

Graphite as a Potential Adsorbent for Ammonium Ions Removal

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ARTICLE HISTORY

Received
22 June 2022

Accepted
6 August 2022

Available online
1 September 2022

ABSTRACT

The main focus of this work is to evaluate the potential of graphite powder as an adsorbent for ammonium ions (NH_4^+ ions) removal. Surface functional groups and thermal analysis of graphite adsorbent were conducted by using FTIR and TGA analyses, respectively. The experimental work covered batch adsorptions of NH_4^+ ions under various adsorption process parameters, which are adsorption contact time, adsorption temperature, initial concentration of NH_4^+ ions, and graphite adsorbent dosage. Detailed adsorption characteristics of NH_4^+ ions using graphite adsorbent were evaluated via adsorption isotherms study, implementing Langmuir and Freundlich isotherms. By adopting a one-factor-at-a-time (OFAT) approach, the best adsorption process parameters identified were 50 min of adsorption contact time, 25 °C of adsorption temperature, 100 mg/L NH_4^+ ions initial concentration, and 0.5 g graphite adsorbent dosage with up to 75 % removal of NH_4^+ ions. Freundlich adsorption isotherm was the best fitted for NH_4^+ adsorption using graphite with R^2 value of 0.9580. The findings of this work could be a benchmark to further develop the characteristics of graphite as a potential adsorbent for NH_4^+ removal.

Keywords: Adsorption, Ammonium ions, Graphite, Isotherms, Batch Process

1. INTRODUCTION

Ground water, surface water, and industrial wastewater contain various type of pollutants. These pollutants include both organic and inorganic substances such as phenolic compounds, petroleum, surfactants, pharmaceutical, medicines, and pesticides [1]. Ammonium (NH_4^+) ions are one of the contaminants found in industrial wastewater that need special management prior to its disposal into water streams. This pollutant originates from industrial activities such as the production of fertiliser, manufacturing of soda, burning of fossil fuels, agricultural management, and production of refrigerator equipment [2]. NH_4^+ ions is a harmful substance because of its corrosive and toxic characteristics that contributes to a number of environmental issues, including contamination to plants, eutrophication, and nitrogen deposition [3]. The presence of NH_4^+ ions in rivers, lakes, and ponds might accelerate the eutrophication process, resulting in algal blooms. This will contribute to a loss in water clarity, and an increase in precipitation rates that led to the destruction of benthic habitat by shadowing submerged plants. The concentration of NH_4^+ ions is higher than the allowable limit in some of surface water supply, such as portable water source. The quality of water supply might be jeopardised if the concentration of NH_4^+ ions in a water stream exceeds the permissible limit [4]. It is recommended that the concentration of NH_4^+ ions in the water not be more than 1.5 mg/L for the most fish species [5]. In light of the aforementioned difficulties, complete removal of NH_4^+ ions from wastewater prior to its discharge into the water stream is necessary.

Among the many available methods (i.e., absorption, air stripping, ion-exchange, and biological processes), the most attractive approach is adsorption process [2]. Adsorption is the most well-established method since it is economical, easy to operate, and simple. The performance of adsorption process is highly influenced by the surface area, pore structure, surface functional groups, and thermal stability of the adsorbent employed. Several types of commercially available adsorbents, which include natural zeolites [4], activated carbon [6], coal ash [7], and graphene oxide [8], have been studied to control the emission of ammonia in industries.

Graphite is a crystalline form of carbons that are arranged in a layered and planar structure. The work by Mirahsani et al. [8] successfully removed 32 mg/g of NH_4^+ by using sodium functionalized graphene oxide. The isotherms studied suggested that the Langmuir adsorption isotherm is the most prevalent model for predicting the behaviour of NH_4^+ particles adsorbed on the surface of nano adsorbents, which applies to monolayer and homogeneous adsorption. The potential of graphite as an adsorbent has also been tested by our previous work [9], where eggshell was impregnated into graphite oxide for fluoride removal application with 48 mg F^-/g adsorption capacity. The removal of F^- ions by using graphite was proposed for the physisorption of F^- ions onto graphite structure, in which surface adsorption as well as intra-particle diffusion were physically transferred. To date, there is no work reported on the utilization of pristine graphite in NH_4^+ ions removal. Hence, the capability of graphite as an adsorbent to remove NH_4^+ ions is anticipated. The main objective of this work is to explore the potential of graphite adsorbent for NH_4^+ ions removal, while understanding the adsorption behaviour at various parameters and its adsorption isotherms.

2. METHODOLOGY

2.1 Material and Chemicals

In this work, graphite powder (size < 20 μm , Sigma Aldrich) was used as an adsorbent and ammonium chloride (NH_4Cl) (AR 99.8%, Merck) was used to vary the concentration of NH_4^+ ions in aqueous solution. Deionized water was used for all experiments as prepared by the laboratory of Centre of Chemical Engineering Studies.

2.2 Characterization of Graphite Adsorbent

The functional groups of graphite's surfaces were determined by the Fourier transform infrared (FTIR) spectroscopy in the spectra range from 4000 – 500 cm^{-1} (Nicolet, 6700). The thermal decomposition properties were analysed using Thermogravimetric Analyzer (TGA) (SDT Q600). The temperature for measuring the weight derivatives of graphite was set up to 1000 $^\circ\text{C}$ by using atmospheric air flow at 50 ml/min.

2.3 Batch Adsorption of NH_4^+ Ions

A 1000 mg/L of NH_4^+ aqueous stock solution was prepared by dissolving a 3.819 g of NH_4Cl in a 1000 mL of volumetric flask filled with deionized water. The concentrations of the aqueous solution were varied by diluting the stock solution with deionized water when necessary.

