation removal from aqueous solution was investigated and its performance was compared with common adsorbents such as zeolites and resins.

The main objectives of this study were to:

- Synthesize and characterize graphene oxide (GO) and modified GO through its surface functionalization by sodium to be employed as a potential adsorbent for ammonium uptake from wastewater.
- Investigate the performance of sodium functionalized graphene oxide (GO-Na) in ammonium adsorption and determine the behavior and mechanism of TAN adsorption by GO-Na (isotherm, kinetic, and thermodynamic study).
- Study the feasibility of regeneration of GO-Na with NaCl.
- Apply central composite design and response surface methodology (RSM) to optimize the solid phase concentration (q_e mg/g) and the removal percentage (R%) of the process for the effect of pH and temperature.
- Assess ion competition on ammonium removal from a simulated explosive impacted mining wastewater by sodium functionalized graphene oxide.
- Investigate the role of pH in ammonium uptake in the presence of other cations in a multi-component system.

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- Determine the adsorption performance of GO-Na for multi-component system during the consecutive cycles of regeneration.
- Immobilize the adsorbent by making a graphene-based hydrogel to facilitate its application to wastewater treatment.

1.3. Novelty or Significance

Graphene oxide could present high potential as an adsorbent since it could contain various oxygen containing functional groups on its surface. Its application has been reported for removal of some contaminants from wastewater, such as dyes, heavy metals, and pharmaceuticals [13-16]. However, limited studies have been conducted on the performance of this material for ammonia removal from aqueous phase, which is the main objective of this research.

1.4. Thesis organization and outline

This thesis is divided into six chapters to facilitate the clarification of the key factors in this study. **Chapter one** presents the statement of the problem, research objectives, and the outline. **Chapter two** contains a literature review on different techniques for TAN removal, the merits and demerits of each method, the benefits of adsorption and ion/exchange process compared to other techniques, and graphene based material as a potential adsorbent for ammonium uptake from wastewater. **Chapters three, four, and five** are written in paper-based format which present the results of the research carried out. Writing the technical part in research paper format causes some overlaps between various sections of these three chapters. Therefore, it is recommended to focus on each chapter separately. **Chapter three (the first technical paper)** studies the synthesis and functionalization of graphene oxide and its application on ammonium uptake from aqueous solution. It also investigates the behavior and mechanism of adsorption process through isotherm, kinetic, and thermodynamic studies. At the end, the feasibility of

application of NaCl for regeneration of the adsorbent was studied. **Chapter four (the second technical paper)** deals with the optimization of influential parameters on the adsorption process. By considering the impacts of two critical factors including pH and temperature, factorial design and response surface methodology (*RSM*) was employed to optimize the solid phase concentration (q_e mg/g) and removal percentage ($R\%$) of the process. **Chapter five (the third technical paper)** is intended to assess the effects of ion competition on ammonium removal from the explosive impacted mining wastewater by sodium functionalized graphene oxide. Finally, the main conclusions drawn from different phases of this study are summarized in **Chapter six**. Also, some helpful recommendations that could be practical for future works were presented in this chapter. At the end, the synthesis methods of some potential adsorbents for ammonium removal are explained in **Appendix 1**. The extra results related to immobilization of GO with sodium alginate and lignin are presented in **Appendix 2** and the additional information about synthesis and analytical methods is provided in **Appendix 3**. Figure 1.2 depicts the outline of this research study.

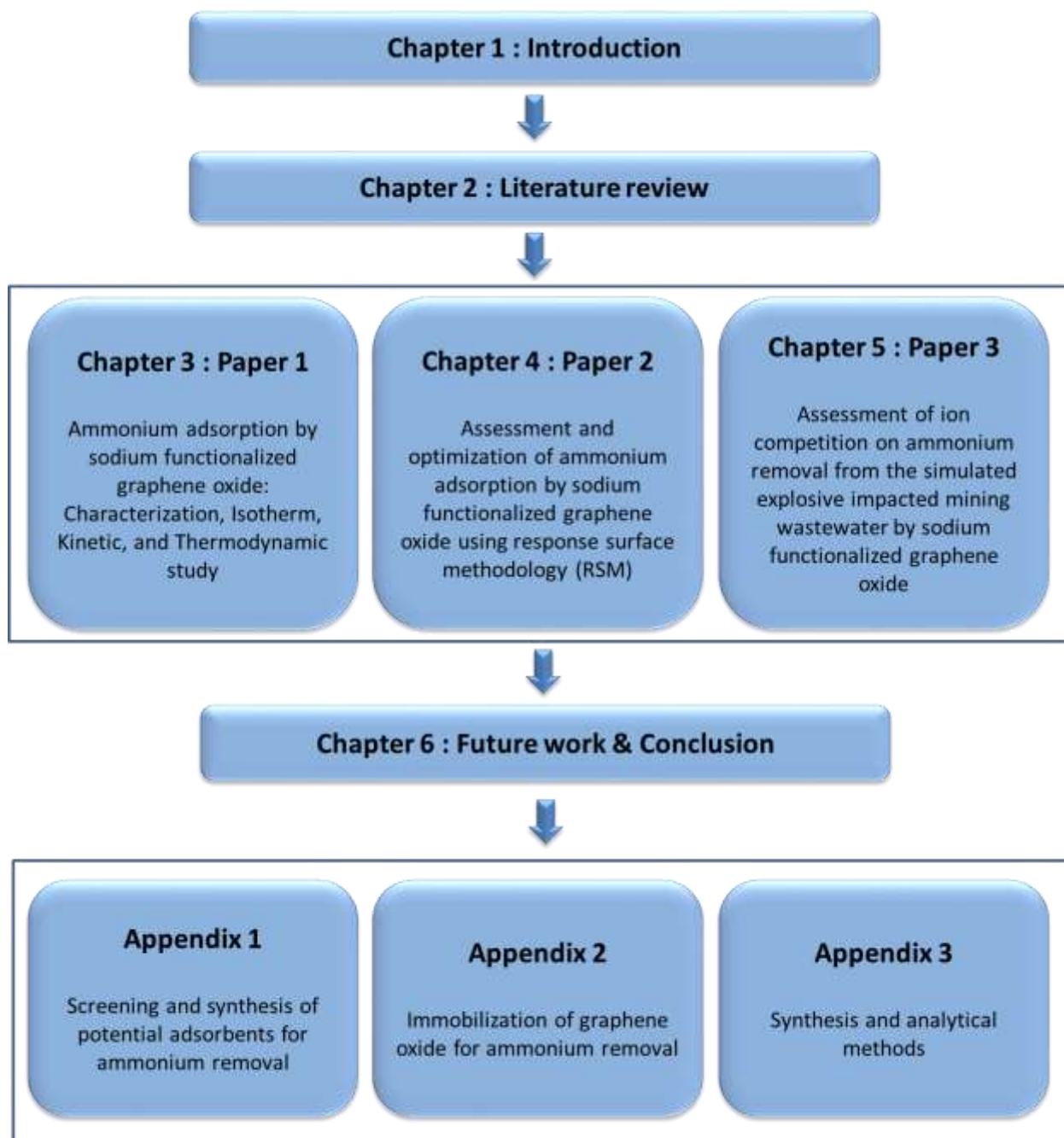


Figure 1.2. Outline of the Thesis

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2.1. Nitrogen cycle in environment

Figure 2.1 illustrates the nitrogen cycle in the environment. There are two natural ways for ammonia generation in the environment. In the first way, the nitrogen-fixing bacteria living in the soil or in the plants' roots reduce the molecular nitrogen N_2 available in the atmosphere to ammonia (NH_3). As the second way, the existing organic nitrogen in soil is degraded by some microorganisms to produce amino acids. Then, the amino acids are converted to ammonia through an ammonification process.

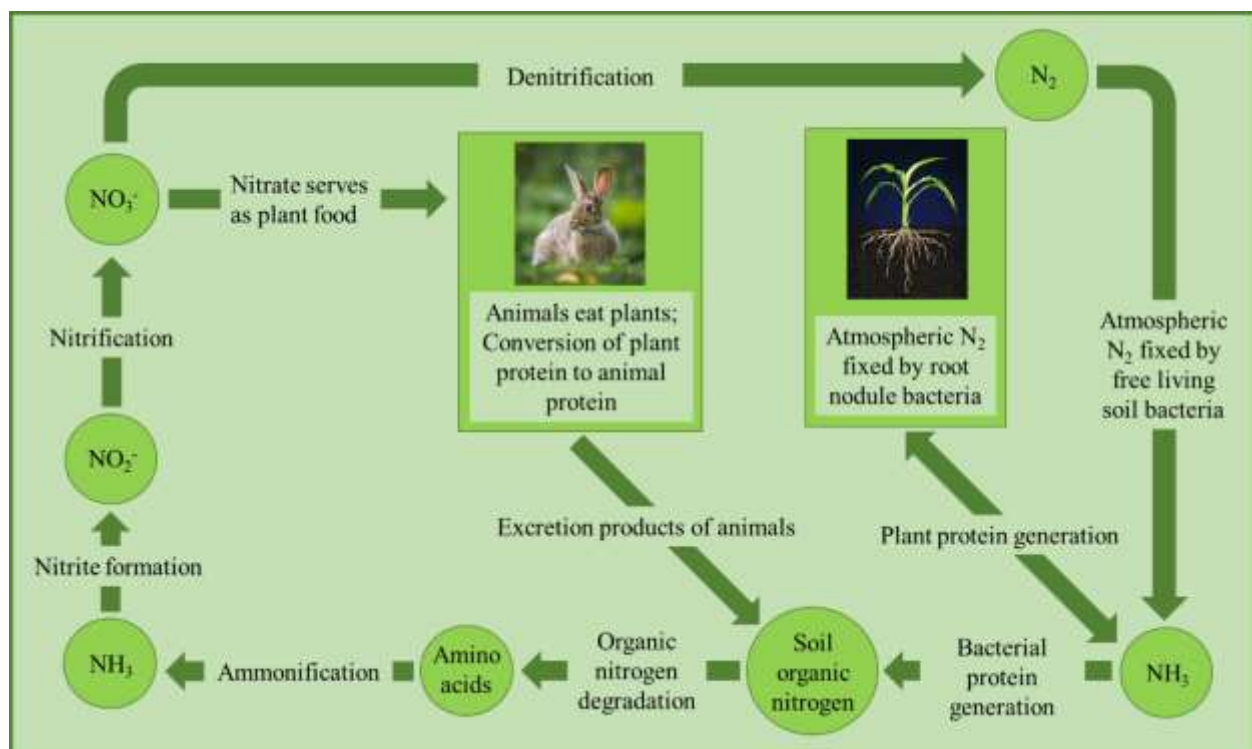


Figure 2.1. Nitrogen cycle in the environment

2.2. TAN toxicity and discharge criteria

Annually a huge amount of TAN, the most abundant form of nitrogen pollutant in the wastewater, enters the effluent through industrial and municipal discharges. Moreover, agricultural practices such as the land application of fertilizers and concentration of crop production result in increase in nitrogenous nutrient pollutant [1]. The major environmental concerns of TAN are listed below:

- Toxicity to fish and other aquatic species [2-4],
- Negative effects on biological treatment of wastewater, because, it is one of the most common toxic substances to bacteria specially in large amounts [5, 6],
- Eutrophication [7, 8],
- Depletion of dissolved oxygen in water resources [1, 9],
- Air pollution problems because of ammonia volatilization and odor emission [3, 10].

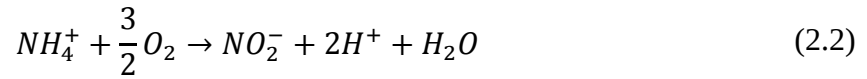
With the rapid growth of environmental awareness over the past century, many environmental standard limits were set to control the release of ammonia into the environment. Total Ammonia Nitrogen (TAN) toxicity is mainly related to dissolved ammonia in water bodies and the distribution of dissolved ammonia to ammonium cation is a function of two important factors; pH and temperature. US EPA has set two standard limits as acute and chronic limits to protect the aquatic life based on pH and temperature. At pH of 7 and temperature of 20°C, the US EPA acute criterion and the chronic levels are 17 mg TAN/L and 1.9 mg TAN/L, respectively [11].

To meet these standard ranges several methods have been proposed for ammonium uptake from wastewater which can be placed in three categories: biological, physical, and chemical techniques.

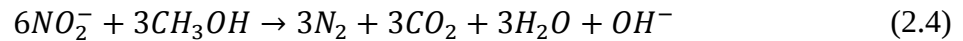
2.3. Biological methods

2.3.1. Conventional nitrification/denitrification

Nitrification is defined as the conversion of ammonium to nitrate through two oxidation reactions, which include oxidation of ammonium to nitrite and oxidation of nitrite to nitrate shown in Equations 2.1 and 2.2, *respectively*. These reactions are carried out by two main types of autotrophic organisms generally termed nitrifiers. The nitrifier bacteria involved in the first and second oxidation reactions are named as Nitrosomonas and Nitrobacter, respectively [12].



Denitrification is the conversion of nitrate to nitrogen gas with the presence of heterotrophic denitrifier bacteria. Equation 2.3 expresses the fact that this process has two significant requirements: anoxic condition and an organic carbon source [13].



Conventional nitrification/denitrification is the most widely used biological ammonium removal procedure at relatively low concentrations of ammonia. However, it has some limitations mentioned below.

- It needs a vast area to provide sufficient land for a series of reactors for nitrification, denitrification, BOD decomposition, and solid liquid separation.
- It is sensitive to pH, temperature, halogen compounds, cyanides, and other heavy metals [14].

- High concentrations of ammonia are toxic to the bacteria that participates in the treatment process [5].

2.3.2. Anaerobic ammonium oxidation (Anommax)

As providing adequate oxygen for conventional nitrification/denitrification in the large scale is not usually economical, the Anommax method was presented as a cost effective alternative for ammonia removal. In this process, ammonia nitrogen is directly oxidized to nitrogen gas under anaerobic conditions according to Equation 2.4. Due to the fact that this process is not oxygen demanding the major part of the overall cost during the biological removal processes will be saved [15]. However, the slow bacteria growth rate and long set up time for Anommax reactor to reach the maximum capacity is the main disadvantage of this method [16].



2.3.3. Removal by algae

In wastewater treatment plants, algae can be used for ammonia removal by converting the inorganic nitrogen, especially ammonium, to biomass through the photosynthesis process. This method has three main advantages listed as below:

- Inorganic nitrogen removal
- Consuming CO₂ by photosynthetic microorganisms and oxygen production
- Valuable biomass generation for animal feed or biodiesel production [17].

One of the major drawbacks of this process is separating the biomass from treated effluent. To address this problem many studies have been performed to immobilized the algae cells by chitosan [18] or alginate beads [19]. However, Chevalier and de la Noüe claimed that only the

cells located on the surface of the beads are active for ammonium uptake and the cells in deeper part of the beads are unable to do photosynthesis [20].

2.3.4. Removal by microbial fuel cell

Microbial fuel cell reactors contain two parts, which are the anode chamber and the cathode chamber separated by a cation exchange membrane. The wastewater with high concentration of ammonium and COD is introduced to the anode chamber containing anaerobic bacteria. The bacteria produce free electrons by degrading the COD under anaerobic conditions. The free electrons are transferred to the surface of anode and they create a voltage between the anode and the cathode. Then, ammonium cations can be uptake by passing through the exchange membrane and attracting to the cathode [21]. Although, the membranes are expensive and some limitations based on irreversible reactions in anode and cathode chamber severely affect the performance of this method [22], energy saving and sludge minimization are the main advantages of this method [23]. Nevertheless, the application of this method has been mainly limited to research scale.

2.4. Physical separation methods

2.4.1. Ammonia stripping

Ammonia stripping is a desorption process used to reduce the ammonia concentration in wastewater. In this process, some alkaline substances such as lime are added to the wastewater system, to increase the pH to 10.8 - 11.5 range. In this pH range, ammonium ions are converted to dissolved ammonia following the reaction below.



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Air and the wastewater are injected through a tower to transfer ammonia gas from liquid to gas phase. Then an air stream containing ammonia gas enters the atmosphere from the top of the tower while the wastewater is being discharged from the bottom. [24].

In comparison with other techniques this method has the advantages listed below:

- It is unaffected by wastewater fluctuation under the steady state pH and air temperature.
- No backwash is created and no regeneration is required.
- It is not affected by toxic compounds which can impede the performance of biological system.
- Ammonia stripping can be applied for selected ammonia removal since it is a controlled process.

On the other hand, there are some limitations restricting its application consisting of:

- High energy and maintenance are required to re-pump the water to the stripping tower.
- The efficiency of ammonia stripping could be significantly affected in cold conditions because of the effect of temperature on distribution of ammonia species.
- Discharging the ammonia to the atmosphere results in air pollution
- This method just reduces the concentration of ammonium ions in wastewater. It means that it is not applicable for nitrite and organic nitrogen removal.
- Noise problems
- The addition of lime to control pH can create operation and maintenance concerns because the high pH of wastewater may damage the wood packing of the stripping tower [24].

2.4.2. Membrane distillation

Membrane distillation has been known as an efficient method for the removal of volatile compounds such as ammonia. It has been used in some industrial applications to remove undesired impurities from water [25, 26], however, it cannot be used in a large-scale operation [27]. Two different thermal sides associated with ammonia removal consist of the feed water tank (hot side) and the permeate tank (cool side) [28].

In this technique, a microporous hydrophobic membrane is employed to separate vapor molecules of ammonia as a result of a thermal gradient between hot and cold side. The hydrophobicity of the membrane prevents liquid phase to pass through the membrane's pores. Therefore, the concentration and temperature differences between two sides of the membrane, creates a pressure gradient, which forces ammonia gas molecules to migrate from feed side to the permeate side [29]. Depending on the configuration of membrane distillation, the ammonia molecules existed in permeate side are either condensed or removed from the system [30-32].

The major benefits of this approach are:

- To achieve a pure product
- Has energy efficiency
- There are no chemical demands
- Has simple and versatile membrane structure

And the main drawbacks are:

- High initial cost
- Down performance with time
- Sediment clogging

- Reduce power penetration in the effect of sediment [33].

2.4.3. Microwave radiation

Recently, few studies have been performed on ammonia removal by microwave radiation. The mechanism of remediation process occurs through two main pathways.

- Non-thermal process which is related to the biological, chemical, and physical behavior of a system.
- Thermal process in which the energy of microwave can be converted to heat by an adsorption process.

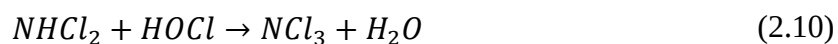
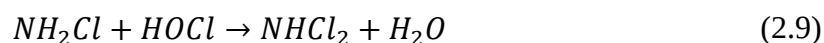
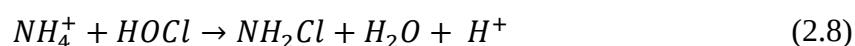
According to the literature, pH and temperature have significant effects on the efficiency of the process. In this method first by increasing the pH of the solution, most of the ionized ammonium converts to unionized ammonia at pH of greater than 9. Then, the energy of microwave can be adsorbed by water molecules and other polar molecules and resulted in heat generation in the system. Subsequently, increasing the temperature accelerates the molecular motion rate in the solution and provides favorable condition for free ammonia molecules to diffuse from the system in the form of ammonia gas [34].

Ammonia uptake by microwave is fast and efficient removal with removal percentage of above 95%. But, due to high energy demand, this method is not economical for large scale applications. In addition, the glass tubes used in this research were not sufficiently tolerant to the high temperature tested. Therefore, there are extra costs associated with replacing the glass tubes frequently [35].

2.5. Chemical methods

2.5.1. Breakpoint chlorination

Oxidation of ammonium by chlorine has been known as the breakpoint chlorination method. Equations 2.6 to 2.8 represent the whole process. When chlorine is added to the wastewater, it reacts with water molecules and produces hypochlorous acid. Then, hydrochlorous acid reacts with ammonium ions and chloramine will be generated. At last, chloramine reacts with hydrochloride acids and the final product will be nitrogen gas.



In this process, chlorine addition to the system is continuous until passing the "breakpoint" which is determined by observing the formation of free chlorine in the system [36]. The main drawback of this method is that a large amount of chlorine is required for ammonia oxidation [14]. This method has been mainly used at research scale and there are no reports of its common industrial application for ammonia removal.

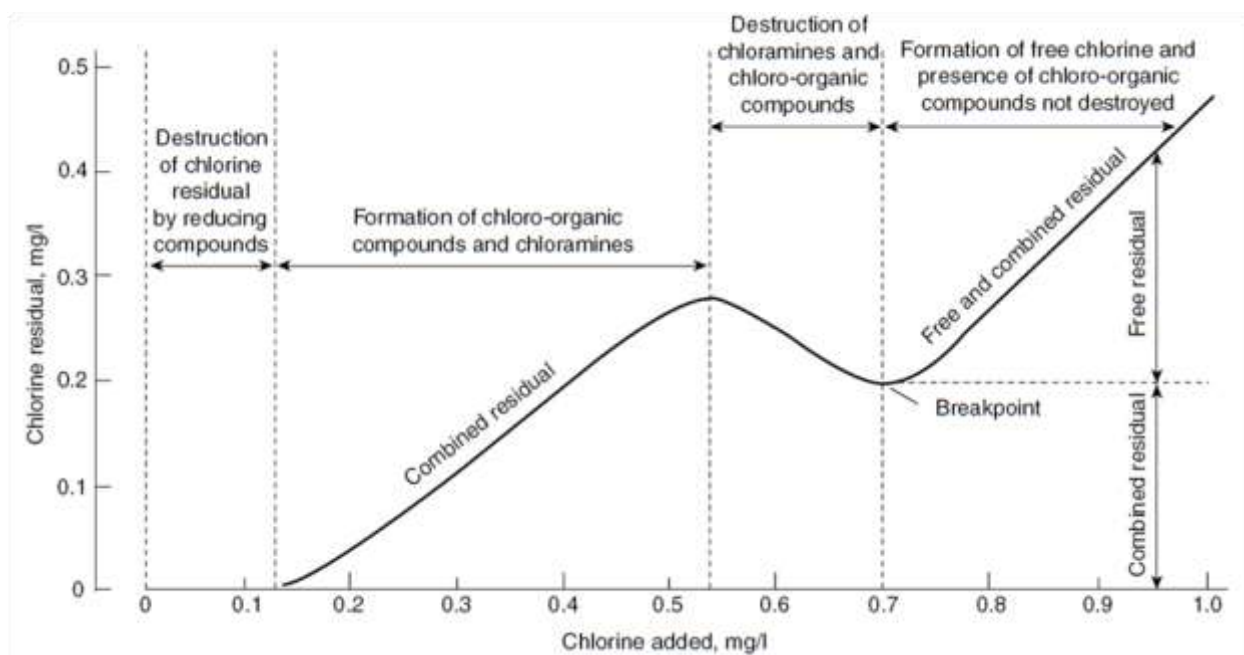


Figure 2.2. Typical curve for breakpoint chlorination [37]

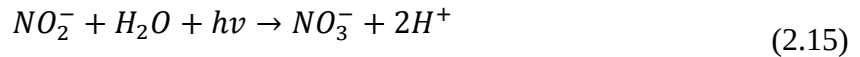
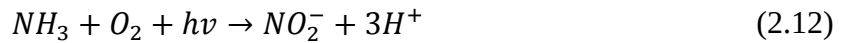
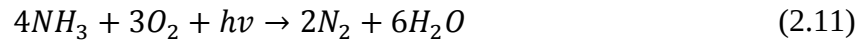
2.5.2. Electrochemical oxidation of ammonia

Chemical oxidation of ammonia by passing an electric current through a solution containing ammonium ions is called electrolysis [21]. The efficiency of this process is a function of many factors such as electrode composition, current density, ion concentration, and pH [38, 39]. Platinum and other noble metals and alloys are usually considered as the most common anode materials in this process [21]. This method is usually used to remove ammonia nitrogen from wastewaters containing high concentrations of ammonia nitrogen (0.1 M or greater) [39, 40], but, high energy demand is the main limitation of electrochemical removal of ammonia [41] and it has been mainly used at research scale.

2.5.3. Photocatalytic oxidation

In photocatalytic oxidation of ammonia, first TiO_2 is activated by UV light. When the surface of TiO_2 adsorbed sufficient energy, an electron in the valence band is promoted to the conduction

band resulting a charge separation on the surface of TiO₂. Then, charge transfer will occur if the recombination of negative and positive charges is not fast enough. This fact facilitates the redox reactions in which ammonia can be oxidized either directly (Equation 2.10 to 2.14) [42] or indirectly by producing active chlorine to oxidize ammonia [43].



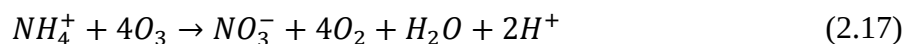
Many factors such as the oxygen concentration, the initial total nitrogen concentration, pH, the intensity of UV irradiation, the activity of different TiO₂ photocatalysts, the concentration of suspended catalyst, and the salinity play vital roles in efficiency of the process [21]. The most significant benefit of this method is that titanium dioxide (TiO₂)-based photocatalytic oxidation is an inexpensive, stable and nontoxic catalyst [44]. According to Abdel-Maksoud, 4%–6% of total solar radiation can be counted as UV radiation and TiO₂ Photocatalysis uses only UV radiation which can be a demerit for this method [45]. This method has been mainly used at research scale and there are no reports of its common industrial application for ammonia removal.

2.5.4. Ozonation

Depletion of dissolved oxygen is one of the significant environmental problems associated with the presence of ammonium ions in the water bodies in accordance with Equation 2.15.



Singer and Zilli in 1974 suggested ozonation as an applicable treatment method for eliminating this problem. In this process ammonium are converted to nitrate as a result of reacting with ozone (Equation 2.16) [46].



During the last decades, many studies have been done on the application of ozonation for ammonia removal from liquid phase, [47-49] however, it's not gone beyond the research scale. Lin and Wu, in a comparative study between the performance of ozonation and ion-exchange process, claimed that the ozonation process is only able to partially remove ammonia from aquatic solution even under its optimal conditions (at pH above 8). While, the ion exchange resins were able to efficiently remove residual ammonia at pH of below 7 [50].

2.5.5. Ultrasonic irradiation

The mechanism of ammonia nitrogen elimination by sono-chemical treatment method can be explained by the fact that ammonia molecules enter the cavitation bubbles and transform to nitrogen and hydrogen molecules [51].

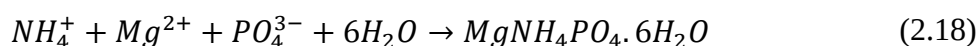
By increasing the height of solution containing ammonia nitrogen, the penetration of ultrasound on the solution will be limited resulting in decreasing the efficiency of process. Therefore, it is necessary to optimize the height of reactor to reach the optimum removal efficiency [52].

Since there is no need to add any additives to the system, there are no byproducts generated which should be concerned about. In contrast, this technology is only feasible on a small scale because of its high energy demand and it's not gone beyond the research scale [53].

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2.5.6. Chemical precipitation

Chemical precipitation consists of formation of a separable solid substance as a result of adding a precipitant substrate to a clear solution. Struvite (ammonium magnesium phosphate) is the most common precipitant used for ammonium precipitation according to Equation 2.17 [21].



There is a lag between solid formations and introducing the suitable molar ratio of precipitant to the solution called induction period. Induction time is a function of supersaturation ratio of the precipitant and pH of the solution [21]. At high supersaturation ratios, due to the high ion concentration homogenous nucleation occurs. In contrast, heterogeneous nucleation occurs when supersaturation ratio is low. Because, at low supersaturation ratio, the impurity in water becomes considerable compare to the amount of ammonium cations and this fact may affect the crystalline formation [54, 55]. Besides, pH adjustment is necessary in this process because increasing the pH decreases the solubility of struvite and the lowest solubility can be obtained at pH of over 10 [56].

2.5.7. Adsorption/Ion-exchange

In recent years, adsorption/ion-exchange process has been widely considered as a method for ammonium removal from wastewater due to the fact that it represented many unique properties such as high treatment capacity/removal efficiency, low cost and fast kinetics. The most popular ion-exchangers/adsorbents for removing ammonium ions from aquatic solution are zeolites [57], polymeric resins [58, 59], and activated carbon [60].

The crystalline structure of zeolite is formed based on three components including silicon, aluminum, and oxygen with a three dimensional framework and a negatively charged lattice.

This structure gives zeolite a large internal surface area. Silicon has the highest oxidation state of +4 while aluminum has +3. Whenever one atom of silicon is replaced by one atom of aluminum an extra cation, such as hydrogen, is required to balance the negative charge of the highly porous framework. Presenting hydrogen in the structure of zeolites creates some potential acid sites which depend on the concentration of aluminum in the crystalline lattice. This acidic feature makes zeolite an active adsorbent [61]. Several studies have reported on ammonium ions removal by different kinds of zeolite [62, 63]. Zhang et al. reported the application of zeolite synthesized from fly ash by a fusion method for removing ammonium [64]. In their latter study, they also investigated the efficiency of zeolite synthesized from low-calcium and high-calcium fly ashes in ammonium removal [65]. Huang et al., Du et al., and Lei et al. used natural Chinese zeolite as an ion exchange for ammonium ions [66-68]. Karadag et al. studied the kinetic and equilibrium isotherm of ammonium exchanging on natural Turkish clinoptilolite zeolite [69]. Wang et al. modified Chinese natural clinoptilolite zeolite and investigated the effects of metal ions in ammonium ion exchange capacity [70]. Vesileva and Viokova reported ammonium ion removal by Bulgarian clinoptilolite zeolite [71].

A solid or highly viscous substance of plants which can be easily converted to polymers called resin. Resins usually are composed of some organic compounds and most of them have a high proportion of acids. These acidic active sites make them as efficient adsorbents for many contaminants such as ammonia. Ding and Sartaj studied the ability of ion-exchange resin for ammonia removal from aqueous solution. They reported the optimum capacity of 28.78 mg/g for Amberlite resin in TAN removal, at pH = 6 and initial TAN concentration of 3000 mg/L. [59]. In another study, Yong et al. investigated the thermodynamic, isotherm, and kinetic of two different resins in ammonia uptake. They claimed that the adsorption of ammonia onto both of the resins

are spontaneous with endothermic reactions which follow Langmuir isotherm and pseudo-second order kinetic model [72]. Narbaitz and Sartaj applied two zeolites (natural clinoptilolite and SIR-600 modified clinoptilolite) and three synthetic resins (Purolite SSTC60, Amberlite IR120 Na and Bojie BC121 H) to remove ammonia from a mining wastewater. They reported that for the single component system the resins showed higher capacity for ammonia uptake than zeolites. While, for the mining wastewater due to the presence of competing ions, such as K and Ca, the performance of zeolites was higher than resins [58].

Activated carbon is a form of carbon with small and low volume pores which creates high surface area available for adsorption. Long et al., studied the performance of activated carbon (AC) in ammonia uptake from aqueous solution with the Langmuir maximum capacity of 17.19 mg/g [60]. The effect of surface chemistry and the amount of oxygen groups on the surface of activated carbon in the removal of ammonia was investigated by Gonçalves et al., using a modified resin-based activated carbon. They reported high improvement in the adsorption behavior at room temperature by modification of the original activated carbon with nitric acid, that is, the incorporation of oxygen surface groups [73]. Niu et al., recently studied the effects of backwashing on granular activated carbon with ammonium removal potential in a full-scale drinking water purification plant. They reported 12% improvement in the ammonium removal after backwashing [74].

In recent decade, the appearance of graphene has provided researchers a new promising material family for contaminant removal from aquatic solutions.

2.6. History of Graphene

In the recent decades, the appearance of graphene has provided researchers a new promising material family for contaminant removal from aquatic solutions. Carbon has three allotropes

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including amorphous carbon, graphite, and diamond [75]. Graphite is formed when sedimentary carbon compounds reduce during metamorphism process [76]. Graphite can be classified into two main groups including natural graphite and synthetic graphite, each of them representing special properties which are suitable for certain applications. Graphite can be naturally found in three forms of vein, amorphous, and flake graphite [77].

Mineral graphite is usually found in different regions of the world including Asia, South America and some parts of North America. Graphite's structure is very similar to diamond's chemical bonds. The only difference between them is that graphite has two dimensional lattice bonds, while diamond contains three dimensional lattice bonds. This means that each atom in each graphite layer has weaker intermolecular bonds in comparison with the one in diamond's structure. Therefore, the layer of graphite can slip through each other and this makes graphite to be a soft material [75].

In 2004, two scientists from University of Manchester, Professor Andre Geim and Professor Konstantin Novoselov, discovered one atomic layer of graphite in which a layer of carbon atoms bonded together in a hexagonal or honeycomb lattice. They named this material as Graphene and in 2010 they received the Nobel Prize in physics for their breakthrough discovery [78, 79].

Although among different carbon compounds graphite shows some unique properties such as high stability and electron conductivity, graphene's excellent features exceed those of graphite. For instance, it is common to use graphite in the manufacturing of steel to increase its strength but due to the fact that it is not hard enough, it cannot be used as a main structural material. In contrast, graphene is the strongest material ever found. It is estimated that it is more than 300 times stronger than A36 structural steel and more than 40 times stronger than diamonds [80]. Moreover, graphene shows much higher electron conductivity than graphite, because, it is much

easier for photons while passing along the planes than when they are passing through the planes. Its electron conductivity is as high as coppers. It is also the best heat conductor. These promising features appeal the scientist's interests to study the potential applications of graphene based materials for different industries [81-85].

2.7. Fabrication of Graphene

In recent years, various methods have been proposed to fabricate graphene, which can be categorized into two main groups: bottom-up and top-down techniques [86]. In bottom-up technique, including Chemical Vapor Deposition (CVD) and Epitaxial growth covalently 2D networks, are built up through chemical reactions. Although the graphene manufactured through bottom-up methods represents high quality and small number of defects, it is not economical to produce it in a large scale [87, 88]. Thus, mechanical exfoliation of graphite in the liquid phase, which is placed in the top-down class, has been presented as an alternative for bottom-up techniques to produce graphene in a large scale at an extremely low cost [86, 89, 90].

2.7.1. Chemical Vapor Deposition (CVD)

As shown in Figure 2.3, the process for creating CVD graphene consists of two steps. First, some carbon containing gases are fed into a reactor chamber in which hydrocarbon precursors decompose to form carbon radicals on a heated metal substrate. Then in the next phase a coating of graphene is created on the surface of the metallic film. The metal substrate plays a vital role in this process. First of all, it keeps the energy barrier lower in the system, as a catalyst. Secondly, it affects the quality of graphene generated in the reactor. Also, it helps to grow the graphene layer on its surface [87].

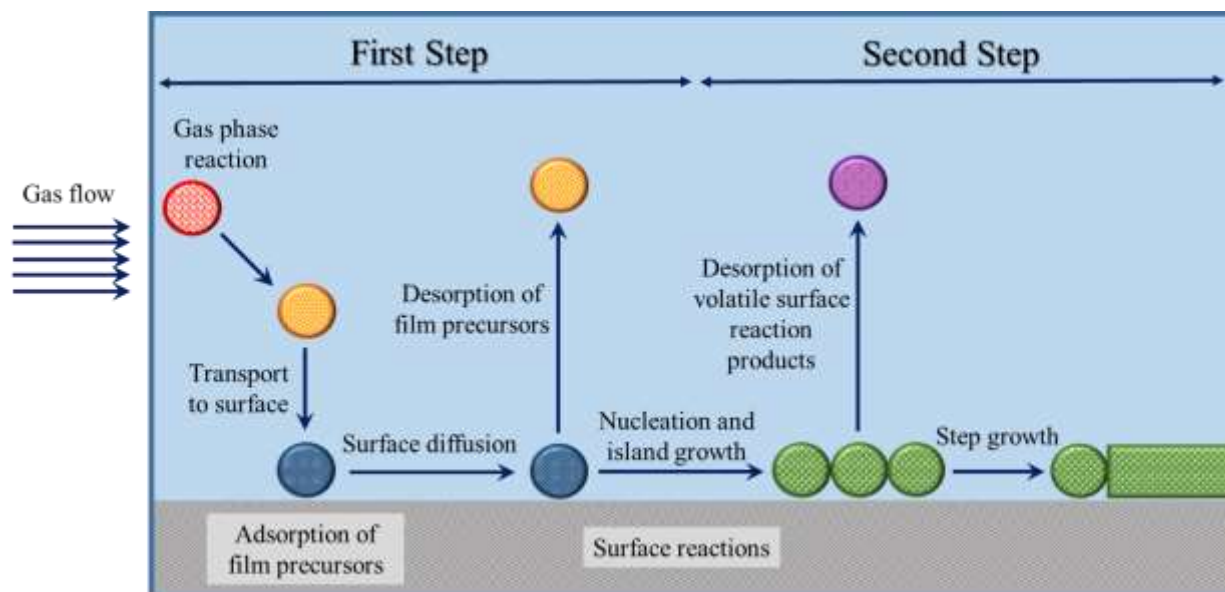


Figure 2.3. Schematic illustration for Chemical Vapor Deposition (Adopted from [91])

CVD is a general form of epitaxial growth which is defined as growing a crystalline layer of one mineral on a crystalline substrate. The main difference between epitaxial growth and Chemical Vapor Deposition is that CVD can be applicable for deposition of almost any type of material-metal, insulator, and semiconductors while epitaxial growth is just suitable for crystalline materials.

2.7.2. Mechanical exfoliation

The main idea in exfoliation process is based on peeling bulk graphite layer by layer to reach the monolayer of graphene. Figure 2.4 illustrates different types of single layer of carbon which are formed by exfoliating multilayer graphite.

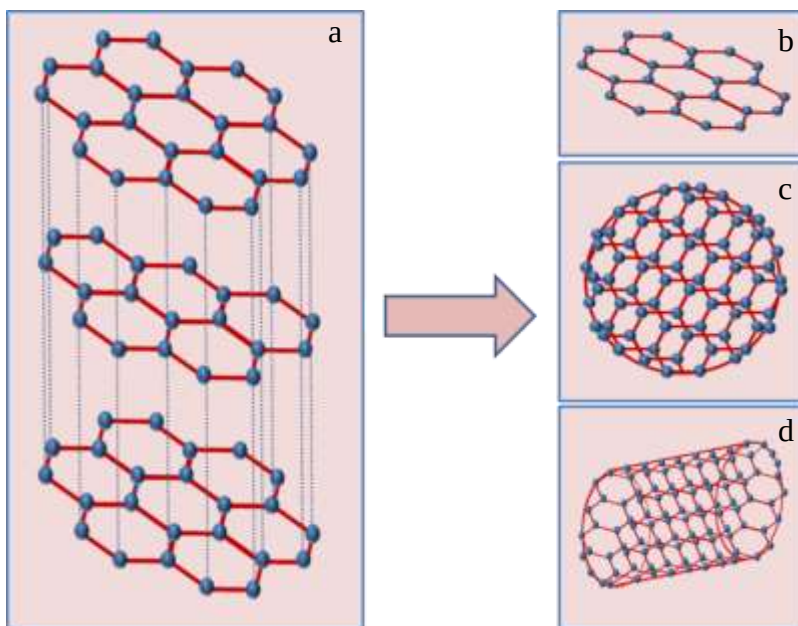


Figure 2.4. Various forms of carbon: (a) Graphite; (b) Graphene; (c) Bucky ball; (d) Nanotube [92]

Generally, two major types of mechanical routes can be followed to overcome the Van der Waals attraction between adjacent graphene flakes, normal force and shear force (Figure 2.5). According to these forces mechanical exfoliation's techniques are classified into four fundamental groups including micromechanical cleavage, sonication, ball milling, and fluid dynamic.

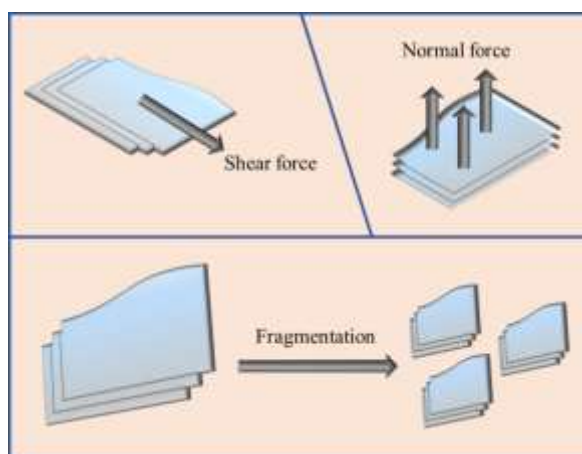


Figure 2.5. Various types of forces associated with mechanical exfoliation of graphene [86]

Micromechanical cleavage of HOPG (Highly Ordered Pyrolytic Graphite) is the primary method to produce graphene. In this procedure a normal force exerts to HOPG surface by applying a scotch tape on its surface. Repeating the process for several times makes graphite thinner and thinner until one-layer of graphene is obtained. The most important disadvantage of this method is that it can be utilized just for generation of graphene in a small scale. In other words, it is impossible to industrialize this method due to the fact that it is extremely labor intensive and time consuming. To eliminate the drawbacks of this method several advanced cleavage methods such as three- roll mill machine with a polymer adhesive and a diamond lathe-like set up for cutting the layers of graphite have been proposed by Jayasena et al. [93], and Chen et al. [94], respectively.

Sonication method, which is the most popular technique for graphene's fabrication, has three main steps including dispersing graphite powder in a specific organic solvent, such as N, N-dimethylformamide (DMF) and N-methylpyrrolidone (NMP), followed by sonication and centrifugation to separate graphene from the final solvent. Finally, with the assistance of characterization images, such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM), the differences between primary graphite powder and the monolayer graphene obtained from this process can be proved. In order to produce more graphene with better quality, many researchers have contributed by modifying this method by adjusting some parameters, such as sonication time, initial graphite concentration, adding suitable surfactant and polymers, mixing organic solvents together, adjusting temperature and pH in the different steps of graphene generation [86, 95].

In the ball milling technique, there are two kinds of forces associated with mechanical exfoliation of graphene to produce graphene powder. The primary force is shear force and the secondary one is vertical force exerted on the surface of graphite layers by the milling balls through the rolling action [86, 96].

Aside from the above methods, fluid dynamics is introduced as an efficient technique to exfoliate graphite flakes by producing shear forces with moving the liquid phase repeatedly at different positions. Different ways can be applied to create shear forces in order to produce the separated graphene's layers including vortex fluidic film, pressure driven fluid dynamics, and mixer driven fluid [86].

2.8. Graphene Oxide (GO) and reduced Graphene Oxide (rGO)

Graphene shows high potential for being used as an ideal basis for oxygen containing functional groups, such as hydroxyl, carboxyl, and epoxy groups, to form graphene oxide (GO) or reduced graphene oxide (rGO). The main properties of these three materials are summarized in Table 2.1. It can be seen from Table 2.1, both GO and rGO are hydrophilic with some oxygen functional groups on the surface, hence support greater adsorption than pure Graphene. Also, C:O ratio represents the amount of oxygen functional groups on the surface of the materials [97].

Table 2.1. Different features of Graphene, GO, and rGO [97]

Properties	Graphene	GO	rGO
C:O ratio	No oxygen	2-4	8-246
Electron conductivity	10000-50000	Insulator	0.05-200
Fabrication method	Graphite exfoliation Chemical Vapor Deposition Epitaxial growth	Oxidation and exfoliation of graphene	Reduction of GO
Functional groups	No functional groups	Hydroxyl Carboxyl Epoxy	Hydroxyl Carboxyl Epoxy
Production cost	High	Low	Low
Color	Black	Brownish	Black
Nature	Hydrophilic	Hydrophilic	Hydrophilic

2.9. Synthesis of Graphene Oxide

Some properties of graphene-based materials, like size, shape, and morphology, play a key role in its application [98, 99]. Therefore, scientists have been looking for an efficient synthesis method not only in order to obtain scalable amounts of this material but also to have a better control on the characteristics of the material.

Brodie was the one who first introduced graphene oxide chemistry by oxidizing natural graphite with KClO_4 and HNO_3 [100, 101]. Later, many other chemists such as Staudenmaier, Hofmann and Frenzel, Hamdi and Hummers tried to improve the synthesis method by utilizing H_2SO_4 , HNO_3 , and KClO_4 [102]. Finally, Hummers and Hoffman reported the easiest way to make graphene oxide. They used H_2SO_4 and KMnO_4 as oxidizer to oxidize the surface of graphene. This method has been known as the modified Hummers method [97, 103]. Six years after modification of Hummer's method, a new technique was introduced as the Improved Hummer method [104]. The only difference between the mentioned methods is the oxidizer agents used to

exfoliate graphene sheets. Among all these methods, improved Hummer method has been recognized as the most efficient and ecofriendly way to produce graphene oxide due to generating less toxic materials [104-106]. For more clarification all the oxidizing agents used in different methods are summarized in Table 2.2.

Table 2.2. Different synthesis method for graphene oxide [107]

Method	Year	Oxidizing agents	C:O ratio
Brodie	1859	KClO ₃ HNO ₃	2.16, 2.28
Staudenmaier	1898	KClO ₃ (or NaClO ₃) HNO ₃ H ₂ SO ₄	1.85
Hummers	1958	NaNO ₃ KMnO ₄ H ₂ SO ₄	2.17, 2.25
Modified Hummers	2004	NaNO ₃ KMnO ₄ H ₂ SO ₄	1.8
Improved Hummers	2010	H ₂ SO ₄ H ₃ PO ₄ KMnO ₄	NA

The procedure of Chemically Derived Graphene Oxide (GO) and then reduced Graphene Oxide (rGO) from Graphite has three main steps. First step contains treating natural graphite's flakes with strong acids, such as sulfuric acid, as an oxidizer to remove an electron. The Hummers and Hoffman's method has been used as the most common technique to produce graphene oxide. In this method a combination of sulfuric acid, sodium nitrate, and potassium permanganate are employed to oxidize the graphite. However, recent studies prove that the oxidation efficiency of graphite can be boosted by increasing the dosage of potassium permanganate in the acid mixture. In the second step, by dispersing and stirring the oxidized compounds in water, graphite oxide is

turned into graphene oxide. In this process, the graphite oxide's layers are completely separated from each other and change into graphene oxide. Aside from stirring, sonication is introduced as a time-efficient way to exfoliate graphite oxide's layers and convert it to graphene oxide. However, this method may damage the graphene's flakes. The last step involves the conversion of graphite oxide to reduced graphene oxide through chemical, thermal, or electrochemical reduction. Although the most scalable way to produce graphene oxide is chemical reduction, the products obtained from this process have been shown to have lower surface area and electron conductivity. On the other hand, rGO generated as a result of thermal reduction have been presented higher surface area but the graphene structure is damaged through heating process when temperature increases to around 1000 °C. In the most recent studies, electrochemical reduction has been introduced as the most effective way to produce reduced graphene oxide and with this method all the foregoing draw backs have been eliminated [108].

2.10. Application of Graphene base materials in wastewater treatment

Annually many organic contaminants discharge to the environment without meeting the standard criteria. Industrial dyes [81], heavy metals [83], pharmaceuticals [97], phosphate [109, 110], and ammonium are examples of main pollutants of concern. These pollutants are serious threats for both aquatic life and human's health. Therefore, finding an effective way to remove them from wastewater before discharge has attracted scientists' attention. In the recent decades, by appearance of graphene into the scientific world, a new door has been opened to the researchers to apply graphene based material as a promising contaminant removal agent from aquatic solutions. The oxygen functional groups make graphene oxide as a promising adsorbent for water purification application due to the fact that they form considerable active sides on the surface of graphene sheets [111-114].

2.10.1. Dyes removal

Guo et al. successfully reported a facile method for preparation of GO/polyethylenimine (PEI) hydrogels and its application in methylene blue (MB) and rhodamine B (RhB) removal. PEI has abundant amine group which can form hydrogen bonds with GO and results in increasing the active sites on GO surface for adsorption of contaminants [81]. GO functionalized by Polyvinyl Alcohol Hydrogels (PVA) was applied to remove MB as a cationic dye [115]. According to some of the scientific reports, GO can be used for decolorization of MB [111, 112]. Also, Travlou's group examined the application of GO/chitosan composite to successfully remove Reactive Black 5 from water [116]. The adsorption capacity of three carbonaceous materials including activated carbon (AC), graphene oxide (GO), and multi-walled carbon nanotubes (CNTs) modified by nitric acid for removal of MB were investigated Li et.al. AC showed the highest adsorption capacity of 270.27 mg/g followed by GO with the capacity of 243.90 mg/g, and finally CNTs with just 188.68 mg/g [117]. GO has been examined as an efficient adsorbent for cationic dyes due to the high surface area and the negative sites available on their surfaces. While, rGO provided active sites for adsorption of dyes [118]. In 2012, Fan et al. created a suitable recipe to synthesize magnetic β -cyclodextrin–chitosan/graphene oxide as a promising adsorbent for dyes. Considering to high surface area of graphene oxide, hydrophobicity of β -cyclodextrin, the abundant amino and hydroxyl functional groups of chitosan, and the magnetic property of Fe_3O_4 , this adsorption showed well performance with the maximum capacity of 84.32 mg/g for cationic dye (MB) removal [119]. In many studies the adsorption performances of magnetic/ graphene oxide and magnetic/reduced graphene oxide were reported for dye removal [120-124]. Adsorption characteristics of the adsorbents that have been reported for dye removals are summarized in Table 2.3.

Table 2.3. Application of graphene based materials for dye removal

Adsorbent	Dye	q_e (mg/g)	Kinetic	Isotherm	Ref
GO/polyethylenimine	Methylene Blue	334.448	Pseudo-second-order	NA	[81]
GO/polyethylenimine	Rhodamine B	131.926	Pseudo-second-order	NA	[81]
Poly (vinyl alcohol)/GO	Methylene Blue	NA	Pseudo-second-order	Freundlich	[115]
GO	Methylene Blue	714	NA	NA	[111]
3D GO	Methylene Blue	397	Pseudo-second-order	NA	[112]
3D GO	Methyl Violet	467	Pseudo-second-order	NA	[112]
GO/Chitosan	Reactive Black 5	277	Brouers-Sotolongo fractal	Langmuir–Freundlich	[116]
Activated Carbon	Methylene Blue	270.27	Pseudo-second-order	Langmuir	[117]
GO	Methylene Blue	243.90	Pseudo-second-order	Langmuir	[117]
Carbon Nanotubes	Methylene Blue	188.68	Pseudo-second-order	Langmuir	[117]
GO	Methylene Blue	17.3	Pseudo-second-order	Langmuir	[118]
GO	Methyl Violet	2.47	Pseudo-second-order	Langmuir	[118]
GO	Rhodamine B	0.54	Pseudo-second-order	Freundlich	[118]
rGO	Orange G	5.98	Pseudo-second-order	Langmuir	[118]
Magnetic β -Cyclodextrin–Chitosan/GO	Methylene Blue	84.32	Pseudo-second-order	Langmuir	[119]
Magnetite/rGO	Rhodamine B	4.23	Pseudo-second-order	Freundlich	[120]
Magnetite/rGO	Malachite Green	6.47	Pseudo-second-order	Freundlich	[120]
MnFe ₂ O ₄ /rGO	Methylene Blue	34.72	Pseudo-second-order	NA	[121]
MnFe ₂ O ₄ /rGO	Rhodamine B	22.52	Pseudo-second-order	NA	[121]
Magnetic/GO	Methylene Blue	64.23	Pseudo-second-order	Langmuir	[122]
Magnetic/GO	Orange G	20.85	Pseudo-second-order	Langmuir	[122]
Fe ₃ O ₄ /rGO	Rhodamine B	44.4	Pseudo-second-order	NA	[123]
Fe ₃ O ₄ /GO	Neutral Red	171.3	NA	NA	[124]
Fe ₃ O ₄ /GO	Methylene Blue	167.2	NA	NA	[124]

2.10.2. Pharmaceuticals removal

The favorable adsorptive properties of GO have attracted the public interests to investigate its adsorption capacity on removal of a variety of pharmaceuticals [113, 125-127]. Nam et al. claimed that the adsorption capacity of GO for the removal of diclofenac and sulfamethoxazole can be considerably improved by sonicating the pristine graphene oxide. They also reported that by increasing the intensity of sonication the removal percentage for diclofenac and sulfamethoxazole increased from 34 to 75% and 12 to 30%, respectively [125]. In 2013, Kyzas et

al introduced a novel method to prepare graphite oxide functionalized with poly acrylic acid grafted with chitosan nanocomposite (GO/CSA) to remove pharmaceutical compounds from biomedical wastewaters. They found that the amine groups of dorzolamide are responsible to interact with the active sides on GO and CSA, while, the abundant carboxyl groups of GO/CSA nanocomposite intensify the adsorption capacity [128]. In a comparative study the adsorption capacity of reduced graphene oxide has been compared with single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), commercial graphene, and graphite. These adsorbents have been tested for the removal of three pharmaceutical and personal care products including ketoprofen, carbamazepine, and bisphenol. The maximum adsorption capacity of these contaminants on the surface of adsorbents followed the order of SWCNTs > rGO > MWCNTs > graphene > graphite [129].

Table 2.4. summarizes the adsorption capacity, isotherm, and kinetic model of different graphene based materials used for pharmaceutical contaminants removal.

Table 2.4. Application of graphene based materials for pharmaceutical removal

Adsorbent	Drugs name	q_e (mg/g)	Kinetic	Isotherm	Ref
GO	Atenolol	91.95	Pseudo-second-order	Langmuir–Freundlich	[126]
GO	Propranolol	58.94	Pseudo-second-order	Langmuir–Freundlich	[126]
GO	Tetracycline	370	Pseudo-second-order	Temkin	[127]
GO	Tetracycline	323	Pseudo-second-order	Langmuir	[113]
GO	Diclofenac	NA	NA	Freundlich	[125]
GO	Sulfamethoxazole	NA	NA	NA	[125]
Magnetite/rGO	Ciprofloxacin	18.22	Pseudo-second-order	Langmuir & Temkin	[130]
Magnetite/rGO	Norfloxacin	22.2	Pseudo-second-order	Langmuir & Temkin	[130]
GO/CSA	Dorzolamide	334	Pseudo-second-order	Langmuir–Freundlich	[128]
GO	Dorzolamide	175	Pseudo-second-order	Langmuir	[128]
CSA	Dorzolamide	229	Pseudo-second-order	Langmuir	[128]
Activated Graphene	Ciprofloxacin	194.6	Pseudo-second-order	Langmuir	[131]
Fe ₃ O ₄ /rGO	Tetracycline	NA	NA	Freundlich	[132]
SWCNT	Ketoprofen	91.5	NA	Dubinin–Ashtakhov	[129]
rGO	Ketoprofen	62.5	NA	Dubinin–Ashtakhov	[129]
MWCNT	Ketoprofen	25.3	NA	Dubinin–Ashtakhov	[129]
Graphene	Ketoprofen	15.3	NA	Dubinin–Ashtakhov	[129]
Graphite	Ketoprofen	1.97	NA	Dubinin–Ashtakhov	[129]
SWCNT	Carbamazepine	185	NA	Dubinin–Ashtakhov	[129]
rGO	Carbamazepine	115	NA	Dubinin–Ashtakhov	[129]
MWCNT	Carbamazepine	55	NA	Dubinin–Ashtakhov	[129]
Graphene	Carbamazepine	22.8	NA	Dubinin–Ashtakhov	[129]
Graphite	Carbamazepine	3.65	NA	Dubinin–Ashtakhov	[129]
SWCNT	Bisphenol	199	NA	Dubinin–Ashtakhov	[129]
rGO	Bisphenol	152	NA	Dubinin–Ashtakhov	[129]
MWCNT	Bisphenol	59.4	NA	Dubinin–Ashtakhov	[129]
Graphene	Bisphenol	26	NA	Dubinin–Ashtakhov	[129]
Graphite	Bisphenol	4.14	NA	Dubinin–Ashtakhov	[129]
Graphene	Aspirin	18.07	Pseudo-second-order	NA	[133]
Graphene	Caffeine	19.72	Pseudo-second-order	NA	[133]
Graphene	Acetaminophen	12.98	Pseudo-second-order	NA	[133]

2.10.3. Heavy metals removal

In recent years the foccus of many studieds were on the adsorption capacity of GO to remove different heavy metals from aquatic solutions[134, 135]. The application of GO in removing Zn²⁺ was investigated by Wang et al. They claimed that Zn²⁺ sorption on GO is exothermic and

spontaneous process in nature also the optimum dosage and pH for this process is 2 and 7 g/L, respectively. Different acids were applied to recover GO for reuse. The results indicate that the best acid for this purpose was hydrochloric acid [114]. In another study few-layered graphene oxide nanosheet was used to treat Cd(II) and Co(II) from wastewater[136]. Calcium alginate was employed for copper removal from synthetic wastewater. This study shows the adsorption capacity of calcium alginate will be improved from 42.7 to 60.2 mg/g by encapsulating it with graphene oxide[137]. Different graphene oxide composites such as Graphene oxide cross linked by ferric hydroxide[138], magnetic chitosan/GO[139], Magnetic cyclodextrin-chitosan/GO[140], Calcined graphene/MgAl layered double hydroxide (CG-MgAl-LDH)[141], magnetic graphene oxide[122], magnetite graphene oxide[142], and GO-TiO₂[143] were applied to adsorb various metal ions. Table 2.5 presents a summary on different heavy metals removed by graphene-based materials.

Table 2.5. Application of graphene based materials for heavy metal removal

Adsorbent	Metal	q_e (mg/g)	Kinetic	Isotherm	Ref
GO	Cu(II)	19	Pseudo-second-order	Langmuir	[134]
GO	Cu(II)	46.6	NA	Langmuir	[135]
GO	Zn(II)	246	Pseudo-second-order	Langmuir	[114]
Few-layered GO	Co(II)	106.3	NA	Langmuir	[136]
Few-layered GO	Cd(II)	68.2	NA	Langmuir	[136]
Calcium Alginate/GO	Cu(II)	60.2	Pseudo-second-order	Langmuir	[137]
GO/ferric hydroxide	As(V)	23.78	NA	NA	[138]
Magnetic chitosan/GO	Pb(II)	76.94	Pseudo-second-order	Langmuir	[139]
Magnetic cyclodextrin-chitosan/GO	Cr(VI)	67.66	Pseudo-second-order	Langmuir	[140]
CG-MgAl-LDH	Cr(VI)	172.55	Pseudo-second-order	Freundlich	[141]
Magnetic GO	Cd(II)	91.29	Pseudo-second-order	Langmuir	[122]
Magnetite GO	Co(II)	12.98	Pseudo-second-order	Langmuir	[142]
Magnetite rGO	As(III)	13.1	Pseudo-second-order	Langmuir–Freundlich	[144]
Magnetite rGO	As(V)	5.83	Pseudo-second-order	Langmuir–Freundlich	[144]
GO-TiO ₂	Zn(II)	88.9	NA	NA	[143]
GO	Zn(II)	30.1	NA	NA	[143]
GO-TiO ₂	Cd(II)	72.8	NA	NA	[143]
GO	Cd(II)	14.9	NA	NA	[143]
GO-TiO ₂	Pb(II)	65	NA	NA	[143]
GO	Pb(II)	35.6	NA	NA	[143]

2.10.4. Phosphate removal

In 2015, Tran et al. synthesized 3-dimensional graphene aerogels decorated with goethite (aFeOOH) and magnetite (Fe₃O₄) nanoparticles. They reported these materials had superior capacity for phosphate removal, up to 350 mg/g. They also noticed that pH could strongly affect the adsorption capacity [145]. Phosphate existed in water can be found in four different forms including H₃PO₄, H₂PO₄⁻, HPO₄²⁻, and PO₄³⁻ depending on pH [146]. They stated that maximum adsorption capacity was reached at lower pH, because, in lower pH the hydroxylation occurs on the surface of aerogel nanoparticles and makes it strongly positive. So, the electrostatics attraction between highly positive aerogel surface and phosphate anions boosts the capacity of adsorption [145, 147]. Additionally, according to a study performed by Jun et al. showed the

removal efficiency of phosphate by graphene oxide could be improved from 70% to 80% with assist of iron nano particles [148].

In another studies the adsorption capacity of phosphate by lanthanum oxide decorated graphene composite, graphene nanosheets supported lanthanum hydroxide, and lanthanum hydroxide doped onto magnetic reduced graphene oxide were investigated [149-151]. These studies claimed that coexistence of anionic species such as Cl^- , SO_4^{2-} , and NO_3^- in water had no significant effect on phosphate removal [149, 151].

Anionic contaminants can be adsorbed on adsorbent surface through specific or non-specific adsorption [152, 153]. The specific adsorption occurs when anionic contaminants were exchanged by hydroxyl groups (-OH) existing on the surface of adsorbent [152, 153]. While the non-specific adsorption associates with coulombic forces [153, 154]. Vasudevan et al. proved that the adsorption of phosphate on graphene was mainly specific adsorption and the thermodynamic results indicated that the adsorption reaction was a spontaneous, endothermic and irreversible process [153]. Sakulpaisan et al. improved the phosphate adsorption performance of graphene oxide by functionalizing it with titania through a sol gel process. They also reported that the removal efficiency improved by the appearance of sodium ions, because, Na^+ made the surface of adsorbent positively charged [155].

Batch and column adsorption experiments for phosphate removal by zirconia functionalized graphite oxide and reduced graphene oxide were investigated [109, 110]. The results revealed that phosphate removal was more favorable under acidic conditions. In addition, the adsorbent showed high stability in 11 consecutive adsorption desorption cycles [109]. Table 2.6 provides a summary of different graphene based adsorbents for phosphate removal.

Table 2.6. Application of graphene based materials for phosphate removal

Adsorbent	q_e (mg/g)	Kinetic	Isotherm	Ref
GN- α FeOOH	352	Pseudo-second-order	Freundlich	[145]
GN-Fe ₃ O ₄	311	Pseudo-second-order	Freundlich	[145]
3D Graphene-La ₂ O ₃	82.6	Pseudo-second-order	Langmuir	[149]
GNS-LaOH	41.96	Pseudo-second-order	Langmuir	[150]
GM@La	116.28	Pseudo-second-order	Langmuir	[151]
GO	89.37	NA	Freundlich	[148]
Graphene	89.37	Pseudo-second-order	Langmuir	[153]
T-F-GO	33.11	NA	Langmuir	[155]
Zr-GO	132	Pseudo-second-order	Langmuir	[109]
Zr-rGO	27.71	Pseudo-second-order	Langmuir	[110]

2.11. Summary and research gap

According to the previous studies, graphene base materials showed great potential for being an effective adsorbent to remove the wide range of contaminants from wastewater such as dyes, pharmaceuticals, heavy metals, and phosphate. However, limited studies have been reported so far to investigate the application of graphene base materials in TAN uptake from aqueous solution. Therefore, there is a need to study the performance of graphene based materials in TAN removal from wastewater.

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Chapter 3: Ammonia removal from aqueous solution by sodium functionalized graphene oxide: Isotherm, Kinetics, and Thermodynamics¹

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Abstract

Municipal, industrial and agricultural wastewaters contain high concentrations of nitrogen in the form of ammonia and ammonium ions. This nitrogen has a range of polluting effects and must be removed before discharge. Multiple methods are currently under investigation for the removal or capture of total ammonia nitrogen (TAN). TAN in aqueous media shows unique behavior making it necessary to study its interactions with potential adsorbents in detail. In this study, sodium functionalized graphene oxide (GO-Na) was used for TAN removal from aqueous media by ion exchange. Batch adsorption experiments were performed to investigate the adsorption capacity of GO-Na. The mechanism of adsorption was investigated using multiple models including Elovich and Intra Particle Diffusion models. The adsorption kinetics followed pseudo second order model. Experimental data was well described by a Langmuir isotherm model with a maximum adsorption capacity of 32 mg/g. The adsorption energies and thermodynamic parameters indicated weak interactions were dominant with an overall exothermic and

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spontaneous process. The weak interactions resulted from ion-exchange of sodium cation on the surface of GO with ammonium cations in the liquid phase, which also results in the easy regeneration of the adsorbent with NaCl which is a non-toxic, environmental friendly, and inexpensive salt in nature.

Keyword: Graphene Oxide, Ammonia, Adsorption, TAN Removal, Isotherms, Kinetics, Thermodynamics

3.1. Introduction

Ammonia (NH_3) is the most abundant nitrogen containing pollutant in the environment. It enters water resources through industrial, municipal, and agricultural discharges on a yearly basis. In aquatic chemistry, ammonia can be found in the form of ammonium cations (NH_4^+) and molecular ammonia (NH_3); the sum of these two forms is expressed as total ammonia nitrogen (TAN). The range and average of TAN in municipal wastewaters is reported to be 12 - 50 mg/L and 30 mg-N/L, respectively [1]. The major environmental concerns of ammonia include eutrophication [2], depletion of dissolved oxygen in water resources [3], and toxicity to fish and other aquatic species even at concentration as low as 0.2 mg/L [4]. In addition, TAN has several harmful effects on human skin, eyes, and the respiratory system [5, 6].

With the rapid growth of environmental awareness over the past century, many environmental standard limits were set to control the release of ammonia into the water bodies. Total Ammonia Nitrogen (TAN) toxicity is mainly related to dissolved ammonia in water bodies and the distribution of dissolved ammonia to ammonium cation is a function of two important factors; pH and temperature. US EPA has set two standard limits as acute and chronic limits to protect

the aquatic life based on pH and temperature. At pH of 7 and temperature of 20°C, the US EPA acute criterion and the chronic levels are 17 mg TAN/L and 1.9 mg TAN/L, respectively [7]. Methods proposed for TAN removal from wastewater include biological nitrification-denitrification process [8], air stripping [9], chemical precipitation [10], ultra-sonication and microwave [11], ion exchange and adsorption [12-22]. Adsorption is one of the viable technology for ammonia removal and its main advantages are simple and economical operation, less sludge production resulting in less disposal problems, and the potential for recovery of ammonium cations [23, 24]. The most widely use adsorbents and/or ion exchangers are zeolites [12-22], mesoporous silica materials [25, 26], and resins [27, 28]. Rat-Valdambrini et al. investigated the application of Arene-Sulphonic acid functionalized SBA-15 on ammonium cation removal from aquatic solution. They reported the maximum adsorption capacity can be reached at 5°C and it was estimated around 19 mg NH_4^+ /g of adsorbent [26]. Ding and Sartaj also optimized the operational conditions for TAN removal by zeolite [29] and resin [27] and compared the performances of these two ion exchangers. They claimed the optimum TAN uptake by a natural zeolite was 22.9 mg/g [29], while for resins it was 28.78 mg/g [30].

In the last decade, the appearance of graphene has provided researchers a new emerging family of materials for contaminant removal from aquatic solutions by incorporation of these new materials into a variety of technologies [31]. Graphene is defined as one atomic layer of graphite in which a layer of carbon atoms bonded together in a hexagonal or honeycomb lattice provides a light and highly functionalizable material [32]. Perhaps the easiest and more versatile way to functionalize graphene is by oxidation, where oxygen containing functional groups such as hydroxyl, carboxyl, and epoxy groups can be added to form graphene oxide (GO).

Previous studies reported on the performance of graphene based material for removing various wastewater contaminants such as dyes [33-37], pharmaceuticals [38, 39], and heavy metals [40-44]. In addition, recently many studies have investigated the application of graphene based materials for ammonia gas adsorption [45-48]. However, the adsorption capacity of graphene-based materials for TAN removal in aquatic media has not been previously reported. TAN in aqueous media shows unique binding and equilibrium behavior making it necessary to study its interactions with the absorbent in detail. In this study, graphene oxide was synthesized and further functionalized with sodium (GO-Na), and its capacity in adsorption of TAN from aqueous solution was investigated. The produced material was characterized and a full kinetic, isotherm, and thermodynamic study was performed to reach a better understanding of the adsorption behavior of TAN on GO-Na.

3.2. Experimental

3.2.1. Chemicals and materials

Synthetic graphite powder, -20+80 mesh, 99.9% (metals basis) was obtained from Alfa Aesar. Sulfuric acid (98%) and potassium permanganate were purchased from Anachemia. Phosphoric acid (85%), hydrochloric acid, and hydrogen peroxide (30%) were purchased from Fisher Scientific. Ammonia TNTplus Vials (HR 2-47mg/L NH₃-N) were purchased from HACH.

3.2.2. Graphene oxide synthesis by Improved Hummer's Method

Graphene oxide was prepared according to an Improved Hummer's Method at room temperature (24°C) [49]. In a beaker, 360 mL of H₂SO₄, 40 ml of H₃PO₄, 37 g of KMnO₄, and 7 g of graphite powder were mixed together with a stirrer for a week at room temperature. Due to the exothermicity of the reaction, the temperature of the suspension initially increased to 40°C and then slowly dropped back to room temperature. During this step, the color of the suspension was

initially purplish green and gradually turned to dark brown. After a week, the suspension became light brown, indicating that a high oxidation level had been achieved. Then, 2L of de-ionized (DI) water and 80 mL of H_2O_2 30% were added to the mixture to end the oxidation process. For safety and to control the temperature, water was added drop by drop and slowly. The resulting solution was centrifuged at 12,000 rpm for 15 min. Upon removal of the supernatant, the material was treated with 400 mL of HCl (1M) and put under stirring for 2 hr to remove all impurities. The mixture was centrifuged again at 12,000 rpm and the brown deposit was washed with DI water under filtration until pH of the solution reached 4. The resulting washed material is hereby labelled as graphene oxide (GO).

3.2.3. Sodium functionalized Graphene Oxide

1.5g of GO was added to 150 mL of NaOH (1M) at 40 °C and put under stirring for 30 min until the brownish GO completely turned to black. The suspension was centrifuged at 12,000 rpm and then mixed with 250 mL of NaCl (10%w) at room temperature and stirred for another 30 min in order to fully saturate all active sites with sodium. Finally, the mixture was centrifuged and washed with DI water until pH 9 was obtained. The resulting material was dried at room temperature and labelled GO-Na.

3.2.4. Material Characterization

Samples were characterized during the preparation process (GO and GO-Na) as well as after adsorption (GO-Na-N). Morphological structures of samples were examined by transmission electron microscopy (TEM) with a Tecnai Spirit TEM instrument. The Fourier Transform Infrared (FT-IR) spectra were collected on a Nicolet 6700 FT-IR spectrometer using an Attenuated Total Reflection (ATR) accessory. The spectra were recorded for suspended material in aqueous solution from 4000 to 400 cm^{-1} (128 co-added scans). Raman spectroscopy of three

samples was collected with a Thermo Scientific Raman Microscope. X-ray Photoelectron Spectroscopy (XPS) measurements were obtained on a Kratos AXIS UltraDLD 39-3061 using a monochromated Al source.

3.2.5. Adsorption Studies

A stock solution of NH_4Cl was used to study the adsorption properties of TAN by GO-Na. Batch-adsorption experiments were performed in 100 mL beakers magnetically stirred. The adsorption isotherms were obtained using NH_4Cl solutions with initial concentrations of 10-100 mg/L and an adsorbent dosage of 1 g/L, with each test replicated 3 times. A kinetic analysis was performed with intermediate TAN concentration (50 mg/L) and an adsorbent loading of 1 g/L, measuring TAN uptake as a function of time for 20 minutes at different time intervals. A thermodynamic investigation was performed by conducting adsorption tests with intermediate TAN concentration (50 mg/L) and adsorbent dosage of 1 g/L, under three different temperatures (7, 24, and 42 °C), results of which were used to calculate enthalpy and entropy parameters. The pH of all batch adsorption experiments were around neutral in which ammonia nitrogen is mostly in the form of ammonium cations. In all cases, after the adsorption experiments all the solutions were filtered through a PTFE (0.2 Micron) filter over vacuum.

TAN concentrations were measured using HACH Ammonia TNTplus Vials (HR 2-47mg/L $\text{NH}_3\text{-N}$) and a DR6000TM UV VIS HACH Spectrophotometer with RFID Technology according to the salicylate method (Method: 10205). The removal percentage (R%) and solid phase concentration (q_e in mg/g) were calculated as follow:

$$R\% = \left(\frac{C_0 - C_e}{C_0} \right) \times 100 \quad (3.1)$$

$$q_e = \left(\frac{C_0 - C_e}{W} \right) \times V \quad (3.2)$$

where C_0 and C_e (mg/L) are the initial and equilibrium concentration of TAN in solution, respectively, W (g) is the mass of adsorbent, and V (L) is the volume of solution.

To study the regeneration capacity, the used adsorbent for kinetic part was added to sodium chloride solution (10%w) and remained under stirring for 4 hr. Then, it was washed with DI water over vacuum filter. Finally, it was dried at room temperature and used for a subsequent cycle of adsorption tests with an adsorbent dose of 1g/L, initial TAN concentration of 50 mg/L, around neutral pH.

3.3. Results and Discussion

3.3.1. Adsorbent Characterization

The nature of the adsorbent was determined using typical characterization features for graphene oxide as reference. Figure 3.1 shows the Raman spectra for the synthesized GO, sodium functionalized graphene oxide (GO-Na) and the used GO-Na after adsorption (GO-Na-N). The characteristic graphite Raman spectrum is shown for comparison. The different forms of GO can be evaluated by the ratio of D to G bands in the spectra, which are related to the degree of disruption of the hexagonal network (D = defective, sp^3 or disordered carbon; G = sp^2 carbon). The as-produced GO shows a ratio of D to G bands at approximately 1 ($I_D/I_G = 1.0$). GO-Na shows an increase in the ratio ($I_D/I_G = 1.1$) emphasizing the additional disruption to the graphene network, and upon exchange with ammonium ions, the ratio remains at approximately that value.

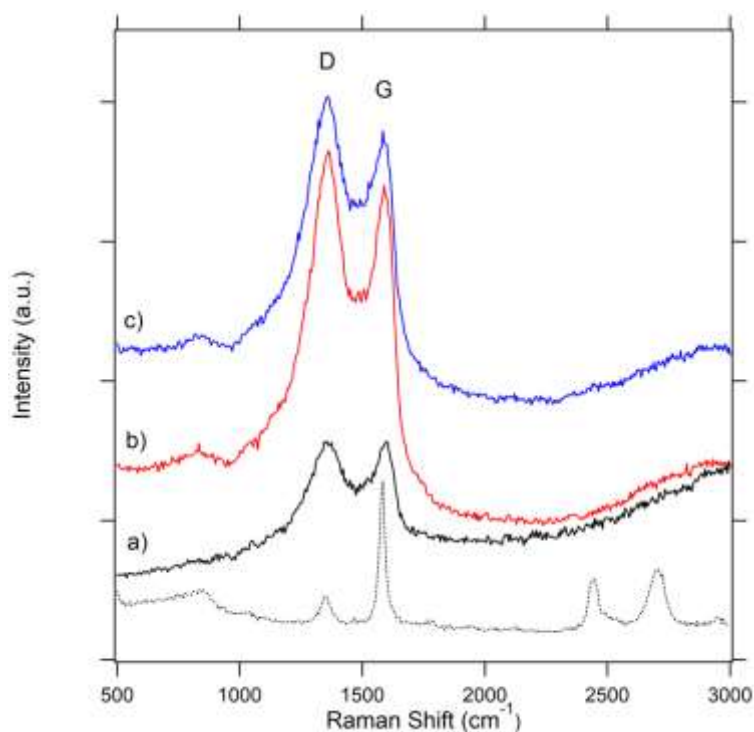


Figure 3.1. Raman spectra of a) GO; b) GO-Na; c) GO-Na-N. Characteristic D and G bands of graphene have been labelled. Dotted spectrum corresponds to graphite, for reference.

The actual functional groups present in the materials were explored by infrared absorption and photoelectron spectroscopy. Figure 3.2 shows the XP spectra for the three materials. Besides the expected carbon and oxygen peaks, GO contains traces of nitrogen. In the case of GO-Na, the typical peaks of sodium are seen in the spectrum. Upon utilization of the GO-Na for adsorption of ammonium, the exchange can be easily identified by the reduction of the sodium peaks and the increase in the nitrogen signal.

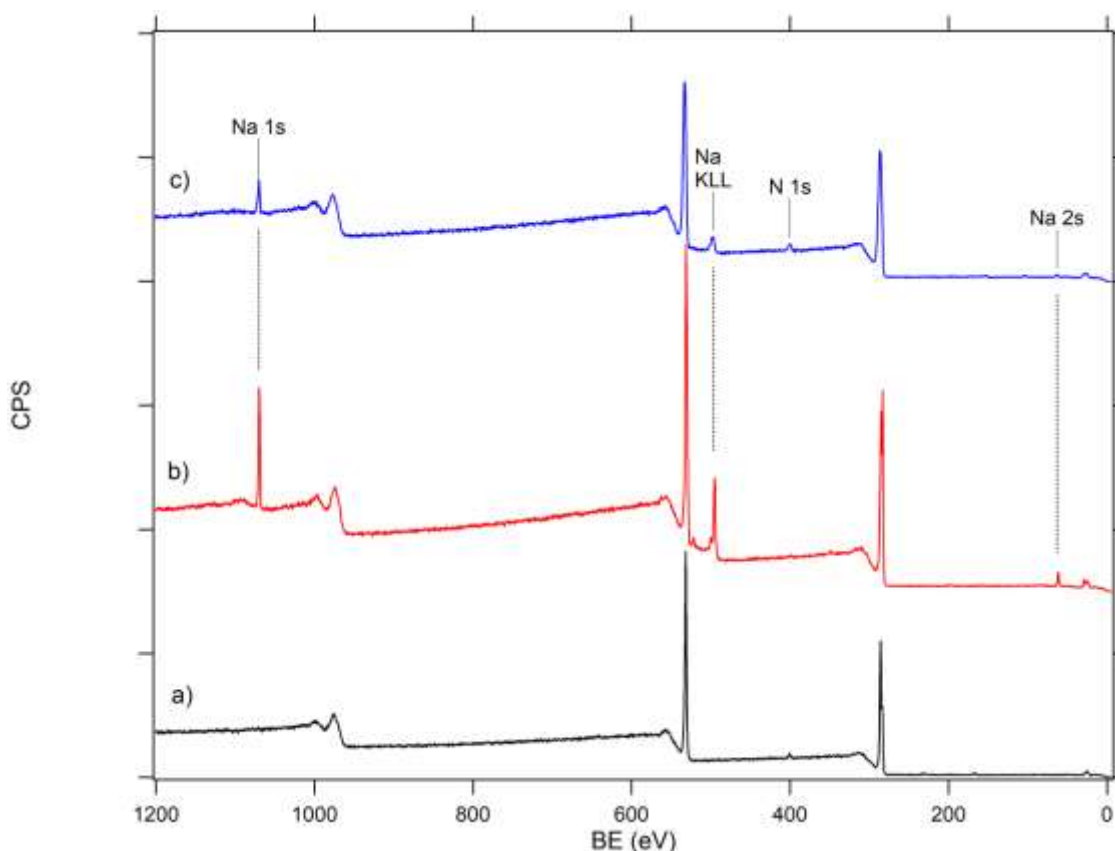


Figure 3.2. XPS surveys for a) GO; b) GO-Na; c) GO-Na-N. Characteristic carbon and oxygen peaks around 285 and 532 eV are not labelled.

Speciation of the functional groups using XPS was performed by considering the C 1s spectra for the three materials. The binding energy spectrum for GO shows two sharp peaks at 283.6 and 285.8 eV, characteristic of C bound to other carbons (as in the graphene backbone) and carbon bound to oxygen via ether like groups (labelled as C-C and C-O-C in Figure 3.3). In addition, a broad high binding energy peak can be seen which includes the contributions of multiple other oxygen bound carbon species (acid, alcohol, and carbonyl). While fitting the spectrum to obtain quantitative identification of potential carbon functional groups is possible, the width of the observed peak prevents an unbiased identification. Thus, considering the qualitative trend is more suitable to understand the characteristics of the material at each step. Upon treatment with

NaOH, a reduction of the GO can be observed by the increase in the C 1s peak at 283.6 eV (increase in C-C) and a decrease in the highly oxygenated species at higher binding energy. It is unclear how the sodium interacts with the carbon framework. Interestingly, the adsorption of TAN shows an increase in the high binding energy peaks as well as a broadening of peaks corresponding to all the species. This is consistent with the appearance of new nitrogen-containing carbon species.

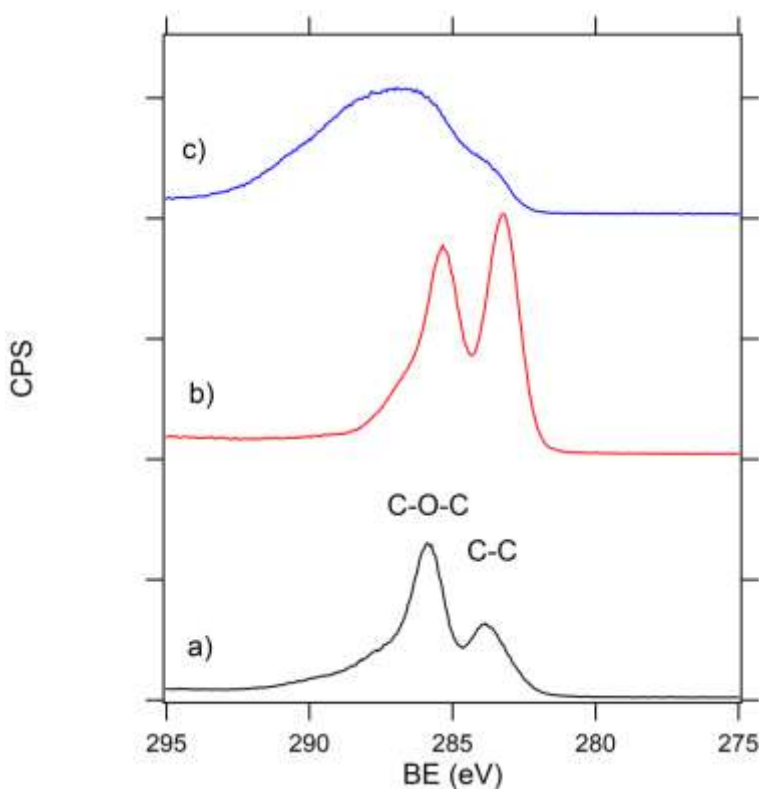


Figure 3.3. C 1s XPS region for a) GO; b) GO-Na; c) GO-Na-N.

The presence of the C-O-C species as dominant in the GO materials was corroborated by FTIR (Figure 3.4). The GO spectrum contains the characteristic peaks at 1750 cm^{-1} , 1616 cm^{-1} , 1214 cm^{-1} and 972 cm^{-1} (with a shoulder at 1050 cm^{-1}). These peaks correspond to the C=O (in -COOH), C=C bend, phenolic C-O and epoxy CO, respectively [50-52]. The OH region is broad,

likely due to ambient water, but a shoulder is also observed at the characteristic 3400 cm^{-1} for alcohol groups in graphene oxide. Upon NaOH treatment, the main change is the disappearance of the peak at 1750 cm^{-1} and a slight shift in the peak at 1616 cm^{-1} consistent with a partial reduction of the material. The graphene oxide structure remains, but changes in the shape of the background are also observed. Adsorption of ammonium ions produces a broadening and decrease in intensity of all peaks, and the appearance of the pairing at 1577 cm^{-1} with a shoulder at 1660 cm^{-1} which can be attributed to the presence of N-H and C=O in amide groups [50].

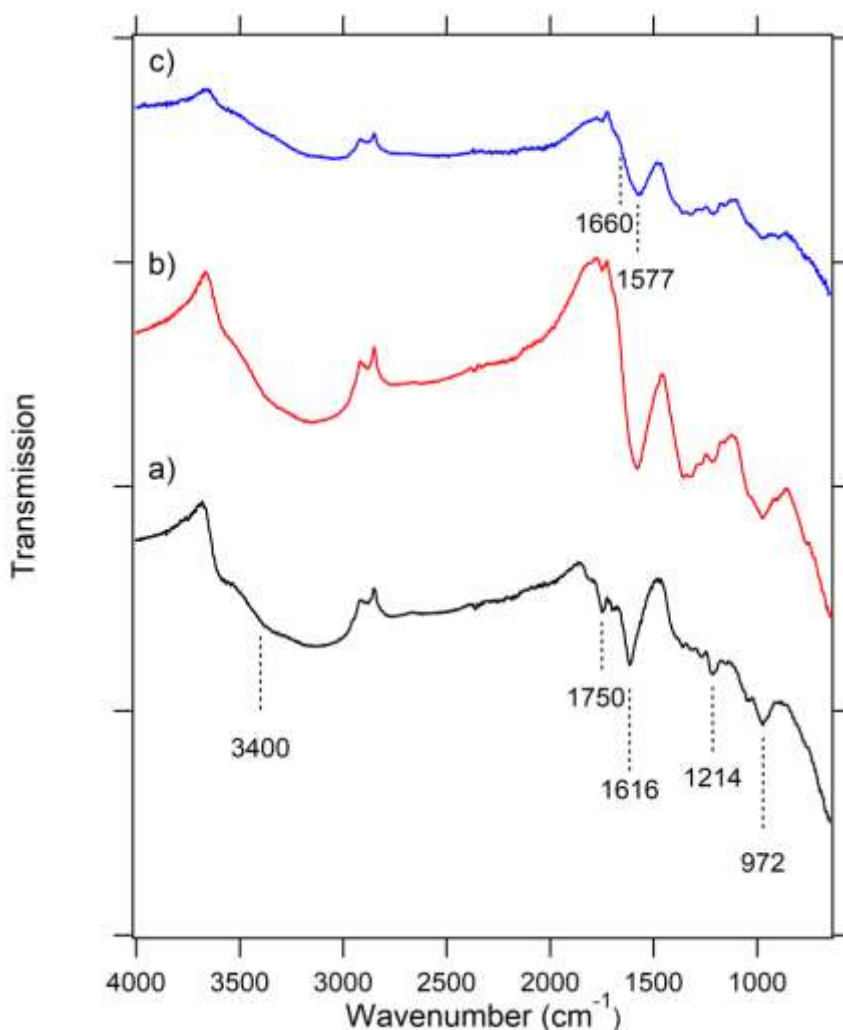


Figure 3.4. FTIR spectra for a) GO; b) GO-Na; c) GO-Na-N. Characteristic peaks have been labelled. Spectra are offset for clarity.

The overall morphology of the GO materials was observed via electron microscopy (TEM). Figure 3.5 shows the characteristic large, thin sheets of GO, which upon treatment with sodium shows folding and aggregation. The material after adsorption (GO-Na-N) appears highly aggregated consistent with the chemical changes. This might be a reason for the slight decrease in adsorption performance upon regeneration of the GO-Na. This is discussed in more details in section 3.3.6.

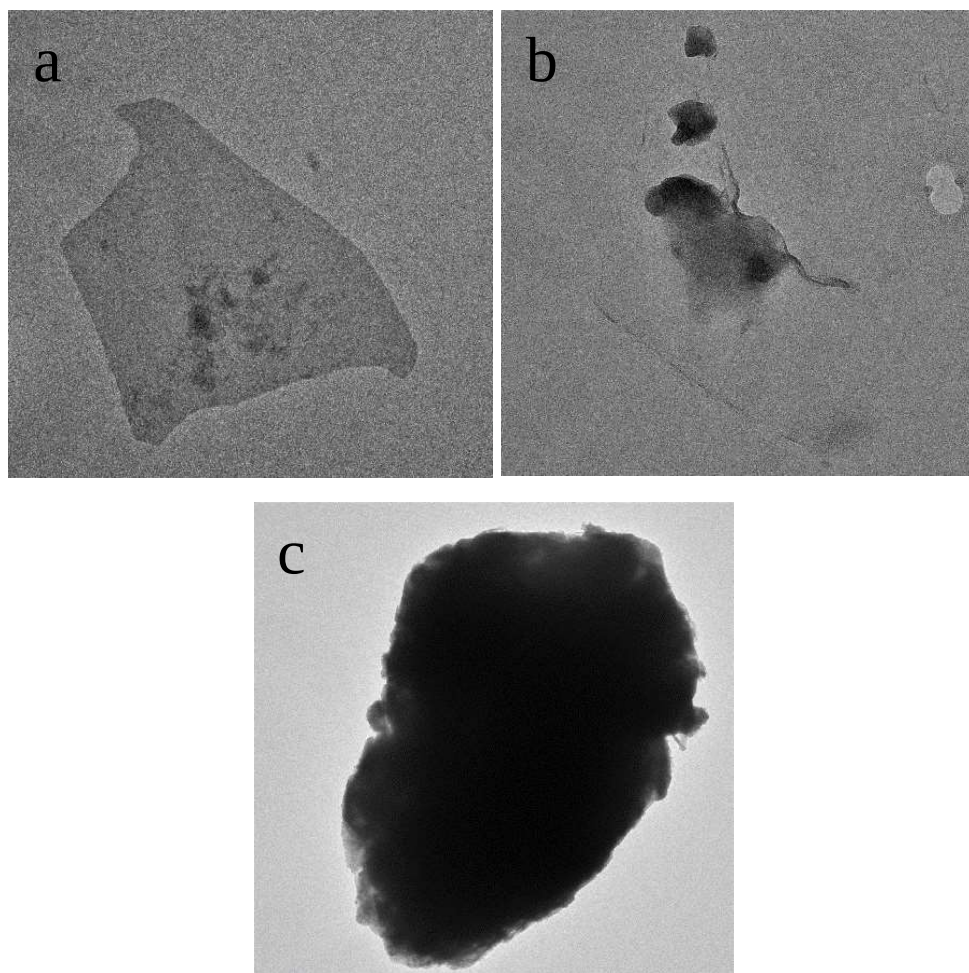


Figure 3.5. TEM images for a) GO, b) GO-Na, and c) GO-Na-N.

3.3.2. Adsorption Isotherm

To study TAN adsorption patterns in the liquid/solid phase at equilibrium conditions, adsorption isotherm tests were carried out under different initial concentration. The adsorption isotherm was fitted according to five common isotherm models, Langmuir, Freundlich, Sips, Redlich-Peterson, and Langmuir-Freundlich (Table 3.1). The isotherm equations are defined below [26, 53]:

$$\text{Langmuir Equation: } q_e = \frac{K_{ad} q_{Max} C_e}{1 + K_{ad} C_e} \quad (3.3)$$

$$\text{Freundlich Equation: } q_e = K_F C_e^{\frac{1}{n}} \quad (3.4)$$

$$\text{Sips Equation: } q_e = \frac{q_{Max} (K_{ad} C_e)^n}{1 + (K_{ad} C_e)^n} \quad (3.5)$$

$$\text{Redlich-Peterson Equation: } q_e = \frac{a C_e}{1 + K_{ad} C_e^n} \quad (3.6)$$

$$\text{Langmuir-Freundlich Equation: } q_e = \frac{K_{ad} q_{Max} C_e^{\frac{1}{n}}}{1 + K_{ad} C_e^{\frac{1}{n}}} \quad (3.7)$$

where q_e (mg/g) is the equilibrium solid phase concentration of GO-Na; K_{ad} (L/mg) is the adsorption equilibrium constant related to the affinity of the binding site and energy of adsorption; q_{max} (mg/g) is the maximum adsorption capacity in Langmuir model; C_e (mg/L) is the equilibrium TAN concentration; K_F (mg^{(n-1)/n}/g.L) is the Freundlich adsorption constant related to adsorption capacity; n is a constant related to surface heterogeneity, and a is the constant in the Redlich–Peterson equation ($a=K_{ad} q_{max}$) [53].

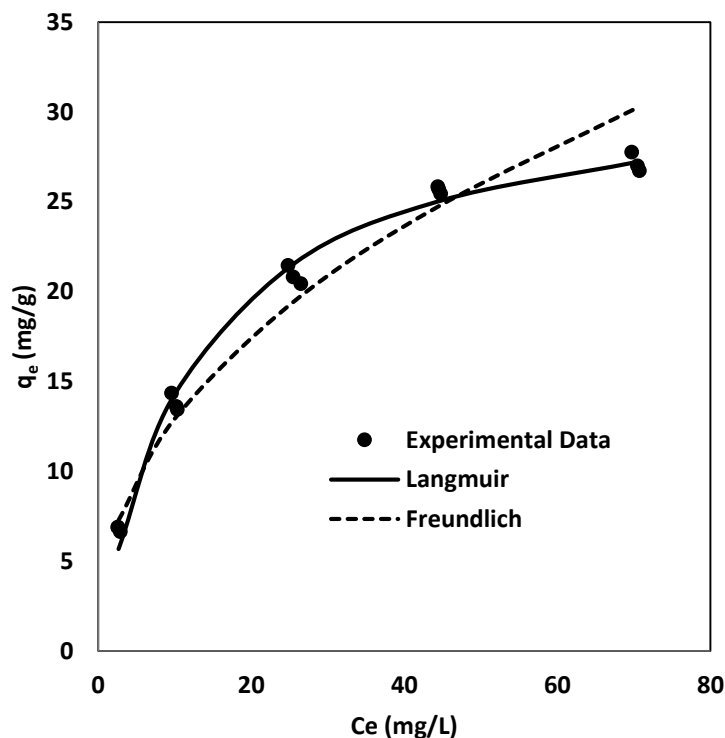


Figure 3.6. Empirical and theoretical TAN adsorption isotherms on GO-Na
Conditions: at room temperature, pH=7, and dose = 1g GO-Na/ L

The two most common and contrasting isotherms (Langmuir and Freundlich) are plotted in Figure 3.6. The Langmuir adsorption isotherm is the most prevalent model for recognizing the behavioral pattern of particles adsorbed on the surface of nano adsorbents in liquid phase. This model is applicable to monolayer and homogeneous adsorption. This implies that all molecules have fixed positions in the adsorbent's structure and just one layer participates in the adsorption process (monolayer) [28]. Additionally, in this model there is no interaction between molecules adsorbed on adjacent sites. The maximum adsorbent capacity reaches a saturation point under equilibrium conditions where no more adsorption can occur [54]. An alternative widely used empirical equation to describe experimental adsorption data is the Freundlich isotherm model. This model is based on multilayer and heterogeneous adsorption with interaction between

adsorbed molecules [55]. According to this isotherm, the adsorption capacity will be boosted with an increase in pollutant concentration [54].

Sips, Redlich-Peterson, and Langmuir-Freundlich isotherms can be thought of as suitable combinations of the Langmuir and Freundlich isotherms applicable under different sets of conditions. The five isotherms provide a good fit to the experimental data (Table 3.1). However, the Langmuir model better describes the physical behavior of TAN adsorption on GO-Na. The implication of the Langmuir isotherm is that the adsorption process titrates fairly similar sites on the GO-Na material, and therefore a single layer of adsorbent participates in the adsorption [28, 54], in accordance with the physical characteristics of GO-Na. From the fit of the TAN removal data following a monolayer adsorption process as described in the Langmuir model, the maximum capacity of GO-Na was determined to be 32 mg/g.

Table 3.1. Isotherm constants and regression correlations

Isotherm Model	q_{Max} (mg/g)	K_{ad} or K_{f}	n	a	R^2
Langmuir	32	0.09	-	-	0.99
Freundlich	-	4.73	2.29	-	0.98
Sips	40	0.04	0.74	-	0.99
Redlich-Peterson	-	4.26	0.81	0.31	0.99
Langmuir-Freundlich	33.6	0.09	1.12	-	0.99

The maximum capacity of sodium functionalized graphene oxide calculated from the Langmuir model was compared with the maximum Langmuir capacity of various adsorbents from literature, as determined under similar conditions. TAN adsorption on natural and modified zeolites vary, but typical values are $q_{\text{max}} < 20$ mg/g [21, 56-58], volcanic tuff has values in the same range [59], and resins can show values of q_{max} in the high twenties [60]. These typical values emphasize the potential of GO-Na synthesized in this study, which show higher maximum

adsorption capacities ($q_{\max} = 32$). The comparison with activated carbon ($q_{\max} = 6.08$) [61] is particularly significant because it indicates that the nano structure of carbon-based materials with accompanying increase in surface area requires appropriate functionalization (as in the case of GO based materials which can be considered as functionalized single carbon sheets) to produce a significant improvement of ammonium cation adsorption capacity.

As a corollary of the applicability of the Langmuir isotherm for the adsorption of TAN on GO-Na, the separation factor (R_L) can be further calculated according to the following equation [62-65].

$$R_L = \frac{1}{1 + K_{ad}C_0} \quad (3.8)$$

where K_{ad} (L/mg) is the Langmuir adsorption constant and C_0 (mg/L) is the initial TAN concentration. R_L is an indicator to estimate the favorability of a reaction. Variation of R_L between 0 to 1 means favorable process. The R_L approaches 0 if the value of K_{ad} is extremely large which indicates an irreversible reaction. Oppositely, when K_{ad} is infinitely small, the R_L value approaches 1 which means a linear process. A R_L value greater than 1 only occurs in the case that K_{ad} appears to be negative. Because K_{ad} is obtained from fitting experimental data, this occurs when there is unfavorable adsorption or leaching of contaminants to the solution during the adsorption process [56, 62, 63, 66]. In this study, the values of R_L for increasing TAN concentrations in solution for a fixed dose of adsorbent GO-Na were calculated. The range of R_L (0.1 to 0.55) verifies the favorable adsorption behavior of TAN on GO-Na.

3.3.3. Adsorption Energy

The mean adsorption energy for TAN adsorption by GO-Na was first calculated according to the Dubinin–Radushkevich equation (D-R), which is commonly used in the field, and allows direct comparison with the literature [64, 65]. The D-R approach uses a temperature dependent

isotherm and assumes a Gaussian distribution of adsorption energies on a heterogeneous surface. The model can be described by Eq. 3.9.

$$\text{Ln}q_e = \text{Ln}q_{\text{Max}} - \beta\epsilon^2 \quad (3.9)$$

where q_{Max} and q_e (mg/g) is the theoretical monolayer adsorption capacity and the solid phase concentration at equilibrium, respectively; β is the constant of the adsorption energy (mol^2/J^2), and ϵ is the Polanyi potential, which is expressed as [64]:

$$\epsilon = RT \text{Ln}\left(1 + \frac{1}{C_e}\right) \quad (3.10)$$

where R (J/mol. K) is the gas constant; T (K) is the temperature; and C_e (mg/L) is the equilibrium TAN concentration.

β depends on the average adsorption energy of the adsorbate per mole of adsorbent when the adsorbate molecules in the solution are transferred to the surface of the adsorbent from infinite distance. The value of β can be obtained from the slope of the D-R plot ($\text{Ln}(q_e)$ versus ϵ^2). Finally, the adsorption energy can be reached by the following equation.

$$E = \frac{1}{\sqrt{2\beta}} \quad (3.11)$$

The adsorption processes with E values ranging from 1 to 8 kJ/mol are typically considered as physisorption whereas 9 to 16 kJ/mol are classified as chemisorption [67]. The E value determined for this study by the D-R method was 0.5 kJ/mol, which is a weak interaction.

3.3.4. Thermodynamic

A thermodynamic approach was used to analyze the temperature dependence of adsorption mechanisms in more detail. As temperature increased from 7 to 42 °C, the solid phase concentration decreases from 22.7 to 20.4 mg/g and the removal percentage drops from 47 to 44%. This indicates that the process was exothermic.

The thermodynamic parameters including enthalpy changes (ΔH) and entropy changes (ΔS) were determined using the results at different temperatures of 7, 24, and 42 °C using the van't Hoff Equation shown below [62, 67].

$$\text{Log}K_d = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \quad (3.12)$$

where T is the temperature in Kelvin; R is the universal gas constant (8.314 J/mol. K); ΔH (J/mol) is the enthalpy change; ΔS (J/mol. K) is the entropy change; and K_d is the equilibrium constant determined as [62, 68, 69]:

$$K_d = \frac{q_e}{C_e} \quad (3.13)$$

where q_e (mg/g) and C_e (mg/L) are equilibrium solid phase concentration and equilibrium TAN concentration, respectively.

Thermodynamic parameters are summarized in Table 3.2. The negative value of ΔH (-2.35 kJ/mol) confirms that the adsorption process is exothermic, which is in agreement with the results above [70]. Additionally, some studies have reported that a ΔH value lower than 8 kJ/mol could be an indication of an ion exchange process [22, 26]. This suggests that the adsorption process consisted of ion exchange of NH_4^+ by Na^+ on GO-Na [71]; considering the fact that at neutral pH and room temperature total ammonia nitrogen in solution is mainly ammonium cations. The observation of the process being dominated by ion exchange is in agreement with the results obtained from the D–R isotherm.

Table 3.2. Thermodynamic parameters of TAN adsorption onto GO-Na
Conditions: pH=7, C_0 = 50 mg/L, and dose = 1g GO-Na/ L

T (°K)	ΔH (kJ/mol)	ΔS (kJ/mol. K)	ΔG (kJ/mol)
280	-2.346	0.048	-15.8
297			-16.62
315			-17.48

The positive value of ΔS (0.048 kJ/mol. K) can be explained by the increasing randomness at the solid–liquid interface during the exothermic adsorption of TAN on the adsorbent surface which confirms the favorability of the process [26]. The results obtained and presented for ΔH and ΔS in this study (Table 3.2) are in agreement with results by various previous research (Rat-Valdambrini et al. [26]; Saltali et al. [22]; Boopathy et al. [72]; and Vassileva and Voikova [18]). They also reported the low values of ΔH and ΔS for ammonium uptake by various adsorbent including zeolites and coconut shell-activated carbon indicates that the interaction between NH_4^+ and the active site on the surface of adsorbent is weak. Furthermore, the process with ΔG ranging from -20-0 is generally considered as a physisorption process and the one with a ΔG ranging from -400 to -80 as a chemisorption process. The negative value of ΔG demonstrates the spontaneity of a reaction, and the value obtained is consistent with the weak interaction nature of the process [73, 74].

3.3.5. Adsorption Kinetics

Four consecutive kinetic steps are usually considered in a sorption process, namely transport in the bulk solution (particle diffusion), diffusion across the film surrounding the sorbent particles (film diffusion), intra-particle mass transfer within the particle [75] (intra-particle diffusion), and finally sorption and desorption on the solid surface considered as a kind of chemical reaction [76]. The rate of adsorption is controlled by the slowest step which can usually be classified in two main categories. First, a diffusion controlled process and second, the process controlled by the chemical reaction between adsorbate molecules in the solution and the molecules on the surface of the adsorbent [77]. To investigate if the diffusion steps control the adsorption kinetics, the intra-particle diffusion model was utilized to ascribe the effects of diffusion on the adsorption

mechanism. Moreover, to study the role of the chemical reaction, the adsorption data was fitted using Elovich's reaction model. The equations are expressed as follow:

$$\text{Intra-particle diffusion: } q_t = k_{id}t^{1/2} + C \quad (3.14)$$

where q_t (mg/g) is the solid phase concentration at time t ; k_{id} (mg/g.min^{1/2}) is the intra-particle rate constant; C (mg/g) represents the thickness of boundary layer and it can be obtained from the interception of plot of q_t vs $t^{1/2}$ [78]. If C is equal to zero, it can be interpreted that the intra-particle diffusion is the only controlling factor in the adsorption process. In this study, the nonzero value of C (19.03 mg/g) suggests that in this process more than one factor can play a role in rate controlling of the whole process [75].

$$\text{Elovich's reaction: } q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (3.15)$$

where α (mg/g.min) and β (g/mg) are the Elovich's constant which represents the initial adsorption rate and the desorption coefficient, respectively [79, 80].

To compare these two models, it is essential to have dimensionless parameters that better quantify the likelihood of TAN adsorption on a particular adsorbent. In this regard, intra-particle and Elovich equations were modified. The dimensionless equations were obtained according to the method of Wu et al. [79].

$$\text{Dimensionless Intra-particle diffusion: } \frac{q_t}{q_{ref}} = 1 - R_{id} \left(1 - \left(\frac{t}{t_{ref}}\right)^{1/2}\right) \quad (3.16)$$

$$\text{Dimensionless Elovich equation: } \frac{q_t}{q_{ref}} = \frac{1}{\beta q_{ref}} \ln\left(\frac{t}{t_{ref}}\right) + 1 \quad (3.17)$$

Where t_{ref} is defined as the longest time in the adsorption process and subsequently q_{ref} is the solid phase concentration at time $t=t_{ref}$. R_{id} is a dimensionless starting adsorption factor of the

Intra-particle diffusion model defined as $R_{id} = k_{id} \frac{t_{ref}^{1/2}}{q_{ref}}$.

Figure 3.7 illustrates the best fit of experimental data using the dimensionless form of the Intra-particle and Elovich equations. As it is depicted in Figure 3.7, the Elovich model contains two stages. The first stage, with a steep slope, can be explained by the instant diffusion of ammonium cations through the solution and exchange with sodium containing ligands on the surface of graphene oxide (film diffusion). There are three theories to explain the second portion: (1) after a few minutes, the diffusion term decreases because many ammonium cations are already adsorbed to the surface of the adsorbent decreasing the concentration of ammonium ions in solution at the vicinity of the adsorbent; (2) there is less sodium cations on the surface of the adsorbent to be exchanged by ammonium, because some of them are already exchanged [53, 78]; (3) the reactivity of ammonium with the adsorbent transitions from ion exchange to reaction with the oxygen of the GO backbone which leads to the saturation of the surface by chemisorbed species [71, 81].

The Elovich's equation is usually used to determine whether the chemical reaction on the heterogeneous surface of adsorbent is the rate-limiting step. A better fit of Elovich's model ($R^2 = 0.960$) compared to Intra-particle diffusion ($R^2 = 0.838$) suggests that chemical reaction is rate-limiting for this process.

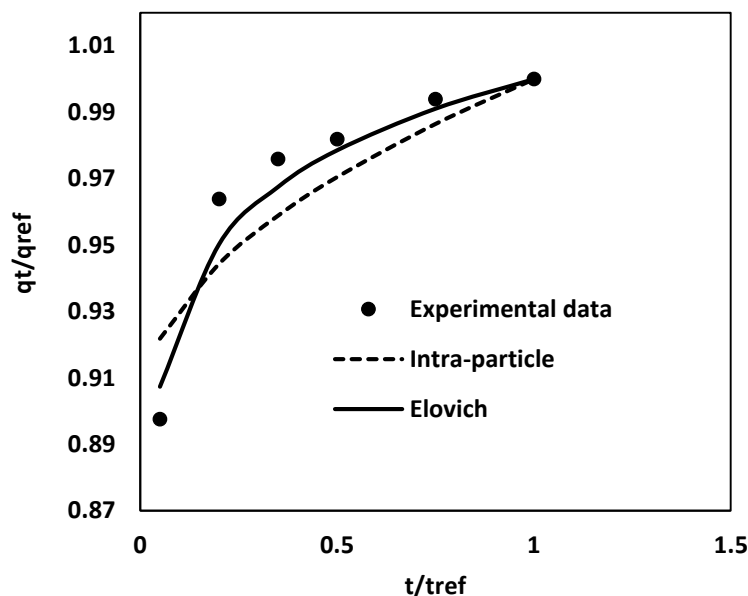


Figure 3.7. Fitting of experimental data with dimensionless form of Intra-particle and Elovich equation
Conditions: at room temperature, pH=7, $C_0=50$ mg/L, and dose = 1g GO-Na/ L

A kinetic analysis was used to determine the optimum operating time to reach equilibrium for the full scale batch adsorption process [19]. The kinetic parameters specify the effect of contact time on the removal percentage and solid phase concentration of adsorbent. The adsorption mechanism of TAN on GO-Na has been examined by pseudo-first order and pseudo-second order models [34, 53, 80, 82-84] which were defined as follow:

$$\text{pseudo-first order: } \ln (q_e - q_t) = -k_1 t + \ln q_e \quad (3.18)$$

$$\text{pseudo-second order: } \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3.19)$$

where q_t , q_e (mg/g) are the solid phase concentration at time t and equilibrium, respectively. k_1 (1/min) and k_2 (g/mg.min) are the rate constant for pseudo first and second order model, respectively.

The experimental data were plotted according to pseudo first and second order models shown in Figure 3.8 and parameters for these models are calculated and summarized in Table 3.3. As

could be expected by the typical adsorption behavior of exchange materials [33, 40, 75], the pseudo second-order model fits with a much higher regression correlation (0.999) indicating that this is the best fitting model for the process. Further strong evidence that the experimental adsorption is best described by pseudo second-order is the theoretical solid phase concentration (q_e) calculated according to the pseudo second-order model matches to the experimentally determined value. The initial adsorption rate V_0 (mg/g min) for pseudo second order is equal to $k_2 q_e^2$. The high value of V_0 (118 mg/g min) verifies the fact that adsorption process is very fast. Also, the batch adsorption experiments revealed that the final equilibrium condition is reached within a few minutes, making the process appealing from a practical point of view [85].

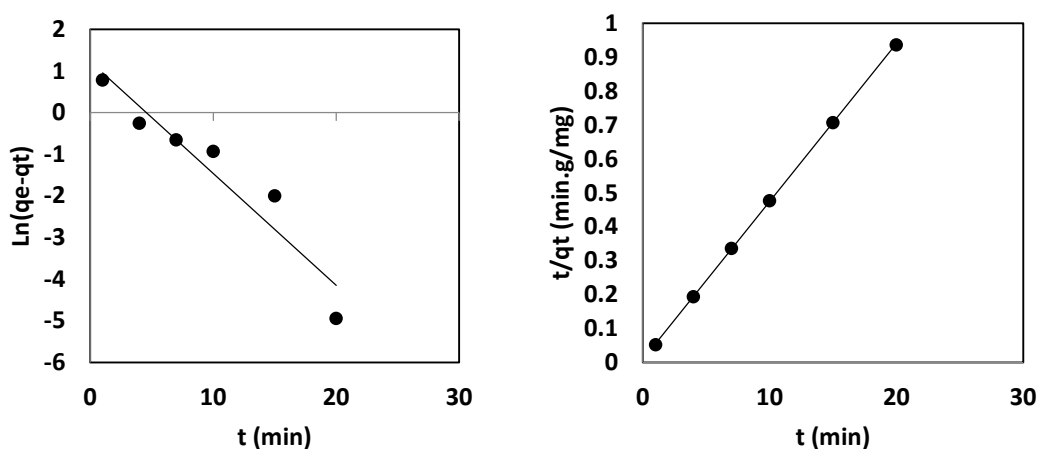


Figure 3.8. Fitting of experimental data with a) pseudo first order, and b) pseudo second order model
Conditions: at room temperature, pH=7, C_0 = 50 mg TAN/L, and dose = 1g GO-Na/ L

Table 3.3. Kinetic parameters of TAN adsorption on GO-Na

Kinetic Model	q_e (mg/g)	k	R^2
Pseudo-first order	3.39	0.27 (1/min)	0.911
Pseudo-second order	21.5	0.25 (min.mg/g)	0.999

Pseudo-second order model is typically indicative of a chemical sorption rate-controlling processes [86]. The chemical sorption process includes valence forces created between adsorbent and adsorbate by sharing or exchanging electrons [40]. The pseudo-second-order model assumes that the rate-controlling step of TAN adsorption process is a consequence of chemical sorption and more than one-step may be involved in sorption processes [80].

There is consistency between the Elovich model and the determined pseudo second order kinetics. That is, the low average value of the adsorption energy suggests a complex adsorption behavior where there is chemical interaction between ammonium ions and different adsorption sites in GO-Na. Binding to each site may have a slightly different rate constant, leading to the overall pseudo second order behaviour, yet the binding shows a weak interaction expected for ion-exchange. This fact makes the adsorbent more promising due to the fact that its regeneration will be more effective and practical.

3.3.6. Regeneration of adsorbent

As the range of adsorption energy and the results obtained from thermodynamic studies confirmed the adsorption process is due to weak interactions, the ion exchange of ammonium and sodium cations can be expected to be reversible. Therefore, sodium chloride, a nontoxic and inexpensive salt in industry, is used for regeneration of the adsorbent to make this process more economical and environmental friendly. The performance of reused adsorbent was studied for several regeneration cycles. Figure 3.9 shows the removal percentage and solid phase concentration of regenerated GO-Na for 3 cycles. Figure 3.9 shows 5% and 2 mg/g loss in removal percentage and incremental solid phase concentration, respectively, in each cycle. It can be concluded that GO-Na can still remain effective after several cycles.

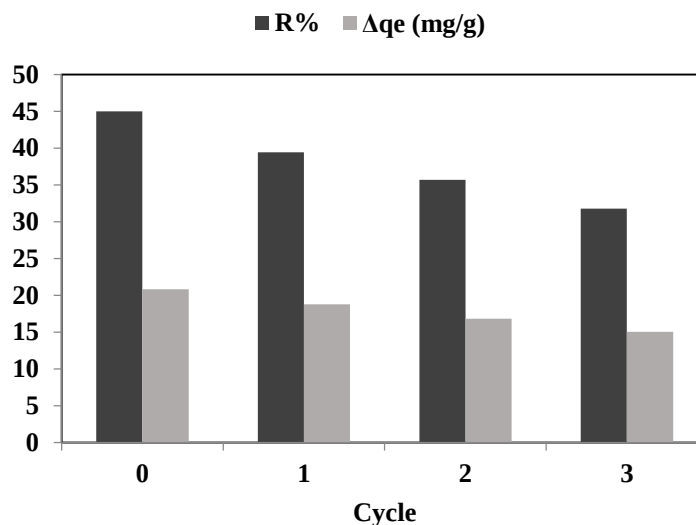


Figure 3.9. Regeneration cycle of GO-Na for TAN removal
 Conditions: $C_0 = 50$ mg/L, dose = 1g GO-Na/ L, neutral pH, and room temperature

3.4. Conclusions

Experimental results indicate that GO-Na is an efficient adsorbent to remove TAN from aqueous solution. The Langmuir model provided the best prediction for the TAN removal process with maximum adsorption capacity of 32mg $\text{NH}_3\text{-N/g}$. The small values of the adsorption energy, enthalpy, entropy, and Gibbs free energy suggest that the adsorption mainly consists of ion exchange processes with weak interaction between adsorbate and adsorbent. A kinetic study shows that this process is very fast which makes GO-Na a promising adsorbent from the practical points of view. This adsorption process is best described by pseudo second order model may indicate that chemisorption is the rate controlling step. The mechanism of adsorbent is well described by the Elovich model suggesting that the rate-controlling step in this process is chemical reaction, which occurs with a slower rate rather than ion exchange of NH_4^+ with Na^+ on the surface of the adsorbent. Thermodynamic studies indicate that adsorption of TAN on GO-Na is exothermic with an increasing randomness at the solid-liquid interface. The negative values of

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Gibbs free energy indicate that this adsorption process is spontaneous in nature. The weak interactions between adsorbate and adsorbent facilitate the regeneration of GO-Na in an efficient way.

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Chapter 4: Assessment and optimization of total ammonia nitrogen adsorption in aqueous phase by sodium functionalized graphene oxide using response surface methodology²

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Abstract

Total ammonia nitrogen (TAN) uptake by sodium functionalized graphene oxide as an efficient adsorbent was evaluated and optimized using response surface methodology (RSM). Batch adsorption tests were carried out based on a central composite design (CCD) experimental plan at 3 pH levels (6, 7, and 8) and 3 temperature levels (5, 25, and 45 °C). The equilibrium condition was reached within 5 minutes. Quadratic models for percent TAN removal (R%) and solid phase TAN concentration (q_e) as response were obtained and evaluated by statistical analysis to predict the experimental data. The models were reduced by eliminating insignificant terms. The final reduced models were significant (p-value <0.0001) with R^2 values 0.96 for R% and 0.97 for q_e , respectively. The optimum pH and temperature to reach the maximum values for R% (58.23%) and q_e (27.45 mg/g) were predicted by the RSM. The laboratory experiments were in very good agreement with the predicted optimized values for R% and q_e by RMS as the error was 1.2% and 0.3%, respectively.

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Statement of Industrial Relevance: The results for GO-Na showed it to be an effective adsorbent for removal of ammonia from aqueous phase with potential applications for municipal and industrial wastewaters containing ammonia, such as mining wastewater.

Novelty or Significance: There has been extensive research on adsorption of ammonia (it is among the most prevalent contaminants of concern in aquatic phase) from aqueous phase by natural minerals, such as zeolites and commercial adsorbents, such as activated carbon and ion-exchange resins. However, there exists very limited research on the adsorption of ammonia by graphene based materials as more recently developed materials. The existing information of adsorption of ammonia by graphene-based materials deals with gas phase adsorption, not liquid phase, which is the subject of this research. Limited studies have been reported for ammonia removal by graphene oxide from liquid phase.

Keyword: ammonia, nanomaterials, optimization, pH, temperature

4.1. Introduction

Ammonia is one of the most prevalent contaminants in agricultural, domestic and industrial wastewaters and runoff [1]. It is required by guidelines and discharge criteria all around the world to reduce ammonia concentration to discharge limits due to its impacts on eutrophication, oxygen depletion and toxicity to fish and aquatic species [1-5]. In aquatic phase, ammonia exists in two forms, molecular unionized ammonia (NH_3) and ammonium cations (NH_4^+), which can be described by the reversible reaction expressed as follow.



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NH_3 has been reported to be toxic to living organisms. It is common in aquatic chemistry to refer to and express the sum of the two as simply ammonia or total ammonia nitrogen (TAN) [6]. pH and temperature are the main factors playing a role on the distribution of the two forms.

Reported techniques for the removal of TAN from aqueous phase include biological nitrification and denitrification [7], chemical precipitation [8], electrochemical coagulation [9], anaerobic ammonia removal [10], in-situ nitrification in aerated landfill bioreactor [11], ammonia stripping [12], membrane distillation [13], microwave [14], and adsorption and ion exchange [15-25]. The biological process is the most commonly used method for removal of ammonia from wastewaters; however, it could be impacted by microbial inhibition due to ammonia toxicity [1, 26]. Adsorption and ion exchange processes are not impacted by ammonia toxicity, operate over a wider range of temperature, and offer many advantages including low cost, simple operation and fast kinetics [1, 4]. The most commonly used materials for TAN uptake from aqueous phase are zeolites and ion-exchange resins. Their application and the impacts of pH and temperature on the behavior of TAN uptake from aquatic solution by these adsorbents have been investigated before [4, 25, 27].

In recent years, there has been a growing interest in developing new nano-materials such as graphene for different technologies, including water purification. Graphene was introduced in the early 2000s and its importance was recognized by the Nobel Prize in physics in 2010. Graphene can be described as a two dimensional sheet of sp^2 -bonded carbon atoms arranged in a honeycomb lattice [28-30]. The excellent physicochemical properties of the oxidized form of graphene, called graphene oxide (GO), has attracted considerable attention for its application for contaminant removal of heavy metals [31-34], dyes [35-38], and pharmaceuticals [39, 40]. However, there is limited literature on the performance of GO as an adsorbent to uptake TAN

from aqueous phases. A recently developed sodium modified graphene oxide (GO-Na) has shown promising TAN removal and reasonable regeneration potential [41].

The traditional approach of studying removal of pollutants from water involves “one variable at a time” changes. This approach has been widely exercised and its initial validity has been demonstrated. However, this approach cannot determine the interactions between different influential factors in the system. Alternative methods, such as factorial design and response surface methodology (RSM), have been applied to address this issue and eliminate this drawback [42]. RSM, which is a collection of statistical and mathematical techniques, has been proven as an efficient experimental design and statistical analysis method to optimize and predict the interactions between process variables [4, 14, 42, 43].

The main objectives of this study were to investigate the performance of sodium functionalized graphene oxide for ammonia adsorption from aqueous solution and to apply response surface methodology to assess and optimize the effects of pH and temperature.

4.2. Materials and Methods

4.2.1. Preparation of adsorbent and its characteristics

The synthesis of GO-Na has been previously described in detail [41]. Briefly, graphene oxide (GO) was prepared using an improved Hummer method which utilizes H_2SO_4 , H_3PO_4 and KMnO_4 in the initial oxidation step and H_2O_2 (30%) to quench the process. After washing and isolating the GO, sodium functionalization was performed by treatment with NaOH and NaCl . Then the resulting GO-Na was washed and dried prior to use in ammonium adsorption experiments.

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The GO-Na adsorbent characterization has been discussed in detail in previous work in relation to its precursor and spent species [41]. Characteristic properties relevant to this manuscript are presented in the Supporting Information. In summary, GO-Na can be described as having a high surface area, and a D/G Raman band intensity ratio of 1.1 indicating a highly defective carbon network. This was corroborated by XPS, which shows not only a high Na content but also a high content of oxygen bound carbon species [41]. These characteristics make this material suitable for ammonium ion adsorption via ion exchange and amide formation with the GO framework.

4.2.2. Batch adsorption experiment

All stock solutions with selected TAN concentration were made by dissolving NH_4Cl in distilled water. To estimate the equilibrium condition and the role of contact time in the adsorption process, a preliminary set of tests was performed with TAN concentration of 50 mg/L, adsorbent loading of 1 g/L, at neutral pH, and room temperature (25 °C), measuring TAN uptake as a function of time at different time intervals. A second set of preliminary tests was carried out to assess the effect of adsorbent dosage. Adsorbent dosage of 0.5, 1, 2, 3 g/L GO-Na were added to a 50 mL of ammonia solution containing of 50 mg TAN/L, at neutral pH and room temperature. Based on the results of kinetic tests, all the solutions were stirred for 1 hour at 250 rpm to make sure they reach the equilibrium condition. In order to study the impact of initial concentration, the adsorption tests were performed using solutions of 10-100 mg TAN/L, at neutral pH, room temperature, and adsorbent dosage of 1 g/L. In addition, the effect of pH on the adsorption process was investigated over a pH range from 2 to 11, while, other conditions were kept constant (at room temperature, $C_0=50$ mg TAN/L, adsorbent dosage = 1g/L, and contact time= 1 hr). NaOH or HCl was used in order to adjust the pH value. Additionally, extra tests were performed under the same conditions with pH ranging from 7 to 11 with no adsorbent to

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determine and correct any TAN loss due to volatilization at high pH values. The main phase of experiments was conducted based on a Central Composite Design experimental plan explained below and results were analyzed by response surface methodology.

In all cases, after vacuum filtration of the solution by Polytetrafluoroethylene (PTFE) filter (0.2 Micron) obtained from Van Waters and Rogers (VWR), equilibrium TAN concentration was determined by Salicylate method (Method: 10031) TNTplus 832 test using a Hach DR6000 spectrophotometer. The removal percentage (R%) and solid phase concentration, q_e (mg/g, TAN adsorbed per gram of adsorbent), were calculated as follow:

$$R\% = \left(\frac{C_0 - C_e}{C_0} \right) \times 100 \quad (4.2)$$

$$q_e = \left(\frac{C_0 - C_e}{W} \right) \times V \quad (4.3)$$

where C_0 and C_e (mg/L) are the initial and equilibrium concentration of TAN in solution, respectively, W (g) is the mass of adsorbent, and V (L) is the volume of solution.

4.2.3. Experimental design and analysis

In this study, the statistical analysis was carried out by Design-Expert® software to analyze the experimental data based on the Central Composite Design (CCD). CCD is an experimental design approach, useful for building a quadratic model for the response variable without needing to use a complete factorial experiment, which significantly reduces the number of required tests. For each independent variable, i.e. pH and temperature, 3 coded levels were chosen to study the behavior of TAN removal as shown in Table 4.1. pH levels of 6, 7 and 8 and temperature levels of 5, 25, 45 °C were selected. The temperatures at 5 and 45 °C were maintained by using an ice bath and oil bath, respectively. An initial TAN concentration of 50 mg/L, adsorbent dosage of 1

g/L, and contact time of 1 hour was used for each test. The total number of experiments needed to design a model can be calculated as 2^k+2k+R where, k is the number of factors (in this study $k = 2$) and R is the number of replications to assess the pure error (in this case $R = 5$) [2]. The quadratic equation below was used to describe the behavior of the system [4, 44].

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i \leq j}^k \sum_j^k \beta_{ij} X_i X_j + e \quad (4.4)$$

where, Y is the outcome response; X_i and X_j are the independent variables (pH and temperature); β_0 is the value of the fixed response at the center point of the design; β_i , β_{ii} , β_{ij} represents the interaction coefficients of linear, quadratic and second-order terms, respectively; k is the number of independent variables; and e is the random error. Coefficient of determination (R^2) was used as the goodness-of-fit statistic or the indicator to measure of how well the observed outcomes are replicated by the polynomial model. Then, the statistical significance of the model as well as model terms were checked by F-value (Fisher variation ratio) and p-value (probability value, Prob>F), respectively. Finally, three-dimensional surface plots and two-dimensional contour plots were obtained and optimum values of pH and temperature to achieve optimum R% and q_e were predicted by the software.

Table 4.1. Independent variables of CCD design

Level of value	pH	Temperature (°C)
-1	6	5
0	7	25
+1	8	45

Abbreviation: CCD, central composite design.

4.3. Results and Discussion

The material properties of the GO-Na absorbent used for all experiments and models were previously studied in detail. Typical results are shown in the Supporting Information. Figure 4.S1 shows TEM images of a thin GO-Na sheet of typical size and an example of a folded sheet. Figure 4.S2 combines infrared and Raman data showing normal GO functional groups and its D/G band structure. It is important to keep in mind that the same material is being used in the exploration of influential factors leading to optimal performance of this efficient adsorbent.

4.3.1. Effect of contact time

As shown in Figure 4.1, adsorption of TAN on the surface of GO-Na increases with a steep slope at the beginning indicating that the TAN adsorption by GO-Na is very fast and the equilibrium condition is reached within 5 minutes, which is promising from practical point of view. Fast kinetics of ammonia adsorption by activated carbon as another carbon-based adsorbent has been reported before [45]. After 5 minutes, the adsorption slows down and just a slight further increase can be observed. This can be explained by the fact that as adsorption proceeds, less free active sites remain and the probability for ammonium cations to be attached to the surface of the adsorbent decreases significantly. Details of the adsorption kinetics, which showed that the process is well described by a pseudo second order model, are presented elsewhere [41].

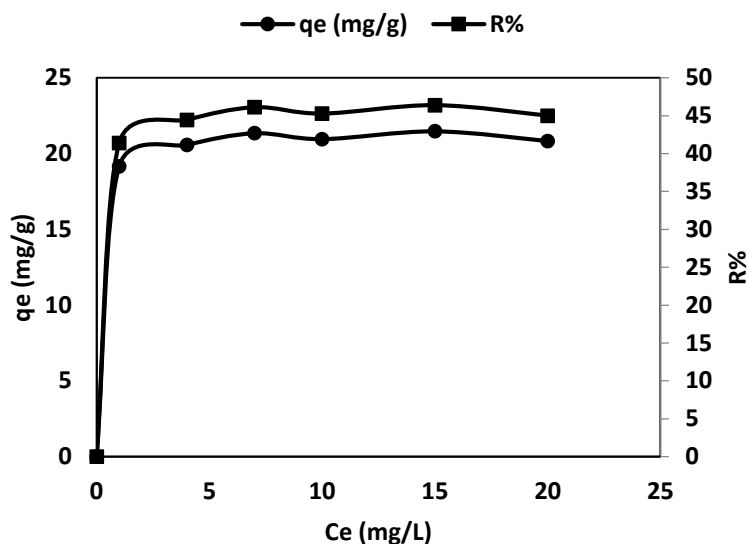


Figure 4.1. Effect of contact time on R% and q_e
 Conditions: pH=7, room temperature, $C_0 = 50$ mg TAN/L, and dose = 1 g GO-Na/ L

4.3.2. Effect of Adsorbent Dosage

Table 4.2 presents the results for the effect of adsorbent loading on TAN removal (R%) and solid phase concentration (q_e). The results of preliminary tests showed that at neutral pH, room temperature, and an initial concentration of 50 mg TAN/L, the removal percentage increased from 27.03% to 66.59% by increasing the adsorbent loading from 0.5 to 3 g/L. At a higher dosage there are more active sites available to uptake TAN from the solution. However, the adsorption capacity declined from 25.71 to 10.33 mg/g by increasing the adsorbent dosage from 0.5 to 3 g/L. This means that all the active sites for TAN adsorption are not fully utilized and some of them remained unsaturated. As adsorption capacity and removal percentage have reverse trends, the dosage for subsequent tests was selected at 1 g /L of GO-Na, the point that both removal percentage and solid phase concentration have reasonable values.

Table 4.2. Effect of adsorbent loading on R% and q_e
Conditions: pH=7, room temperature, and $C_0 = 50$ mg TAN/L

Ads Dose (g/L)	R%	q_e (mg/g)
0.5	27.03	25.71
1	43.56	20.44
2	57.84	13.76
3	66.57	10.33

Note: Conditions: pH=7, room temperature, and $C_0 = 50$ mg TAN/L

4.3.3. Effect of initial TAN concentration

Table 4.3 displays the effect of initial TAN concentration on the adsorption capacity and removal percentage. Increasing the initial ammonium concentration can enhance the adsorption capacity; however, the removal percentage drops. Increasing the ammonium concentration forces the equilibrium to be moved toward more adsorption on the GO-Na surface. This results in more active sites being occupied by ammonium cations and higher adsorption capacity. At each adsorbent dosage, there is a saturation limit (i.e., there is a limited number of active sites that can be occupied by ammonium cations). After reaching the saturation point, the rest of ammonium cations will remain in the solution. Thus, by further increasing the ammonium concentration, more ammonium cations would remain in solution, which causes ammonium removal to decrease. Over the range of initial TAN concentrations of 10-100 mg/L, the solid phase concentration increased from 6.80 to 27.17 mg/g, while removal efficiency decreased from 71.77 to 27.88%.

Table 4.3. Effect of initial TAN concentration on R% and q_e

$C_0 \text{ NH}_4^+$ (mg/L)	R%	q_e (mg/g)
10	71.77	6.80
25	57.91	13.80
50	44.98	20.91
70	36.57	25.67
100	27.88	27.17

Note: Conditions: pH=7, room temperature, and dose = 1g GO-Na/ L

Abbreviation: TAN, total ammonia nitrogen.

4.3.4. Effect of pH

As stated above, depending on pH, ammonia nitrogen can be found in aquatic solutions either in the form of ammonium cations or aqueous ammonia. At pH values lower than 7, ammonia nitrogen is almost entirely in form of ammonium cations, while at pH values higher than 11, the molecular (unionized) form predominates. By increasing the pH from 7 to 11 ammonium cations start converting to dissolved ammonia. pKa for $\text{NH}_4^+/\text{NH}_3$ at ambient temperature is 9.4, which means that at this pH, 50 % of ammonia nitrogen is in the form of ammonium and 50% is in form of ammonia [19, 27]. The effect of pH on ammonium adsorption by GO-Na was investigated at pH values ranging between 2 to 11. As it is depicted in Figure 4.2, the removal percentage increases as pH increases from 2 to 11. When pH increases to values higher than 8, a portion of the ammonium cations are adsorbed by the GO-Na and a portion may convert to dissolved ammonia and then ammonia gas and exit the system. This was quantified by running control samples at the same conditions, but with no GO-Na added. The nitrogen loss was measured and subtracted from the TAN removal in order to determine the net contribution of adsorption in the ammonium removal process at basic pH values. The results show that up to pH of 8.0 there is no significant ammonia gas volatilization, but at a pH values larger than 8.0 the contribution of ammonia volatilization has to be considered. After applying the contribution of ammonia gas volatilization, a noticeable drop in ammonium uptake is observed at high pH. This could be attributed to the fact that ammonia volatilization would result in lower concentration of ammonia in solution and hence lower uptake by the adsorbent. The effect is more obvious when increasing pH beyond 9.4, when more than 50% of the ammonium ions are converted to ammonia gas and therefore, less ammonium cations are available in the solution to be adsorbed by GO-Na. This leads to a decrease in solid phase concentration. This reduction in adsorption

can also be attributed to partial dissolution of GO at high pH values as a similar behavior has been reported by some researchers for zeolite [19] and mesoporous silica materials [27].

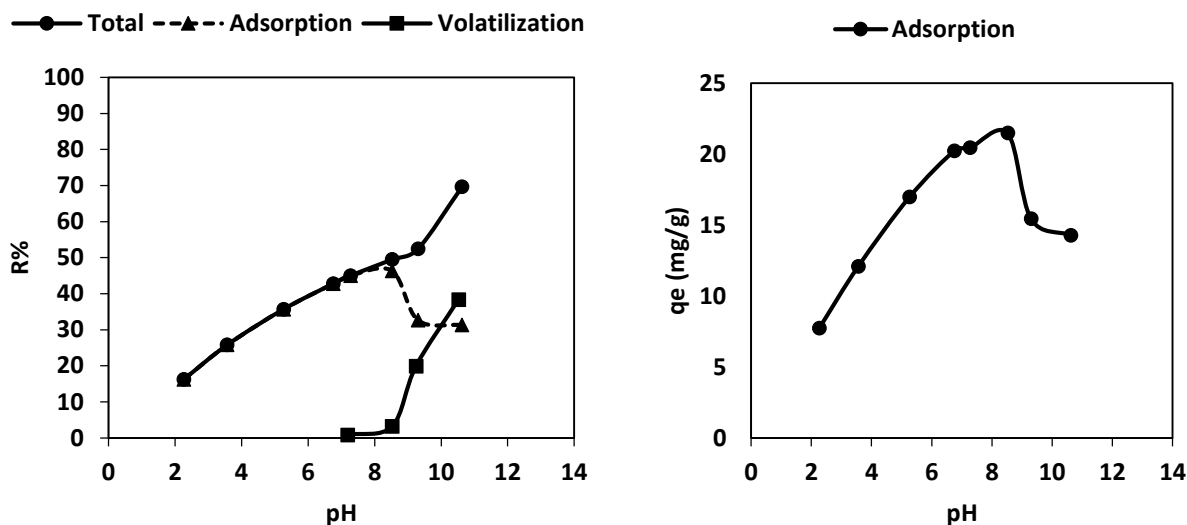


Figure 4.2. Effect of pH on ammonium adsorption onto GO-Na. Lines are used to guide the eye. Conditions: room temperature, $C_0 = 50$ mg/L, and dose = 1g GO-Na/ L

4.3.5. Statistical analysis and modeling

Response values for removal percentage (R%) and solid phase concentration (q_e) for 13 experimental runs, based on the CCD and using pH and temperature at 3 levels, are presented in Table 4.4.

Table 4.4. Response value for different experimental conditions

Run No.	Factor 1	Factor 2	R%	q _e (mg/g)
	pH	Temperature (°C)		
1	7	25	43.56	20.44
2	6	25	37.26	17.48
3	6	45	20.04	13.63
4	7	25	45.00	20.83
5	7	45	44.17	20.44
6	7	25	46.39	21.47
7	8	45	57.57	27.38
8	7	25	45.55	21.10
9	7	5	46.94	21.73
10	8	5	48.22	22.63
11	6	5	39.45	18.51
12	8	25	51.62	24.56
13	7	25	46.11	21.34

The results of regression analysis of the quadratic model for both responses are presented in Tables 4.5 and 4.6. In each table, the analysis of variance (ANOVA) for predicted model for the full and reduced model (after eliminating the insignificant terms) for each response is presented. The p-values of <0.0001 for the full model for both R% and q_e imply that both of the models are statistically significant and there is only a 0.01% chance that an F-value this large could occur due to noise. However, the p-value for some of the model terms is greater than 0.05 (95% confidence) showing these terms are not significant [2]. Model reduction, elimination of non-significant terms, is necessary to improve the model. For both R% and q_e response models, only pH and pH×Temperature are the significant model terms.

Table 4.5. ANOVA of R% for full and reduced quadratic model

Source	Full quadratic					Reduced				
	Sum of Square	DF	Mean Square	F-value	p-value	Sum of Square	DF	Mean Square	F-value	p-value
Model	560.46	7	80.07	68.30	0.0001	542.41	2	271.20	113.43	<0.0001
pH	103.10	1	103.10	87.96	0.0002	444.79	1	444.79	186.03	<0.0001
Temperature	3.84	1	3.84	3.27	0.1302	-	-	-	-	-
pH × Temperature	97.61	1	97.61	83.28	0.0003	97.61	1	97.61	40.83	<0.0001
pH ²	5.53	1	5.53	4.71	0.0820	-	-	-	-	-
Temperature ²	0.2477	1	0.2477	0.2113	0.6650	-	-	-	-	-
pH ² × Temperature	1.67	1	1.67	1.43	0.2858	-	-	-	-	-
pH × Temperature ²	6.13	1	6.13	5.23	0.0709	-	-	-	-	-
Residual	5.86	5	1.17			23.91	10	2.39		
Lack of fit	0.8390	1	0.8390	0.6683	0.4595	18.89	6	3.15	2.51	0.1964
Pure Error	5.02	4	1.26			5.02	4	1.26		
Core Total	566.32	12				566.32	12			
C.V.% = 2.42						C.V.% = 3.46				
R ² = 0.99						R ² = 0.96				
R ² Adjusted = 0.97						R ² Adjusted = 0.95				
Predicted R ² = 0.81						Predicted R ² = 0.91				
Adequate precision = 33.59						Adequate precision = 36.48				

Table 4.6. ANOVA of q_e for full quadratic and reduced model

Source	Full quadratic					Reduced				
	Sum of Square	DF	Mean Square	F-value	p-value	Sum of Square	DF	Mean Square	F-value	p-value
Model	129.44	7	18.49	105.38	< 0.0001	126.93	2	63.47	187.82	< 0.0001
pH	25.06	1	25.06	142.84	< 0.0001	103.75	1	103.75	307.03	< 0.0001
Temperature	0.8321	1	0.8321	4.74	0.0814	-	-	-	-	-
pH × Temperature	23.18	1	23.18	132.13	< 0.0001	23.18	1	23.18	68.61	< 0.0001
pH ²	0.2052	1	0.2052	1.17	0.3289	-	-	-	-	-
Temperature ²	0.1190	1	0.1190	0.6783	0.4477	-	-	-	-	-
pH ² × Temperature	0.5002	1	0.5002	2.85	0.1521	-	-	-	-	-
pH × Temperature ²	1.15	1	1.15	6.54	0.0508	-	-	-	-	-
Residual	0.8773	5	0.1755			3.38	10	0.3379		
Lack of fit	0.1948	1	0.1948	1.14	0.3455	2.70	6	0.4494	2.63	0.1838
Pure Error	0.6825	4	0.1706			0.6825	4	0.1706		
Core Total	130.31	12				130.31	12			
C.V.% = 2.01						C.V.% = 2.78				
R ² = 0.99						R ² = 0.97				
R ² Adjusted = 0.98						R ² Adjusted = 0.97				
Predicted R ² = 0.82						Predicted R ² = 0.95				
Adequate precision = 41.84						Adequate precision = 47.02				

Abbreviations: ANOVA, analysis of variance; CV, coefficient of variance.

The Equations 4.5 and 4.6 present R% and q_e reduced models.

$$R\% = 44.68 + 8.61 \text{ pH} + 4.94 \text{ pH} \times \text{Temperature} \quad (4.5)$$

$$q_e = 20.89 + 4.16 \text{ pH} + 2.41 \text{ pH} \times \text{Temperature} \quad (4.6)$$

The “lack of fit test” provides a comparison between the “Residual Error” and the “Pure Error” obtained from the replicated experimental design points [42]. The significant lack of fit F-value suggests that there are still some unaccounted influential factors in the reduced models and adding additional terms might improve the model. This may also be due to the close replicate values that provide an estimate of pure error. Introducing a higher order term to the model could result in a more complicated model, with higher number of terms and insignificant lack-of-fit [4]. However, the resulting regression model would be a more complex model with more number of terms. Nevertheless, as it can be seen from Table 4.5 and 4.6, reduced models of R% and q_e indicate significant improvement in terms of lack of fit since the corresponding p-values were reduced from 0.456 to 0.196 for R% and from 0.346 to 0.183 for q_e , respectively. In addition, the R^2 values for reduced models for R% and q_e were calculated as 0.96 and 0.97, respectively, showing the goodness of fit and the accuracy of the model to predict the experimental data. Figure 4.3 shows the predicted vs. measured values for both models. According to Table 4.5 and 4.6, the difference between Adjusted R^2 and Predicted R^2 for both reduced models were less than 0.2 that showed a reasonable agreement of Adjusted R^2 with Predicted R^2 .

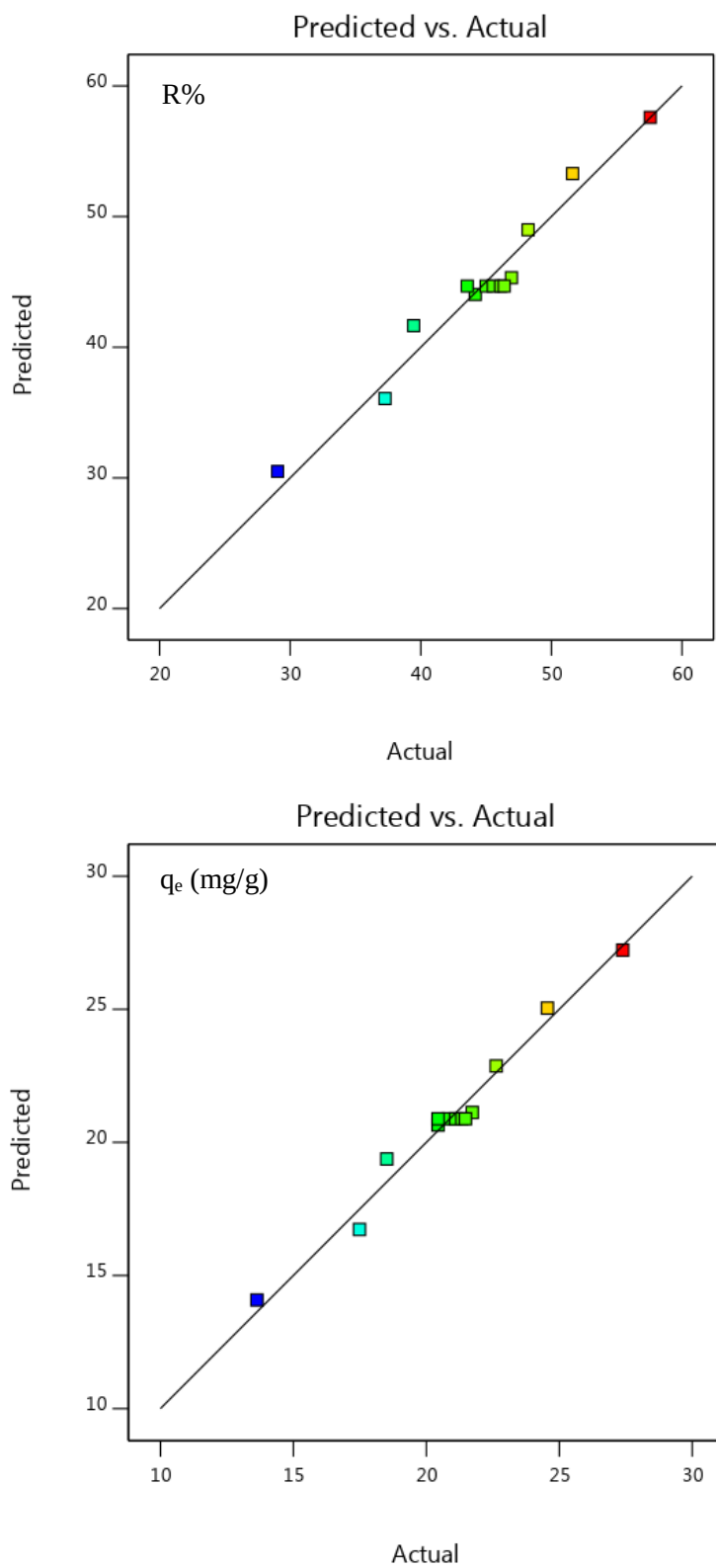


Figure 4.3. Predicted versus actual values for $R\%$ and q_e

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The signal to noise ratio can be checked by the Adequate Precision value. An adequate precision value greater than 4 confirms enough experimental design points and the qualification of the model to navigate the design space [44]. In this study, the Adequate Precision values for both reduced models are significantly larger than 4 (36.48 for R% and 47.02 for q_e) that confirms the models are satisfactory.

The coefficient of variance (C.V.%) compares the standard error of estimate to the mean value of the actual response. This parameter is usually employed to determine the reproducibility of a model. Normally a model with C.V.% less than 10% is considered as a reproducible model [44]. In this study, the C.V.% values for R% and q_e reduced models are estimated as 3.46 and 2.78 (C.V.% <10), respectively.

The normal probability of externally studentized residuals for R% and q_e , shown in Figure 4.4, was used to check whether the residuals follow the normal distribution or not. All points are approximately located in a straight line with reasonable scattering which proving a good fit [2].

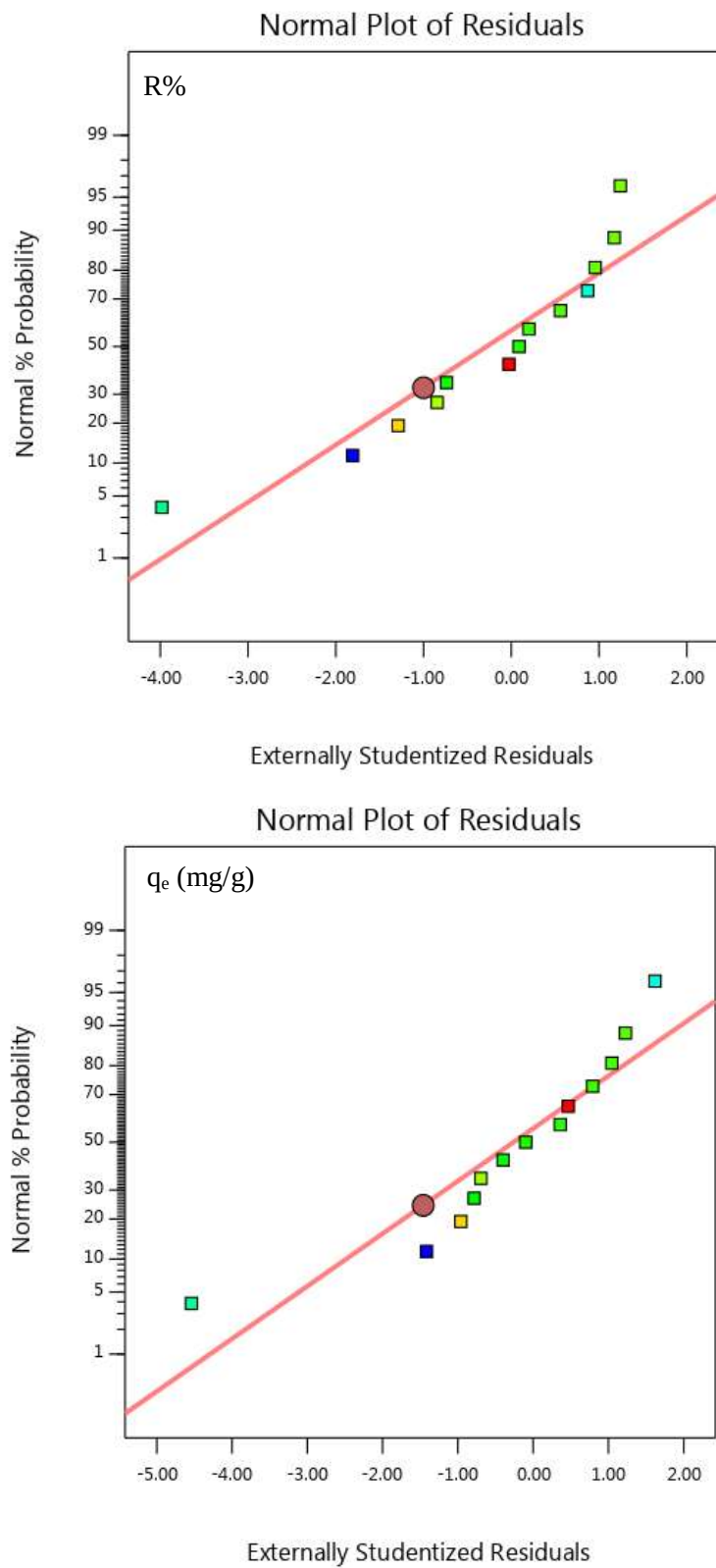


Figure 4.4. Normal probability of externally studentized residuals for R% and q_e

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To confirm that the assumptions for the ANOVA are met, diagnostic plots of residuals were produced and evaluated. The standardized residual versus runs (Figure 4.5) shows that there is no obvious pattern in any of the plots. A specific pattern would indicate that another influential factor is not accounted for in the model. The randomly scattered points across the graph prove the accuracy of both models and confirms that all assumptions for ANOVA analysis are met [6]. Considering the above discussion, the reduced quadratic models were considered to be appropriate.

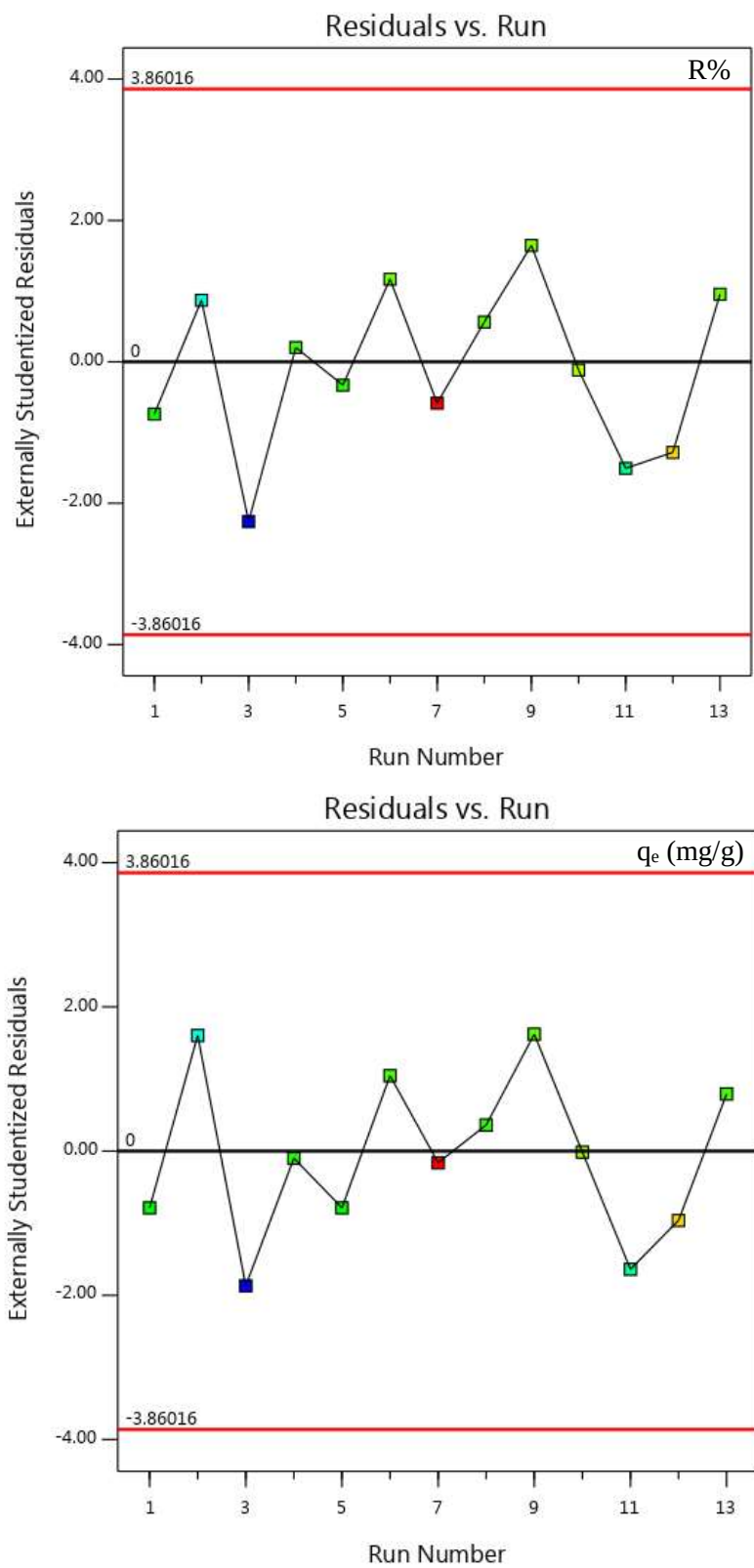


Figure 4.5. Diagnostic plot of studentized residuals versus runs for $R\%$ and q_e

4.3.6. Response surface methodology

Figures 4.6 and 4.7 show the three-dimensional response surface plots and two-dimensional contour plots for TAN removal (R%) and solid phase concentration (q_e). It can be concluded from the figures that TAN removal and solid phase concentration increase as the pH increases. However, the effect of temperature varies at different pH levels. At acidic and neutral pH, by reducing the temperature from 45 to 5 °C a slight increase in R% and q_e values can be observed. While at basic values of pH, R% and q_e values increase with increasing temperature. This behavior might be explained by the fact that at basic pH and higher temperature, due to the existence of more OH^- ions and the endothermic chemical reaction between OH^- ions and GO surface results in improving the adsorbent's performance [46, 47].

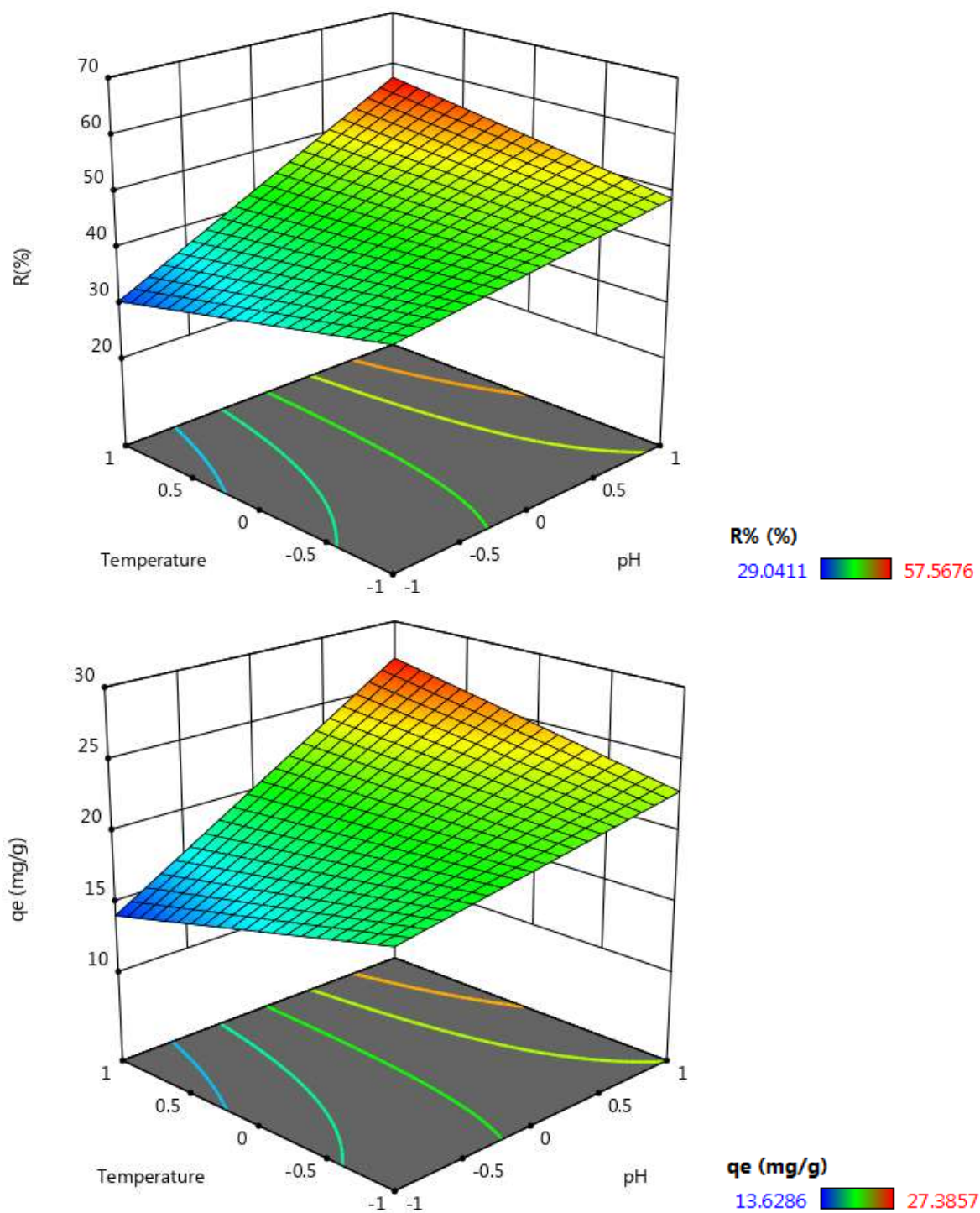


Figure 4.6. Three dimensional surface plot for $R\%$ and q_e

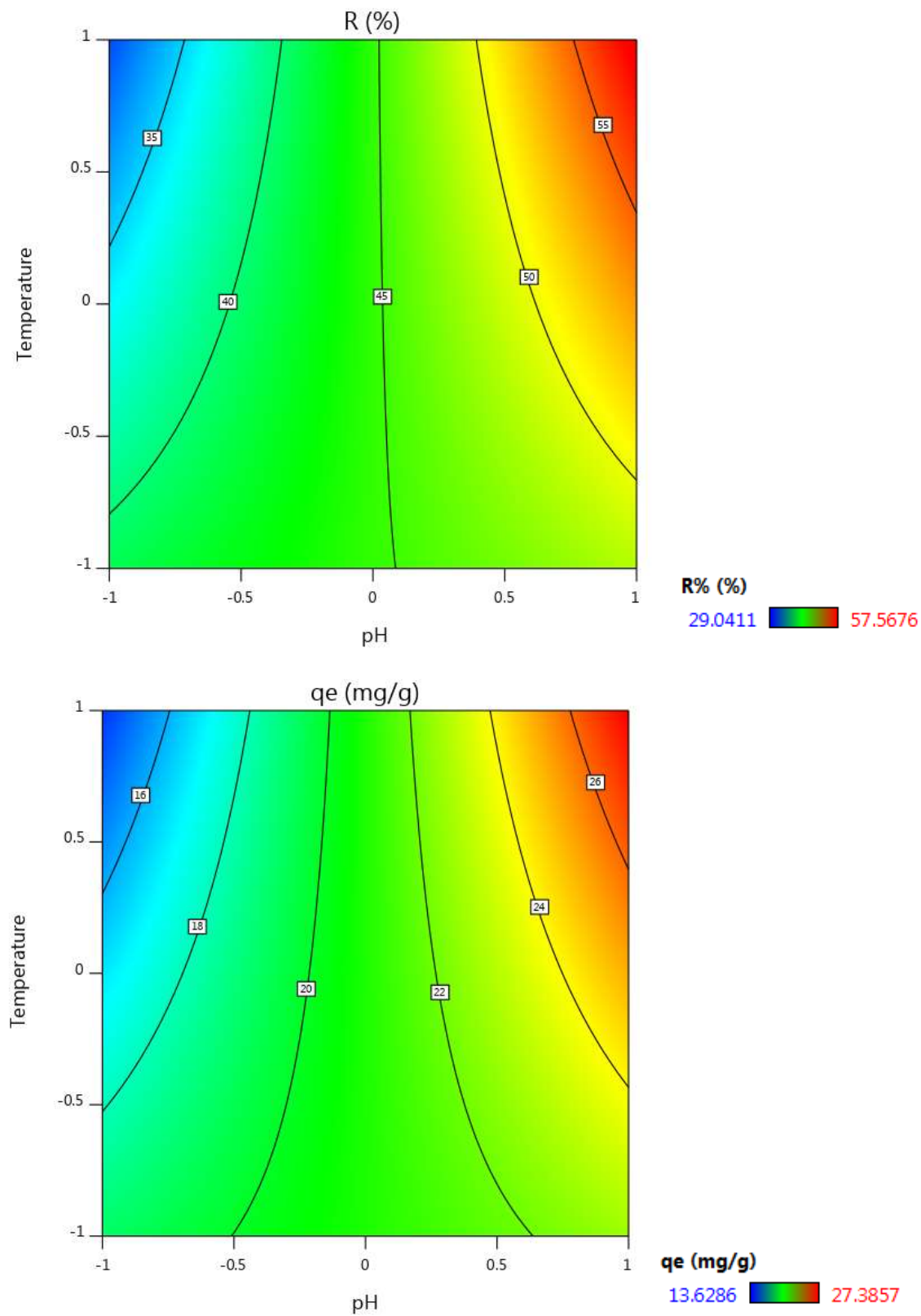


Figure 4.7. Two dimensional contour plot for R% and q_e

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Based on RSM, the optimum pH and temperature for TAN adsorption by GO-Na in terms of R^2 and q_e were determined as pH value of 8 and a temperature of 45 °C. The predicted values for R^2 and q_e at optimum conditions were verified by performing an additional experiment at optimum conditions. The results are summarized in Table 4.7. The laboratory experiments were in very good agreement with the predicted values by Design Expert as the error was 1.2% and 0.3% for R^2 and q_e , respectively. In addition, it is worth noting that the TAN adsorption capacity of GO-Na measured in this research is significantly higher compared to activated carbon reported by Li et al. [45].

Table 4.7. Verification of experiment at optimum pH and temperature
($C_0=50\text{mg/L}$ and adsorbent dose = 1g/L)

pH optimum = 8 and T optimum = 45 °C	R^2	q_e (mg/g)
Experimental value	57.56	27.38
Model response	58.23	27.45
Error	0.67 (1.2%)	0.08 (0.3%)

Note: ($C_0=50\text{mg/L}$ and adsorbent dose = 1g/L)

4.4. Conclusion

The present experimental study aimed at investigating the effects of influential factors on the application of sodium functionalized graphene oxide in TAN removal from aqueous phase. The adsorption process proved to be fast, the equilibrium condition was reached within 5 minutes, which can be promising from practical point of view. The statistical analysis of experimental data based on RSM showed that while temperature was not a significant factor, pH and the interaction of pH and temperature had a significant effect on TAN adsorption from aqueous solution. Coefficient of determination (R^2) values of 0.96 and 0.97 for R^2 and q_e , respectively, showed that the models were in very good agreement with the experimental data and the quadratic model was appropriate to describe the observed data. The optimum pH and

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temperature to reach the maximum values for R% (58.23%) and q_e (27.45 mg/g) were predicted by the model at 8 and 45 °C, respectively, and verified by laboratory experiments.

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4.SI. Supporting Information

4.SI.1. Chemicals

Ammonia TNTplus Vials (HR 2-47mg/L $\text{NH}_3\text{-N}$) were purchased from HACH. Synthetic graphite powder, -20+80 mesh, 99.9% (metals basis) was purchased from Alfa Aesar. Sulfuric acid (98%) and potassium permanganate were obtained from Anachemia. Phosphoric acid (85%) and hydrogen peroxide (30%) were purchased from Fisher Scientific.

4.SI.2. Instruments used in material characterization

The surface morphology of GO-Na adsorbent was observed by transmission electron microscopy (TEM, Tecnai Spirit TEM instrument). A Thermo Scientific Raman Microscope was utilized to collect Raman spectroscopy of the GO-Na. A Nicolet 6700 FT-IR spectrometer using an Attenuated Total Reflection (ATR) accessory was applied to record the Fourier Transform Infrared (FT-IR) spectra of GO-Na sample in the range of 4000 to 400 cm^{-1} (128 co-added scans).

4.SI.3. Material characterization

The morphology of GO-Na was shown in Figure S1. Single layer sheets of several hundreds of nanometers size are present together in this figure with folded and agglomerated sheets. It is also important to note that the quantification of specific surface area is difficult for graphene oxide materials because of their tendency to aggregation. As such, BET measurement are not relevant to the surface area of the material in solution. However, the observation of large numbers of thin sheets by microscopy allows the qualitative assessment that the adsorbent can be assumed to have a high surface area for ammonia removal.

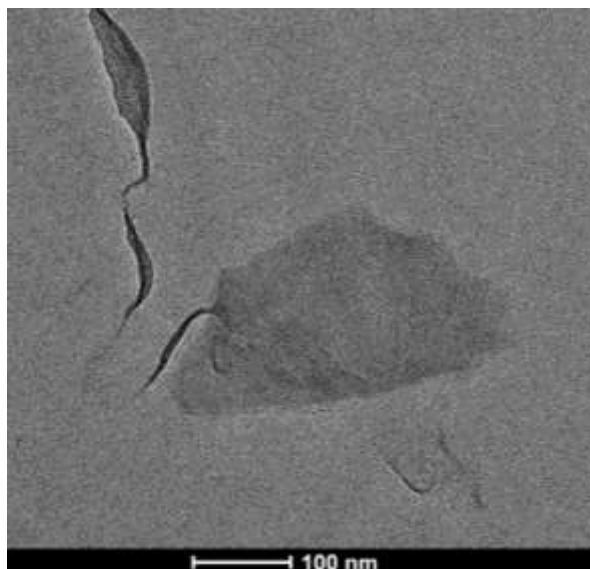


Figure SI.1. Typical TEM image of GO-Na.

The FTIR and Raman are the most common techniques to determine the typical characteristics of the GO material surface, which confirms the possibility of the adsorption process. Figure S2 illustrates the FTIR and Raman spectra of the adsorbent (GO-Na). The typical peaks for the main carbon species of GO can be seen in FTIR spectra. The band at 1750, 1577, 1214, and 972 cm^{-1} are assigned to the C=O stretch of the carboxylic acid group, C=C skeletal stretching, phenolic C-O, and epoxy CO, respectively [1]. Moreover, two typical peaks of GO material in Raman spectroscopy (D band and G band) can be seen in Figure 2. During the oxidation of graphene sheets to produce GO materials some of the C=C double bonds corresponding to sp^3 hybrid carbon atoms are broken and instead some sp^2 hybrid carbon atoms are created. G and D peaks in Raman spectra are the representatives of sp^2 and sp^3 hybrid carbon atoms, respectively [2].

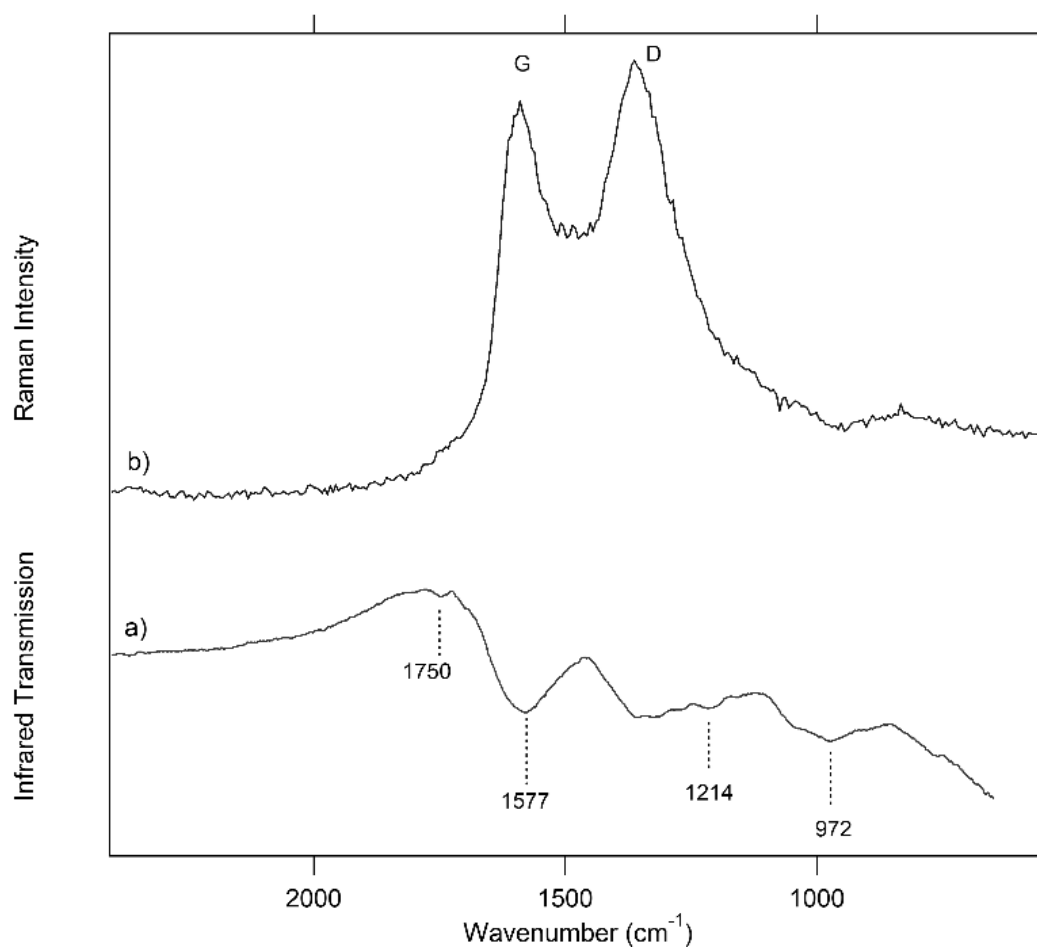


Figure SI.2. Infrared (a) and Raman (b) spectra of Go-Na. Characteristic IR peaks are labelled together with the D and G Raman bands.

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Chapter 5: Assessment of ion competition on ammonium removal from the simulated explosive impacted mining wastewater by sodium functionalized graphene oxide

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Abstract

The effects of competitive ions on ammonium removal from simulated explosive impacted mining wastewater were studied. The adsorption behavior of sodium, Na⁺, potassium, K⁺, and calcium, Ca²⁺, on sodium functionalized graphene oxide were studied in single-component and multi-component systems. The results were fitted on Langmuir isotherm model and showed that the maximum Langmuir adsorption capacities follow the order $K^+ \geq NH_4^+ > Ca^{2+}$ in single-component systems. Also, the reduction rates in multi-component systems fall in the decreasing order $K^+ \geq NH_4^+ \gg Ca^{2+}$. Increasing pH from 7 to 8.5 showed a slight improvement in the contribution of ammonium adsorption in the multi-component system. The results obtained from regeneration of the used material in multi-component system by NaCl showed a significant drop for calcium adsorption from 1.5 to 0.7 meq/g in the first cycle and then remained constant. In case of ammonium and potassium the adsorption capacity remained pretty constant with slight fluctuations.

Keyword: competitive adsorption, ammonium, potassium, calcium, graphene oxide, regeneration, wastewater treatment

5.1. Introduction

One of most essential elements for living organisms is nitrogen. However, the existence of excess nitrogen compounds in aqueous bodies creates some environmental problems such as eutrophication [1], depletion of dissolved oxygen in water resources [2], and toxicity to human and aquatic species [3]. Therefore, effective removal methods for these contaminants from water bodies are essential for the protection of public health and aquatic life. The most abundant nitrogen compounds in wastewater is ammonia nitrogen, which consists of unionized ammonia and ammonium cation, combined together referred to as total ammonia nitrogen (TAN) [4]. Adsorption is one of the most effective methods reported for TAN removal [4-14]. In a previous study, sodium functionalized graphene oxide, which is defined as single-atom layers of carbon with some sodium and oxygen containing functional groups on the surface of the flake, has been found to be as an efficient adsorbent for TAN uptake [15].

Sodium functionalized graphene oxide (GO-Na) is an effective adsorbent for ammonium from aqueous solution. However, the presence of other ions in real wastewater may affect its performance. Therefore, in the path to assess the viability of GO-Na as an adsorbent for TAN removal, there is an essential need to investigate the competitive adsorption of diverse ions on sodium functionalized graphene oxide. Depending on the type of wastewater, there are different kinds of ions that can compete with each other in an adsorption process. Mining wastewater usually contains a considerable amount of TAN because of the extensive use of nitrogen based explosives [16].

This study examines the performance of sodium functionalized graphene oxide for the competitive adsorption of ammonium from simulated explosive impacted mining wastewater (EIMWW). In addition, it is important to note that the main competitive ions in EIMWW are Na,

K, and Ca. Regeneration studies were performed to evaluate the efficiency of GO-Na during the consecutive loading/regeneration cycles.

5.2. Experimental

5.2.1. Materials and reagents

Synthetic graphite powder, -20+80 mesh, 99.9% (metals basis) was obtained from Alfa Aesar. Sulfuric acid (98%) and potassium permanganate were acquired from Anachemia. Nitric acid (70%), phosphoric acid (85%), hydrogen peroxide (30%), ammonium chloride (NH_4Cl), sodium chloride (NaCl), potassium chloride (KCl), calcium chloride (CaCl_2), hydrogen chloride (HCl), and sodium hydroxide (NaOH) were purchased from Fisher Scientific. Nessler reagent and Nessler salt were acquired from Hach.

5.2.2. Analytical methods

The NH_4^+ concentration in the solution was measured by Nessler standard method 4500- NH_3 [17]. In this method, stabilizing Rochelle salt is necessary to prevent precipitation followed by the addition of Nessler reagent to react with NH_4^+ . First, a calibration curve is required prior to the actual TAN measurements. To construct the calibration curve, different solutions with TAN ranging over 1-10 ppm were prepared. Then, the concentrations of the samples were measured and dilutions were performed for the samples with the concentrations of greater than 10 mg/L to become in range of 1-10 ppm. Briefly, 0.25 mL of Rochelle salt was added to 10 mL of each solution (a blank solution, calibration solutions, and experimental solutions). After 5 minutes, 0.2 mL of Nessler reagent was added to the solutions and kept without any agitations for 10 minutes to react with ammonium and turn to yellow. Finally, the blank sample consisting of 10 mL of distilled water, Rochelle salt, and Nessler reagent was used to zero the spectrophotometer at wavelength absorbance of 425 nm followed by measuring the concentrations of the calibration

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and experimental solutions. A PerkinElmer PinAAcle 500 Flame Atomic Adsorption Spectrometer was used to measure the concentrations of Na^+ , K^+ , and Ca^{2+} at wavelength of 589, 766, and 422 nm, respectively.

5.2.3. Preparation of adsorbent

The GO was synthesized by the improved Hummer's method at room temperature (25 °C) [18]. Then, the functionalized GO-Na was prepared according to the procedure of a previous work [15].

5.2.4. Characteristics of the explosive impacted mining wastewater

The characteristics of an explosive impacted mining wastewater (EIMWW) from another study were used as reference to prepare simulated wastewater [18]. According to Table 5.1, the concentrations of Na^+ , K^+ , and Ca^{2+} are considerable and the rest of cations can be neglected. Therefore, the focus of this study is just on the competition of these three cations with ammonium. The simulated wastewater for the adsorption experiments was prepared by dissolving NH_4Cl , NaCl , KCl , and CaCl_2 in deionized water.

Table 5.1. Characteristics of the EIMWW [19]

Parameter	Concentration (mg/L)	Concentration (meq/L)
Si^{4+}	3.56	0.51
Al^{3+}	0.08	0.01
Fe^{3+}	0.70	0.04
B^{3+}	0.07	0.02
Ca^{2+}	78.1	3.90
Mg^{2+}	12.7	1.04
Sr^{2+}	2.10	0.05
NH_4^+	70.2	3.9
Na^+	270	11.8
K^+	112	2.85
HCO_3^-	300	4.92
SO_4^{2-}	1050	21.9

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5.2.5. Batch adsorption experiments

The batch adsorption experiments were performed in 250 mL Erlenmeyer flasks while shaking on a shaker at 150 rpm, neutral pH (around 7), and room temperature (around 25°C). Each experimental data point presented in this study is the average of three replicates. A previous study showed that adsorption by GO-Na was fast and complete in less than 10 minutes [15]. For this study, after 2 hours of mixing, the solutions were filtered through a Van Waters and Rogers (VWR) glass filter over the vacuum filter. The filtrate Na^+ , K^+ , and Ca^{2+} concentrations were measured by atomic adsorption spectroscopy and the NH_4^+ concentration was determined by the Nessler method.

Then, the removal percentage (R%) and solid phase concentration (q_e in mg/g) were calculated according to the following expressions [20, 21]:

$$R\% = \left(\frac{C_0 - C_e}{C_0} \right) \times 100 \quad (5.1)$$

$$q_e = \left(\frac{C_0 - C_e}{W} \right) \times V \quad (5.2)$$

where C_0 and C_e (mg/L) are the initial and equilibrium concentration of the specific ion in solution, respectively, W (g) is the mass of adsorbent, and V (L) is the volume of solution.

5.2.6. Isotherm study

Stock solutions of each ion (1000 mg/L) were prepared separately. Different concentrations of each component were obtained by dilution of 1000 mg/L of stock solution to study the isothermic adsorption of single-component systems in the range of 10 to 500 ppm. Finally, a simulated wastewater which contains 78.1 mg of Ca^{2+} /L, 70.2 mg of NH_4^+ /L, 270 mg of Na^+ /L, and 112 mg of K^+ /L was prepared and diluted 5 times with dilution factor of 3:4 each time to investigate the isothermic adsorption behavior of a multi-component system.

5.2.7. Effect of pH

The effects of pH on the multi-component system were studied at two critical pH points including 7 and 8.5. These were selected based on a previous study [22], which suggests that at acidic pH, the adsorption of ammonium cation decreases by competition of the H^+ in the solution to occupy the free active sites on the surface of GO-Na. Furthermore, at the basic pH of more than 8.5, considerable amounts of ammonium cations convert to dissolved ammonia then ammonia gas in two step process and exit the system through volatilization, causing errors in the adsorption results. In the pH range of 7 to 8.5 most of the TAN exists in the system is in form of ammonium cation, but based on our previous study, adsorption of NH_4^+ is improved in the upper limit [22]. Therefore, these two critical values of pH were selected for this study to investigate their potential effects on the simulated EIMWW wastewater.

5.2.8. Regeneration study

The used adsorbent for multi component system was regenerated by 10%W of NaCl solution for 30 minutes. The regenerated material was filtered in a vacuum filter. The filtrate solution was kept in order to measure the concentrations of ions exchanged through the regeneration process. After washing the regenerated material by deionized water, it was placed in the oven to be dried. Then the dried material was used for the next adsorption cycle. The equilibrium concentration of ions remaining in the multi-component system were measured. Then, the removal percentages and solid phase concentrations of different components were calculated. This process was repeated for 3 consecutive cycles.

5.3. Results and Discussion

5.3.1. Adsorption Isotherms of Single-Component Systems

Based on previous studies, Langmuir isotherm is the most practical model to describe the adsorption pattern of a cation on the surface of GO-Na due to the physical properties of the adsorbent's surface [15, 22]. Therefore, the data from the isothermal adsorption experiments of NH_4^+ , K^+ , and Ca^{2+} on GO-Na were fitted to the Langmuir equation which is expressed as below [20, 23]:

$$\text{Langmuir Equation: } q_e = \frac{K_{ad}q_{Max}C_e}{1 + K_{ad}C_e} \quad (5.3)$$

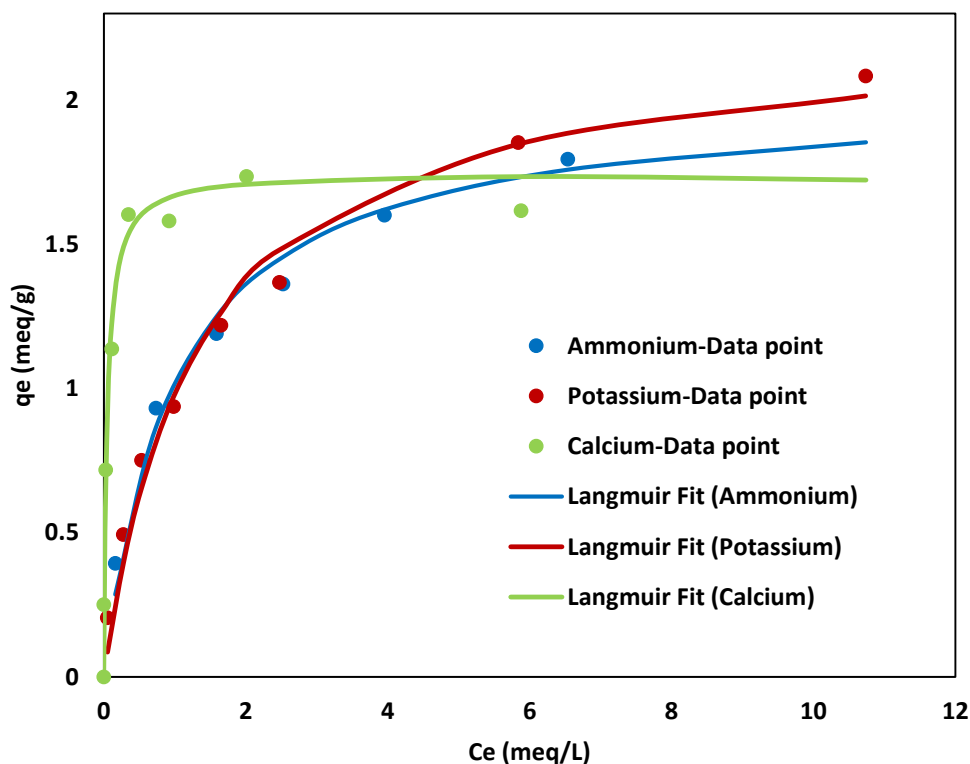
where C_e (meq/L) is the equilibrium liquid phase TAN concentration; K_{ad} (L/meq) is the Langmuir adsorption equilibrium constant related to the affinity of the binding site and energy of adsorption; q_e (meq/g) is the equilibrium solid phase concentration of GO-Na; and q_{max} (meq/g) is the maximum adsorption capacity in the Langmuir model.

Figure 5.1 and Table 5.2 present the adsorption isotherms and the Langmuir isotherm constants of each species measured in single-component solutions, respectively. All adsorption isotherms fit the Langmuir model well with high regression correlation values (>0.99). GO-Na shows much higher affinity to adsorb calcium ($K_{ad} = 20.64$ L/meq) compared to ammonium and potassium with K_{ad} of 1.01 and 0.74, respectively. However, the values of q_{max} from Table 5.2 imply that the maximum adsorption capacity of these three cations follows the order $\text{K}^+ > \text{NH}_4^+ > \text{Ca}^{2+}$.

Although the adsorption behavior of Na^+ was investigated, the observations indicate that GO-Na does not further adsorb any sodium ions. In fact, because GO-Na is saturated with sodium, the adsorbent releases Na^+ into solution at this concentration ranges.

Table 5.2. Isotherm constants and regression correlations in single-component system

Component	K_{ad} (L/meq)	q_{Max} (meq/g)	R^2
NH_4^+	1.01	2.13	0.992
K^+	0.74	2.33	0.996
Ca^{2+}	20.64	1.75	0.991

**Figure 5.1.** Langmuir adsorption isotherms of different single components on GO-Na
Conditions: at room temperature, pH=7, and dose = 1g GO-Na/ L

5.3.2. Adsorption Isotherms of Multi-Component Systems

The isothermal adsorption behavior of NH_4^+ , K^+ , and Ca^{2+} on the surface of GO-Na in a multi-component system was examined in order to investigate the effect of ionic interactions and competition on the sorption process. In this regard, the ratio of $\frac{q_i^{multi}}{q_i^{single}}$ was utilized in which q_i^{multi}

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and q_i^{single} are the sorption capacity for component i in multi- component system and single-component system, respectively [24].

If $\frac{q_i^{multi}}{q_i^{single}} > 1$, it means that the presence of other ions will promote the sorption of component i .

If $\frac{q_i^{multi}}{q_i^{single}} = 1$, it can be concluded that the introduction of other ions does not have any effects on the adsorption of component i .

If $\frac{q_i^{multi}}{q_i^{single}} < 1$, it expresses that other ions compete with component i to occupy the active sites on the surface of the adsorbent, suppressing the adsorption of component i in the multi-component system [25].

The competition of an ion in a multi-component system can also be evaluated by the competitive equilibrium coefficient (a_i^{multi}) which is defined as the equilibrium ratio of adsorbed component i to all adsorbed components in the multi-component system. The competitive equilibrium coefficient of component i among n components can be expressed as follow [24]:

$$a_i^{multi} = \frac{\frac{q_i^{multi}}{C_{0i}}}{\sum_{j=1}^n \frac{q_j^{multi}}{C_{0j}}} \quad (5.4)$$

where q_i^{multi} and q_j^{multi} are the amounts of adsorbed components i and j in the multi-component system at equilibrium, respectively; C_{0i} and C_{0j} are the initial concentrations of component i and j in the multi-component system, respectively.

The non-competitive equilibrium coefficient of component i in the single-component system (a_i^{single}) is calculated as the following equation [24]:

$$a_i^{single} = \frac{\frac{q_i^{single}}{C_{0i}}}{\sum_{j=1}^n \frac{q_j^{single}}{C_{0j}}} \quad (5.5)$$

In which, q_i^{single} and q_j^{single} are the amounts of adsorbed components i and j in the single-component system at equilibrium, respectively; C_{0i} and C_{0j} are the initial concentrations of component i and j in the single-component system, respectively.

The percent of adsorption reduction (ΔY) expressed as follow can be applied in order to compare the adsorption behavior of component i in the multi-component system with the amount in the single-component system [24].

$$\Delta Y = \frac{a_i^{single} - a_i^{multi}}{a_i^{single}} \times 100\% \quad (5.6)$$

where, a_i^{single} and a_i^{multi} are the non-competitive and competitive equilibrium coefficient in single and multi-component system, respectively.

The competitive constants of single and multi-component system are summarized in Table 5.3. Furthermore, for more clarification, the Langmuir fit of NH_4^+ , K^+ , and Ca^{2+} in single and multi-component systems are shown in Figure 5.2.

In all cases, the value of $\frac{q_i^{multi}}{q_i^{single}}$ is found to be < 1 which suggests that the adsorption capacity of GO-Na for all the components is suppressed by the presence of other cations in the multi component system as compared to single component system. However, as can be seen in Figure 5.2, the amount of suppression in multi component system varied for different cations. For instance, calcium with $\frac{q_i^{multi}}{q_i^{single}}$ value of 0.91 shows the lowest decrease compared to potassium and ammonium with the $\frac{q_i^{multi}}{q_i^{single}}$ values of 0.2 and 0.18, respectively. These results confirm the results obtained from the rate of adsorption reduction as calcium has the lowest ΔY value of

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9.42%, while potassium ($\Delta Y = 80.07\%$) and ammonium ($\Delta Y = 81.72\%$) show a much larger decrease. The data in Table 5.3 indicates that there are specified active sites on the surface of GO-Na that can be occupied by different cations and the cation adsorption depends on their selectivity and tendency to be adsorbed on the surface of adsorbent. In case of competitive adsorption in multi component system, calcium has the highest tendency to be adsorbed on the surface of the adsorbent, which limits the available active sites for ammonium and potassium ions. Zheng and Wang have reported the same behavior for ammonium adsorption by chitosan hydrogel in presence of multivalent cations [26]. Also, Rat-Valdambrini et al. supported this idea that the multivalent cations have more negative effect on ammonium adsorption [23].

Table 5.3. The competitive constants of single and multi-component system at pH=7

Component	C_0 (mg/L)	$q_i^{\text{multi}}/q_i^{\text{single}}$	a_i^{single}	a_i^{multi}	ΔY (%)
NH_4^+	70	0.18	0.21	0.07	81.72
K^+	112	0.2	0.25	0.09	80.07
Ca^{2+}	78	0.89	0.54	0.84	11.43

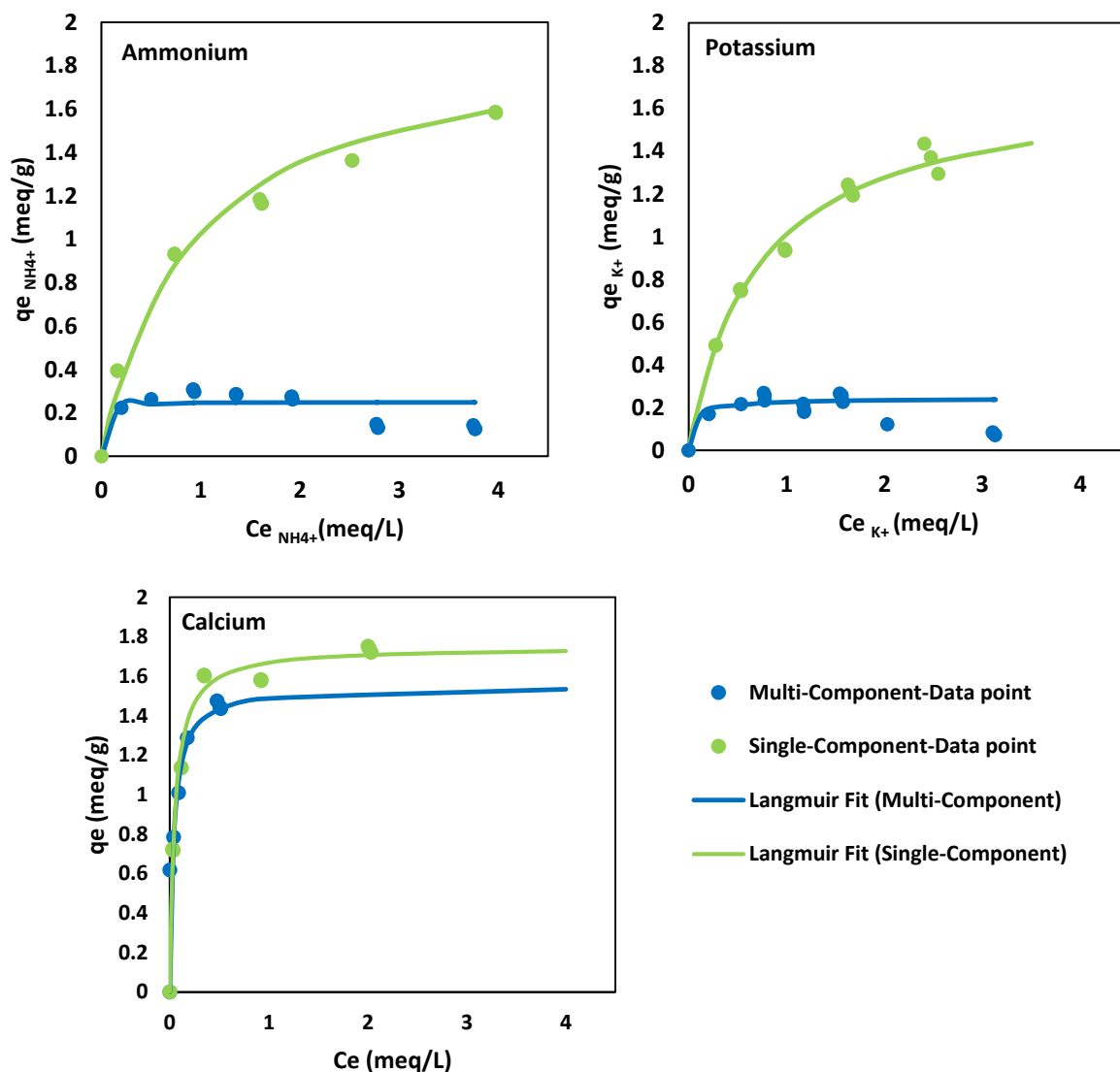


Figure 5.2. Langmuir adsorption isotherms of each component on GO-Na in single and multi-component system

Conditions: at room temperature, pH=7, and dose = 1g GO-Na/ L

5.3.3. Effect of pH

Figure 5.3 shows the effect of pH on solid phase concentration at equilibrium condition and the adsorption contribution percentage of each component in the multi-component system. According to Figure 5.3, increasing the pH causes no significant effect either on the adsorption of potassium or on its contribution percentage. From Figure 5.3, it can be concluded that by

increasing the pH a slight improvement is detected in ammonium and calcium adsorption from 0.08 to 0.2 meq/g and 1.52 to 1.78 meq/g, respectively. However, the contribution percentage of calcium drops while the contribution percentage of ammonium increases which means that increasing the pH has stronger effect on the improvement of ammonium adsorption compared to calcium adsorption in the multi-component system. It can be explained by the fact that at basic pH due to the existence of more OH^- ions and the chemical reaction between OH^- and GO-Na surface might result in creating specific active sites on the surface of adsorbent which can be a favorable location for ammonia to be occupied in forms of amide group [22].

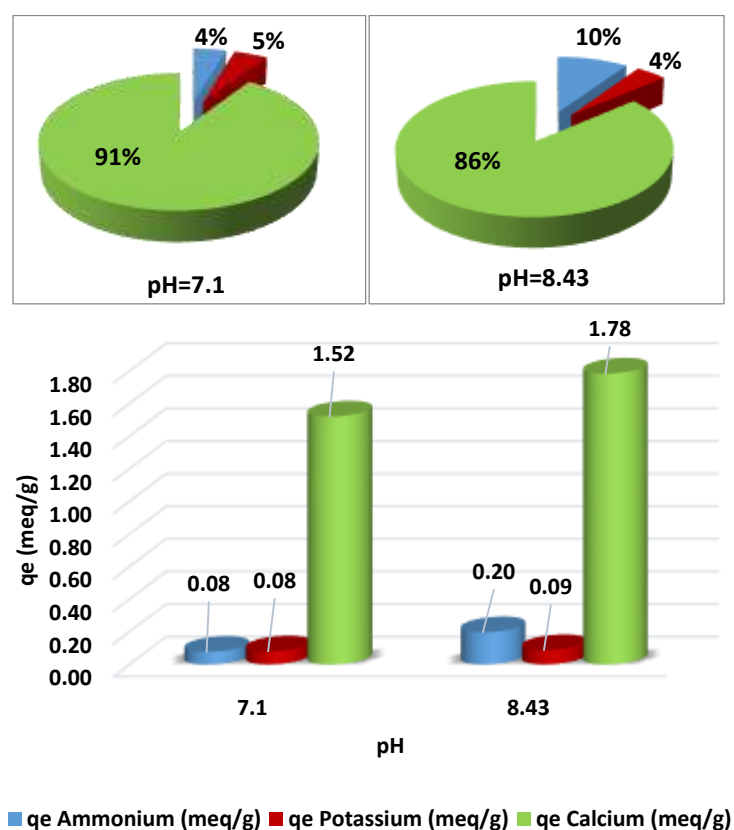


Figure 5.3. Effect of pH on the q_e and the adsorption contribution percentage of each component in the multi-component system ($C_0 \text{ NH}_4^+ = 70 \text{ mg/L}$, $C_0 \text{ K}^+ = 112 \text{ mg/L}$, and $C_0 \text{ Ca}^{2+} = 78 \text{ mg/L}$)
Conditions: at room temperature and dose = 1g GO-Na/L

5.3.4. Regeneration study

Figure 5.4 presents the efficiency of the used adsorbent after regeneration with sodium chloride for the three subsequent regeneration cycles of the multi component system. After regeneration of the used material, the efficiency of GO-Na for the adsorption of calcium significantly dropped from 1.5 to 0.7 meq/g and remains constant in the next subsequent regeneration cycles. However, the capacity of GO-Na for the adsorption of ammonium and potassium stays almost constant with a slight fluctuation in each cycle.

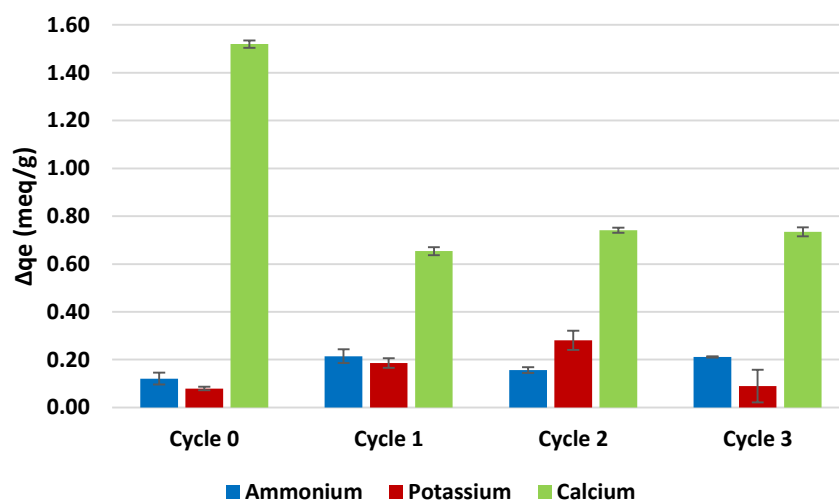


Figure 5.4. Regeneration cycle of GO-Na for cation removal in multi-component system
Conditions: at room temperature, pH=7, and dose = 1g GO-Na/ L

To have a better understanding of the regeneration process and to estimate how much of each ion would be exchanged with sodium during the regeneration process, the equilibrium concentration of each component released to the regeneration solution were measured and summarized in Table 5.4. In the first two cycles no ammonium is exchanged but after two subsequent cycles it starts exchanging with sodium. This might be explained by the existence of two different kinds of sites that contribute to adsorb ammonium on the surface of GO-Na including ion exchange

and formation of amide group [15]. In the multi-component system most of the active sites participating in the ion exchange are occupied by calcium and potassium which can easily be exchange with sodium in the concentrated sodium chloride solution. Under this competitive conditions, the adsorption of ammonia on the surface of GO-Na seems first associated with amide formation on the surface which remains on the structure of GO-Na during the regeneration process. After two cycles, when all the potential active sites related to amide forming are occupied by ammonia, its adsorption is also dominated by ion exchange, which results in the releasing of ammonia to the concentrated sodium chloride solution during regeneration.

Table 5.4. The equilibrium concentrations of each component released to the regeneration solution

Component	C_e (meq/L) Cycle1	C_e (meq/L) Cycle2	C_e (meq/L) Cycle3
NH_4^+	0.00 ± 0.000	0.00 ± 0.000	0.04 ± 0.002
K^+	0.10 ± 0.004	0.10 ± 0.004	0.13 ± 0.004
Ca^{2+}	0.71 ± 0.011	0.47 ± 0.003	0.38 ± 0.008

5.4. Conclusion

The isothermic and competitive adsorption performance of counter ions with ammonium: calcium, potassium, and sodium on the surface of GO-Na in single-component and multi-component system were examined. According to the results obtained from single-component system, calcium shows the lowest value for q_{Max} compared to ammonium and potassium. However, the adsorption affinities of these cations on the surface of GO-Na follow the order $\text{Ca}^{2+} \gg \text{NH}_4^+ > \text{K}^+$. The multi-component results also revealed that calcium has the lower reduction value of around 10 % while, both ammonium and potassium show 80% reduction in a multi-component system, which indicates the fact that most of the active sites on the surface of GO-Na are occupied by calcium cations in the multi-component system.

Based on the pH studies, increasing the pH of the simulated explosive impacted mining wastewater from 7 to 8.5 causes a slight improvement in the contribution of ammonium

Chapter 5: Ion-Competition

adsorption in the multi-component system. In fact, the presence of OH^- ions creates more favorable active sites for ammonium adsorption associated with forming of amide group on the surface of GO-Na.

The adsorption efficiency of the used GO-Na in multi-component system during the consecutive cycles of regeneration with NaCl was studied. The results revealed that the capacity of adsorbent for both ammonium and potassium removal was pretty constant with slight fluctuations during the consecutive cycles of regeneration. But, in case of calcium, the adsorbent capacity showed a significant drop from 1.5 to 0.7 meq/g in the first cycle of regeneration and then remain constant in the next cycles.

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Chapter 6: Conclusions and Recommendations for future work

6.1. Conclusions

The following conclusions can be drawn from this research study for the application of graphene based materials for TAN removal from wastewater:

- In this study, graphene oxide was synthesized according to Improved Hummer's Method. Then, considering the fact that the ammonium cation has high competency with sodium cation, the GO material has been treated by sodium hydroxide in order to obtain sodium functionalized graphene oxide as a potential adsorbent for TAN removal from wastewater.
- The adsorption results indicate that the adsorption isotherm is best fitted to the Langmuir isotherm with the maximum adsorption capacity of 32.02 mg/g. Comparing to other studies on TAN removal, GO-Na showed better performance than many other common used adsorbents such as resins, zeolites, and activated carbon.
- The kinetic study showed that the adsorption process is fast; hence it is favorable from practical points of view. The adsorption kinetics are well fitted to a pseudo-second order model suggesting that the chemical reaction is the rate limiting step. Also, the mechanism of adsorption, best described by the Elovich model, indicates chemical reaction is controlling the rate process which confirms the compatibility with the results obtained from pseudo-second order model.
- Thermodynamic parameters demonstrate that this process is an exothermic and spontaneous reaction in the nature with an increasing randomness at the solid-liquid interface.

Chapter 6: Conclusions and Recommendations

- The ranges of Gibbs free energy and adsorption energy suggest that this process mainly consists of ion exchange with weak interaction between the GO surface and ammonium cation; facilitate the regeneration of GO-Na with a natural, inexpensive, and environmental friendly salt (NaCl). The results implied that GO-Na can still remain effective after several cycles of regeneration.
- The effects of influential factors such as contact time, adsorbent dosage, initial TAN concentration, pH, and temperature on the performance of GO-Na for TAN removal were investigated. The results demonstrated that the adsorption process is very fast and the equilibrium condition can be reached in a few minutes. Increase in adsorbent dosage and decrease in TAN concentration resulted in improvement in removal percentage. However, the solid phase concentration changed in a reverse direction. pH and temperature are the two factors which have some interactions on each other. Therefore, response surface methodology was utilized to study the impacts and interacts of these two critical factors in order to estimate the optimum value for R% and q_e . The optimum pH and temperature to reach the maximum amounts were predicted by the software at 8 and 45 °C, respectively.
- The single solute adsorption performance of three competitive cations (calcium, potassium, and sodium) on the surface of GO-Na in a single-component system were examined. GO-Na has much higher affinity to adsorb calcium with K_{ad} value of 94.02 L/meq while the K_{ad} value for ammonium and potassium was reported around 1.01 and 0.74 L/meq, respectively.
- The behavior of ammonium adsorption on the surface of GO-Na in the presence of competitive cations in a multi component system (a simulated explosive impacted mining

wastewater) was studied. The rate of adsorption reduction in a multi-component system compared to the single-component system indicates that most of the active sites on the surface of GO-Na are occupied by calcium cation with the low reduction value of around 10%, while, both ammonium and potassium show 80% reduction in the multi-component system.

- The impacts of pH on ion-competition in the simulated explosive impacted mining wastewater was investigated. Increasing the pH from 7 to 8.5 causes a slight improvement in the contribution of ammonium adsorption in the multi-component system which is possibly associated with the creation of more active sites in presence of OH^- ion which might be favorable active sites for ammonium adsorption on the surface of GO-Na in the form of amide groups.
- Finally, the efficiency of the used adsorbent during the consecutive cycles of regeneration with NaCl was studied. Both ammonium and potassium show fairly constant behavior with slight fluctuations during the consecutive cycles of regeneration. In the case of calcium, the adsorbent capacity shows a significant drop from 1.5 to 0.7 meq/g in the first cycle of regeneration and then remain constant in the next cycles.

6.2. Recommendations for future works

There are some other aspects that may improve the present study in the future to make this novel material more viable in various industrial sections.

- Considering the fact that GO-Na is an expensive material in terms of production, it would be a good idea to find a way to make a nano-composite of this material with an environmental friendly and economical material such as silica to not only use the benefits

of GO material as an efficient adsorbent for many contaminants removal, but also, reduce the GO demand and cost.

- The micro structure of GO materials makes the filtration process difficult. Therefore, a practical option would be immobilizing GO with an effective immobilizer which itself has the ability to adsorb ammonium. Because, the immobilization may block some of the active sites on the surface of GO powder. By the fact, it may result in facilitating the filtration and separation of GO powder.
- Another option in order to facilitate the separation process is making a magnetic GO-Na material to be able to separate the powder by just a simple magnet.
- According to the present study GO-Na shows high tendency to adsorb multivalent cations. So, this material can be a good choice for the contaminants uptake such as heavy metals and some of the multivalent cationic dyes and pharmaceuticals.

Appendix 1: Screening and synthesis of potential adsorbents for ammonium removal

AP1.1. Introduction

The starting research idea was the application of nanocomposite materials for ammonia removal from the aqueous phase. As such, a number of different kinds of potential adsorbents for ammonium removal including silica-based materials, carbon-based materials, and commercial resins were considered. In this regard, some specific materials from each group were selected to study their potential capacity for ammonium removal from the aqueous phase. SBA-15, Graphene oxide, and Dowex were selected as the representative of silica based materials, carbon based materials, and commercial resins, respectively. Then, some modifications were performed to the structure of the selected materials in order to improve their adsorption performance. Graphene oxide was extensively examined, which is the main focus of the thesis. Relevant information on SBA-15 and Dowex is presented in this appendix.

AP1.2. Material Synthesis

AP1.2.1. Chemicals and Reagents

Pluronic P123 ($\text{PEO}_{20}\text{-PPO}_{70}\text{-PEO}_{20}$, $M_{\text{av}} = 5800$) block copolymer nonionic surfactant, Tetraethyl orthosilicate (TEOS, 99%), and Dowex® 50W X8 were purchased from Sigma Aldrich. Anhydrous ethanol, methanol, succinic anhydride, and 3-aminopropyltriethoxysilane were purchased from Merck. Nitric acid (HNO_3 , 68-70%) and hydrobromic acid (HBr, 48%) were redeemed from VWR. Sulfuric acid (H_2SO_4 , 98%), hydrogen chloride (HCl, 37%), and potassium permanganate (KMnO_4) were purchased from Anachemia. N,N'-dimethylformamide (DMF, 99%), oxalic acid, and Thiourea were redeemed from Alfa Aesar. Hydrogen peroxide

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(H₂O₂), sodium hydroxide (NaOH), and sodium nitrate (NaNO₃) were purchased from Fisher Scientific.

AP1.2.2. Synthesis of SBA-15

In order to synthesize SBA-15, 4 gr of Pluronic (P123) was dissolved in a mixture of 90 mL of HCl (2M) and 21 mL of distilled water and maintained under stirring (700 rpm) for 5 hours at room temperature. Then, 6.4 gr of tetraethyl orthosilicate (TEOS) was gently added to the foregoing solution and stirred for 24 hours at 40 °C. The mixture was poured in a sealed glass bottle and placed in an oven at 100 °C for a day. After allowing the mixture to cool down to room temperature, the white solid product was washed over vacuum filter to remove the surfactant. Finally, the white powder was placed in a furnace to be calcinated in air at 600 °C for 6 hours to completely remove the surfactant template [1].



Figure AP1.1. SBA-15 mesoporous silica

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AP1.2.3. Surface modification of SBA-15 by Carboxylic group

To obtain SBA-15-COOH, it is necessary to first modify the surface of SBA-15 by amine groups and then put the carboxylic functions on its surface. In this regard, 0.1 gr of SBA-15 was dispersed in 20 mL of anhydrous ethanol and stirred for 1 hour at room temperature. Then, 1 mL of 3-aminopropyltriethoxysilane was added to this solution and stirred at 80 °C for 6 hours. The white solid was filtered and washed with ethanol and dried at room temperature [2]. The dried white powder was labeled as SBA-15-NH₂. The next step was carboxylic modification of SBA-15-NH₂. 0.1 gr of amino-functionalized SBA-15 was added to 50 mL of N,N'-dimethylformamide (DMF) solution which contains 2%wt succinic anhydride. The mixture remained under stirring for a day at room temperature. Finally, the product was collected by centrifugation, washed with DMF and dried at room temperature [2].

AP1.2.4. Synthesis of Dowex-silica-nanocomposite

3.96 gr of tetraethyl orthosilicate (TEOS) as a silica source was gently dissolved in a mixture containing 2 mL of distilled water and 0.5 mL of HCl (0.04 M). It was stirred (1000 rpm) for 1 hour at room temperature to completely dissolve chemicals and obtain a homogenous solution. In a separate container, 0.8 gr Dowex resin was added to 2.5 mL of NaOH (0.4 M) and stirred for an hour at room temperature. Then, the solution containing silica source was rapidly added to the solution containing Dowex and stirred at 50-80 °C for half an hour. Increasing the temperature from 50 to 80 °C results in evaporation of the solvent and production of small granular particles of Dowex-SiO₂. Then, the obtained particles were placed in an oven at 95 °C for 2 days. Resulting composite was then acidified by mixing with 1 mL of HCl (3.5 M) and washed with distilled water four times. As a final treatment, the material was treated by HNO₃ (25%wt) for

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overnight at 75 °C and the next day washed with distilled water. Final product was dried under vacuum at 100 °C for a day [3].



Figure AP1.2. Dowex® 50W X8 and Dowex-silica nanocomposite

AP1.2.5. Synthesis of graphene oxide prepared according to Modified Hummer's method

1 gr of graphite was mixed with 46 mL of H_2SO_4 at 10 °C in an ice bath. After 40 minutes, 1 gr of NaNO_3 was added to the acid containing solution and stirred for 2 hours. 6 gr of KMnO_4 was then added to the solution and stirred for 2 extra hours. In order to increase the temperature to 35 °C, the water bath was removed. Then, 80 mL of deionized water was added to the mixture drop by drop, which resulted in rising the temperature to 90 °C. It is important to note that since the addition of water to acid solution is dangerous, an ice bath for controlling the sudden increase in temperature is necessary. After 30 minutes when the temperature started to drop to 40 °C, 200 mL of extra water was added to the mixture which was followed by addition of 20 mL of H_2O_2 to react with the excess KMnO_4 in the solution. The warm solution was washed and centrifuged at 5000 rpm for 10 minutes. The precipitants were dried in oven at 50 °C. Then the powder was dispersed in 100 mL of NaOH (14 Mm) while the temperature was increased to 70 °C. After

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centrifuging the solution at 12000 rpm the material was separated and treated with 100 mL of HCl (14 M) at 70 °C for an hour to remove all the impurities. Finally, the mixture was centrifuged and washed with deionized water and dried at 50 °C [4].

AP1.2.6. Surface modification of GO by Carboxylic group (GO-COOH)

75 mg of GO was dispersed in 30 mL of deionized water and ultrasonicated for 15 minutes. 5 mL of HBr was then added and stirred for 24 hours. 1.5 gr of oxalic acid was added to the previous mixture and stirred for 4 extra hours. Finally, the mixture was filtered and the particles remained on the filter were washed with water and dried at 50 °C in an oven [5].

AP1.2.7. Surface modification of GO by Sulfonic group (GO-SO₃)

20 mL of methanol was mixed with 15 mL of H₂SO₄ (0.5 M) followed by the addition of 0.2 gr of GO. The mixture was sonicated for 1.5 hour. Then, the solution was filtered and washed with water and dried at 100 °C [6].

AP1.2.8. Surface modification of GO by Thiol group (GO-SH)

75 mg of GO was dispersed in 75 mL of deionized water and ultrasonicated for 15 minutes. Then, 5 mL of HBr was added to the GO containing solution and stirred at 30 °C for 2 hours. 5 gr of Thiourea was added to the mixture and remained under stirring at 80 °C for 24 hours. After the solution cooled down to room temperature, 50 mL of NaOH (4 M) was added to the solution and stirred for 30 minutes at room temperature. The mixture was then washed with water and ether over a 0.2 µm PTFE membrane vacuum filter. The obtained solid was re-dispersed in water and ultrasonicated for 15 minutes. Finally, the solution was kept in an oven at 50 °C for a day to be completely dried. The obtained powder was labeled as GO-SH [4].

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AP1.3. Comparison of the adsorbents capacity for ammonium removal

The solid phase concentration and removal percentage of all materials made above are listed in Table AP1.1. As it was expected SBA-15 has no contribution in the adsorption of ammonium because it has no active sites on its surface that can be involved in the adsorption process. In case of amine functionalized SBA-15, however, there are some active sites on the surface of silica material, the sites are not favorable for ammonium adsorption. The results show an improvement in the performance of silica material in ammonium removal after surface modification of SBA-NH₂ with carboxylic group. In fact, the proton (H⁺) existed in the structure of COOH group can be exchanged with NH₄⁺ cation [7].

Dowex has been known as one of the most efficient industrial resins for ammonium removal. Therefore, in this study, silica material as one of the most abundant and environmental friendly materials was applied to make a nanocomposite in order to boost the adsorption performance of the resin through crosslinking process. In a comparative study between Dowex and Dowex nano silica, they show pretty the same performance which means an improvement in the adsorption process since by making a nano-composite material, a considerable portion of Dowex was replaced by silica material which is an economical and environmental friendly substance.

As the third class of adsorbents, graphene oxide synthesized according to Modified Hummer's method and the acid containing functional groups on its surface after modification with different functional groups, didn't show any promising result. Furthermore, it was found that Improved Hummer's method for GO synthesis has some safety issues related to controlling the temperature (high temperature is needed in some steps of synthesis). On the other hand, adding water to acid results in raising the temperature immediately which may cause the danger of exposure. Therefore, the method of synthesis was changed to Improved Hummer's method at room

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temperature which is a safe and more efficient synthesis process. Then, the highly oxidized surface of GO made based on Improved Hummer's method was factionalized by sodium (GO-Na) [8]. Among all graphene based materials, GO-Na shows the highest performance for ammonium removal with q_e of 21.42 mg/g and R% of 42.86% (at pH=7, T=25 °C, C_0 =50 mg/L, and dose=1 g/L).

Table AP1.1. q_e and R% of different adsorbents for ammonium removal
Conditions: at room temperature, pH=7, C_0 =50 mg/L, and dose = 1g GO-Na/ L

Adsorbent	C_e (mg/L)	q_e (mg/g)	R %
SBA-15	50	0.00	0.00
SBA-NH ₂	50.9	-0.90	-1.80
SBA-COOH	44.73	5.27	10.54
Dowex	26.02	23.98	47.96
Dowex-SiO ₂	26.6	23.40	46.80
GO-Modified Hummer's Method	45.5	4.5	9.00
GO-SO ₃	47.69	2.31	4.62
GO-COOH	46.91	3.09	6.18
GO-SH	43.44	6.56	13.12
GO-Improved Hummer's Method	50	0.00	0.00
GO-Na	28.58	21.42	42.84

AP1.4. Conclusions

The adsorption of ammonium cation onto different adsorbents in three categories including SBA, resin, and graphene based material was investigated. The results suggest that Dowex family and GO-Na with q_e values of 23.5 and 21.5 mg/g, respectively, showed the best performance for this application. Since, Dowex based materials have lots of acidic sites on their surfaces, the protons can be easily exchangeable with ammonium cation. On the other hands, sodium shows high compatibility with ammonium which makes the ion-exchange process between ammonium and sodium existed on the surface of GO-Na possible. Based on the above findings, it was decided to focus on GO-Na composite materials as the main topic of this research.

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Appendix 2: Immobilization of Sodium functionalized graphene oxide (GO-Na) for ammonium removal

AP2.1. Introduction

Although GO-Na showed promising performance as an adsorbent for ammonia from liquid phase, its micro size structure makes its separation and recycling process difficult. Additionally, producing the GO is more expensive than many other adsorbents [1]. Therefore, an effective way to make macroscopic GO composite more economical and practical, is immobilizing the GO powder by using a suitable support. However, this might block some active sites on the surface of GO during the polymerization and crosslinking with other materials. One of the most important polysaccharides in nature is sodium alginate (SA) derived from brown sea algae, which consists of a linear chain of mannuronic acid (M) and guluronic acid (G) and has a crosslinking property in the presence of multivalent cations as shown in Figure AP2.1 [1-4].

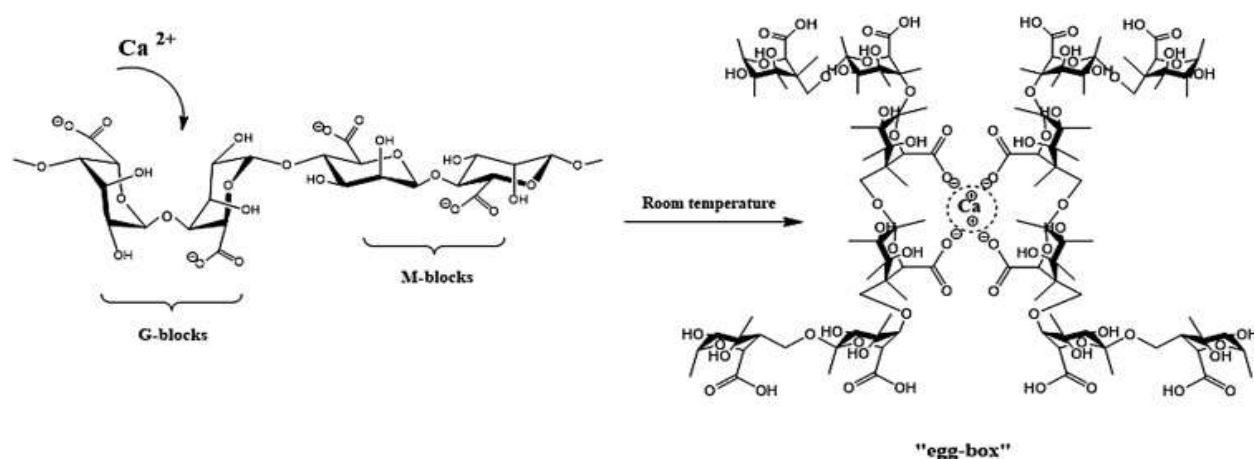


Figure AP2.1. Alginate structure and the egg-box model of hydrogel formation [4].

Appendix 2

Some unique features of SA such as high stability in organic solvents, biodegradability, being easily obtainable, and environmental friendliness makes this material as a good support candidate to immobilize GO [1, 5]. The hydrogel alginate beads can be formed when calcium ions make bridges between the M unit and G unit on adjacent chains [2]. According to Jiwei et.al., the homogenous distribution of GO powders in the Ca-SA matrix can also improve the mechanical stability of the hydrogel beads [1]. Lignin is another heterogeneous biopolymer which is a byproduct of paper-making industry and composed of three kinds of phenylpropanoid including sinapyl alcohols, p-coumaryl, and coniferyl [2, 6]. Lignin has some merits such as being economical, high abundance, low density, environmentally friendly, and bio-renewable [6], which makes it as a suitable filler for graphene alginate beads to improve the stability and biocompatibility of the beads and reduce the costs. All these three materials (GO, SA, and lignin) have many different oxygen containing groups on their surface which create some active sites for adsorption. In this study, alginate materials along with lignin was used to immobilize the GO powder. Then, the capacity of the hydrogel beads for TAN removal was examined.

AP2.2. Material Synthesis

AP2.2.1. Preparation of SA hydrogel beads

1 g of sodium alginate purchased from Sigma Aldrich was added to 25 mL deionized water and stirred vigorously until homogenous SA solution was formed. Then, the homogenous solution was dropped into 100 mL of $\text{Ca}(\text{OH})_2$ (0.1 M) using a burette. The beads were washed with deionized water and labeled as SA.

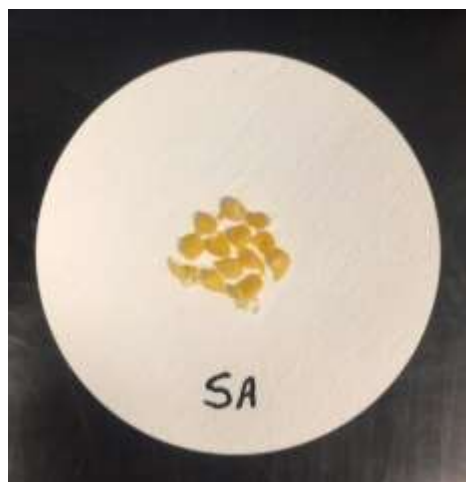


Figure AP2.2. Sodium alginate hydrogel beads

AP2.2.2. Preparation of SA-GO hydrogel beads

GO was prepared from graphite powder using Improved Hummer's methods according to the previous phases. 0.1 g GO was dispersed to 25 mL of DI water and sonicated for 1 hr in sonication bath. Then, 1 g of SA was added to the GO solution and remained under stirring for 1 hr. The homogenous GO-SA solution was dropped into 100 mL of $\text{Ca}(\text{OH})_2$ (0.1 M) by using a burette. After washing the beads, it was labeled as SA-GO.



Figure AP2.3. Sodium alginate-graphene oxide hydrogel beads

Appendix 2

AP.2.2.3. Preparation of SA- L hydrogel beads

To prepare SA- L beads 1 g SA was dissolved to the mixture of 0.5 g of Lignin in 25 mL of DI water based on the same procedure mentioned before.

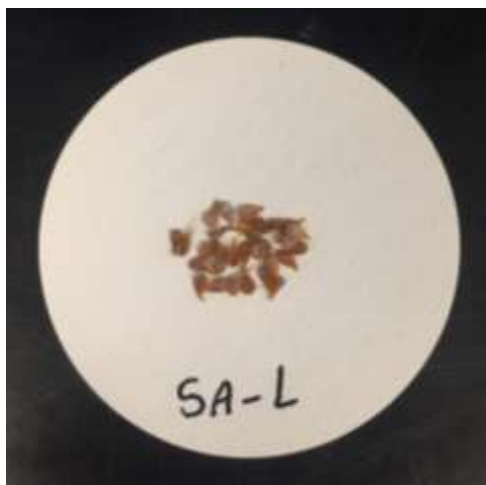


Figure AP2.4. Sodium alginate-lignin hydrogel beads

AP.2.2.4. Preparation of SA-GO-L hydrogel beads

SA-GO-L beads were made according to the same procedure by adding 1 g SA to the mixture of 0.1 g GO and 0.5 g Lignin in 25 mL of DI water.

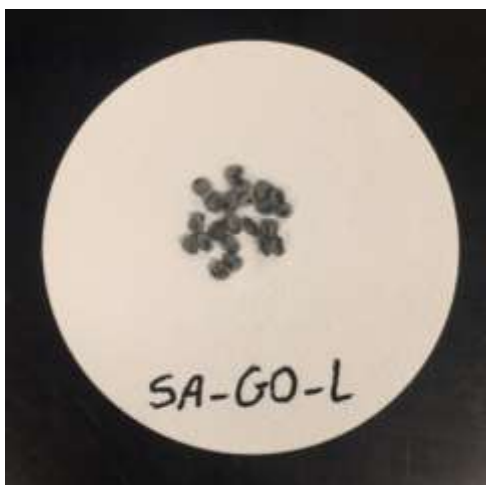


Figure AP2.5. Sodium alginate-graphene oxide-lignin hydrogel beads

AP2.3. Adsorption Results and Conclusions

The adsorption capacity of ammonium on different kinds of sodium alginate beads (with 3 replicates for each point) are shown in Table AP2.1. The results suggest that although all these alginate beads showed promising results in heavy metals [7, 8] and dyes removal [9], they are not good options for ammonium removal due to the fact that the calcium as a multivalent cation has no strong tendency to be exchanged with one positive charge cation of ammonium (Chapter 5) which makes the adsorption process inefficient. Moreover, immobilizing GO and/or lignin with alginate material results in blocking the adsorptive sites on the surface of the powders. However, the addition of GO and lignin improved the stability of alginate beads.

Table AP2.1. q_e and R% of different alginate beads for ammonium removal in a single component system
Conditions: at room temperature, pH=7, C_0 =50 mg/L, and dose = 1g GO-Na/ L

Adsorbent	q_e (mg/g)	R %
SA	2.14 ± 0.44	4.31 ± 0.89
SA-GO	1.04 ± 1.20	2.09 ± 2.41
SA-L	2.53 ± 1.63	5.09 ± 3.28
SA-GO-L	2.23 ± 0.89	4.49 ± 1.8

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Appendix 3: Synthesis and Analytical methods

AP3.1. Synthesis and functionalization

In this study, graphene oxide was synthesized according to Improved Hummer's method from synthetic graphite powder. Then, due to high compatibility of sodium and ammonium this material was treated with sodium hydroxide to obtain sodium functionalized graphene oxide (detailed explanation was provided in Chapter 3) [1]. Figure AP3.1. illustrates the main steps of synthesizing and functionalizing GO from graphite powder to sodium functionalized graphene oxide.

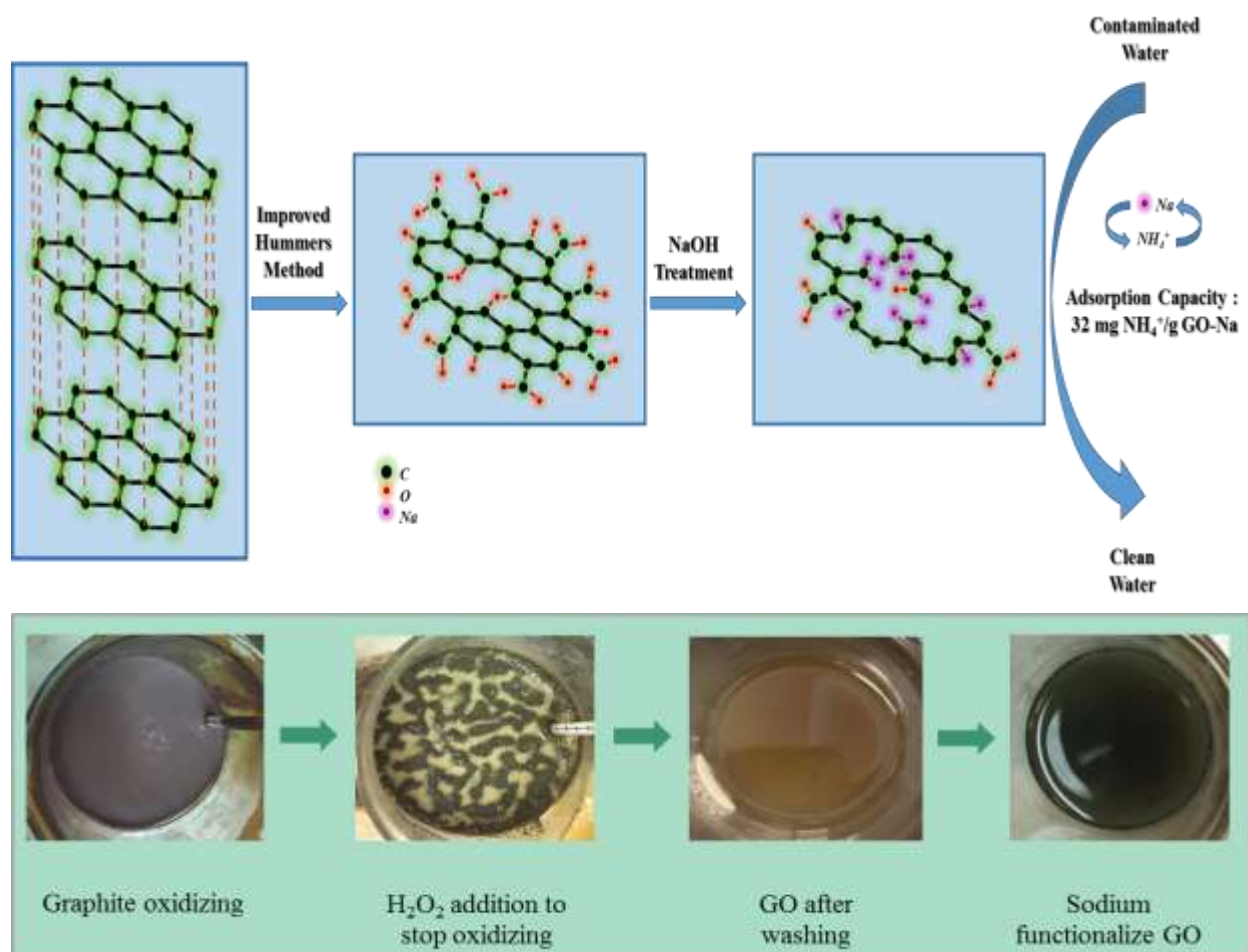


Figure AP3.1. The main steps of synthesizing and functionalizing graphene oxide

AP3.2. Ammonia measurement

Two different techniques were applied to measure the concentration of ammonia in the different phases of this study including Hach TNT ammonia vial high concentration (2-47mg NH₃-N/L) and direct nesslerization standard method 4500-NH₃.

AP3.2.1. Hach TNT ammonia vial high concentration (2-47mg NH₃-N/L)

In this approach, salicylate method was used to determine the concentration of ammonia nitrogen by using Hach Ammonia TNT plus 832 high range (2-47mg NH₃-N/L) vials (Method 10205). In the salicylate method, mono-chloramine formed by the reaction of ammonia and hydrochlorine reacts with salicylate to form blue-green colored 5-aminosalicylate. The color intensity of the solution depends on the amount of ammonical nitrogen in the sample [2]. DR6000-Hach laboratory spectrophotometer was used to measure absorbance at wavelength of 832 nm. The resulting concentration is expressed in NH₃-N in the solutions. Therefore, to convert the concentrations to NH₄, all the numbers should be multiplied by the factor of $\frac{18}{14}$.



Figure AP3.2. Hach Ammonia TNT plus 832 high range (2-47mg NH₃-N/L)



Figure AP3.3. DR6000-Hach Laboratory Spectrophotometer

AP3.2.2. Direct nesslerization standard method 4500-NH₃

In Nessler method a reagent reacts with ammonium to form a yellow color in proportion to TAN concentration that may be assessed colorimetrically. Nessler's reagent, which is a solution consisting of mercury (II) iodide and potassium iodide in highly alkaline solution, is named after Julius Nessler, the German chemist who first made this reagent in 1856 [2, 3]. Prior to add Nessler's reagent the addition of Rochelle salt, potassium sodium tartrate ($\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$), to the solution is necessary to avoid interference hardness cations [2].



Figure 3.4. Different ammonia concentrations measured by Nessler method

Appendix 3

In this method, first a calibration curve should be prepared, explained in chapter 5 in analytical methods section, prior to the actual ammonia measurement of the samples. Then the amount of absorbance in each sample was measured by DR6000-Hach laboratory spectrophotometer at a wavelength of 425 nm and ammonia concentrations were calculated according to the equation extracted from calibration curve illustrated in Figure AP3.5.

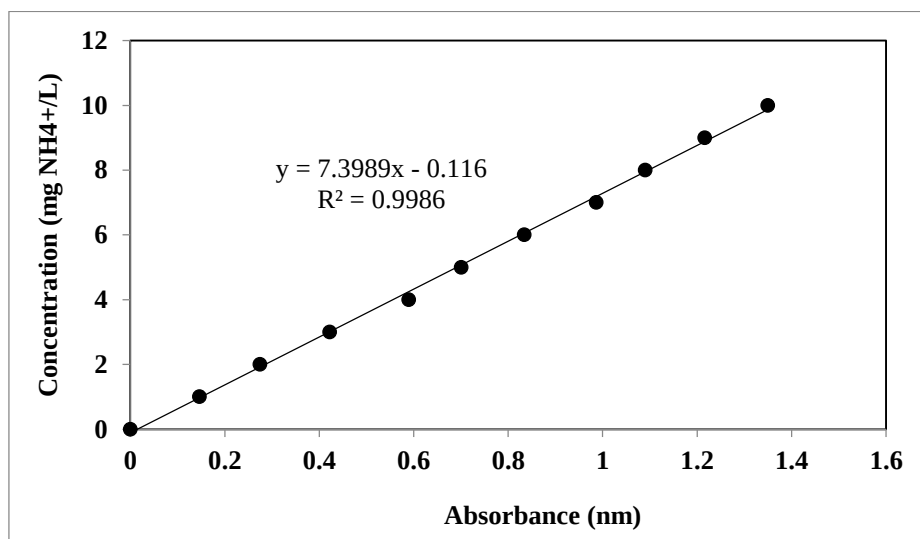


Figure AP3.5. Calibration curve for Nessler method

AP3.3. Na/K/Ca analysis by atomic adsorption

Na/K/Ca concentrations in this study were measured by a flame atomic absorption spectrometer (PinAAcle 500, PerkinElmer, Waltham, MA, United States), following standard methods 3111B [4], which is a Direct Air-Acetylene Flame Method. In this measurement process a liquid sample is aspirated into a flame and atomized and the amount of light absorbed is measured, while the flame is passed through the emission of a hollow cathod elemental lamp [4].

A calibration curve has to be developed for each cation measurement. Prior to each analytical measurement session, fresh standards were prepared and used for calibration. Furthermore, 1 %

Appendix 3

concentrated nitric acid should be added to each solution including blank, standards, and samples for two main reasons. First, to ensure that cations remain dissolved. Second, to clean the capillary tube, spray chamber and burner head and to prevent any residual metals trapped within the instrument which might cause some analytical errors.

As the first step, a blank sample was prepared to establish the baseline concentration. This was followed by the analysis of the standards solutions to conduct a calibration curve. Finally, the concentrations of all samples were measured.



Figure AP3.6. PerkinElmer PinAAcle 500 Flame Atomic Adsorption Spectroscopy

AP3.4. pH measurement

pH of all samples were measured by a pH probe (PHC201, HACH, Loveland, CO) connected to a portable benchtop meter (HQ40d, HACH, Loveland, CO). Three buffer solutions with pH of 4.0, 7.0, and 10.0 were used to calibrate the prob. In order to adjust the pH value in each sample, 0.01M NaOH or HCl was used.



Figure AP3.7. Hach pH meter and its probe

AP3.5. Temperature measurement and control

Temperature of the samples before and after adsorption were measured by the same pH probe introduced in the previous section. Also, during the synthesis and functionalization process, water bath and oil bath were employed to control the temperature of GO solution and to maintain the necessary heat for oxidization, respectively (shown in Figure AP3.8.).



Figure AP3.8. Temperature controlling by water bath

References

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