For batch adsorption experiments, a set of 250 mL conical flasks was used by adding 0.5 g of graphite and 25 ml of NH_4^+ ions from stock solution with the initial concentration of 100 mg/L. The conical flask was sealed with a glass stopper. These samples were then mounted on the

orbital shaker at 25 °C at various contact times. Orbital shaker (230 VAC, JEIO TECH) was used to mix and shake the samples at 150 rpm. Then the samples were filtered by filter papers for NH₄⁺ ions analysis. The initial and final NH₄⁺ ions concentration remained in the solutions were analysed using spectrophotometer (HACH, DR2700) and the absorbance was monitored at a wavelength of maximum absorbance ($\lambda = 430$ nm). The batch adsorption experiments were repeated according to one-factor-at-a-time (OFAT) approach, where the parameters used were contact time (10 – 180 min), adsorption temperature (25 – 45 °C), adsorbent dosage (0.5 – 3 g), and initial concentration of NH₄⁺ ions (20 – 100 mg/L). The percentage of removal (%R) of NH₄⁺ ions from aqueous solution were calculated according to the following equation [8]:

$$\%R = \frac{(C_o - C_e)}{C_e} \times 100 \quad (1)$$

where, C_o is the initial concentration of NH₄⁺ ions in solution (mg/L), C_e is the equilibrium concentration of NH₄⁺ ions in solution (mg/L), V is the volume of solution (L), and m is the mass of the adsorbent (g).

2.4 Adsorption Isotherms

The adsorption concentration data was fitted using Freundlich and Langmuir equations. Langmuir is appropriate for any adsorption occurs at a specific homogeneous surface and there is no interaction between the adsorbate molecules, as shown in Equation (2). Whereas Freundlich equation is suited to nonideal sorption on heterogeneous surface and multi-layer sorption, as shown in Equation (3) [10].

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (2)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (3)$$

where, q_e is the amount of NH₄⁺ ions adsorbed (mg/g), C_e is the equilibrium concentration of NH₄⁺ ions in solution (mg/L), K_L is the Langmuir constant correlated to the energy of adsorption that reflect the affinity of binding sites (L/mg), q_m is the maximum adsorption at monolayer coverage (mg/g), K_F is the Freundlich constant representing the adsorption capacity (mg/g) and n is the constant representing the adsorption intensity.

3. RESULTS AND DISCUSSION

3.1 Functional Groups and Thermal Analysis of Graphite Adsorbent

Figure 1 represents the analysis of surface chemistry for graphite adsorbent by using FTIR spectra before and after NH₄⁺ ions batch adsorption. From the figure, the spectra indicate various functional groups represent the presence of –OH stretching groups (water) at 3420 cm⁻¹, and the intensive peak at 2354 cm⁻¹ for vibrations of carbon dioxide (CO₂), the valence of C–H vibrations at 3000 cm⁻¹, several peaks near 1600 cm⁻¹ corresponding to the vibrations of C=C and vibrations of C=O at region 1720-1740 cm⁻¹ were observed [11]. The –OH groups are either attached to carbon or representing the adsorbed water. High intensity spectra were observed after adsorption of NH₄⁺ ions by graphite. Seredych and Badosz discussed on the characteristics of graphene oxide after ammonia adsorption, where a small

peak at 1415 cm^{-1} along with a broad band at 3255 cm^{-1} (N–H stretching) and a broad band between 1600 and 1700 cm^{-1} are seen representing the presence of ammonia ions [12]. According to their findings, it can be concluded that the adsorption of NH_4^+ ions might have happened due to the interaction between –OH stretching groups and the double bonds of C=C and C=O.

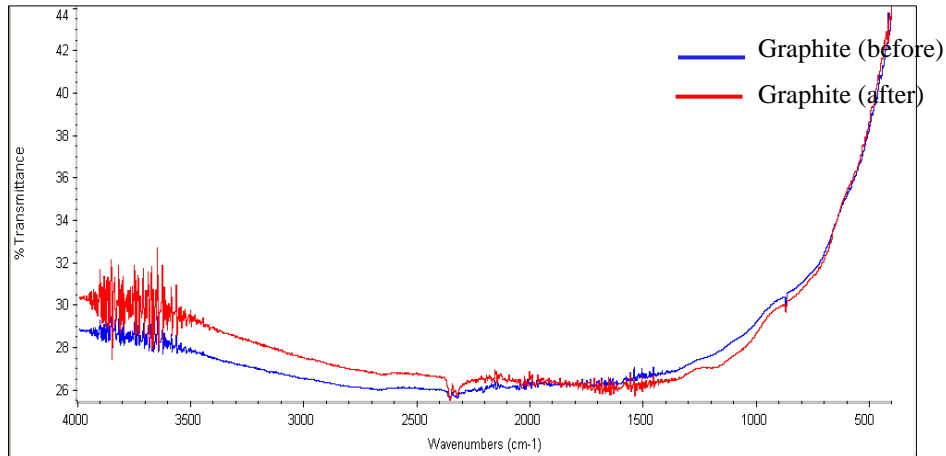


Figure 1: FTIR spectra of graphite adsorbent before and after NH_4^+ batch adsorption

Further understanding of the surface chemistry of the adsorbents can be supported by thermal gravimetric analysis (TGA). Figure 2 displays the graphite adsorbent's thermal analysis. It was observed that there was a very slight change in weight (%) until the temperature reached $633\text{ }^\circ\text{C}$. The variations in temperature from 0 to $633\text{ }^\circ\text{C}$ might not have an effect on the graphite's weight reduction. The possible causes of the minimal shift in weight include the loss of a trace amount of moisture as well as volatile organic compounds (VOCs). This specifies that graphite is thermally stable up to $633\text{ }^\circ\text{C}$. The sharp decreases of temperature from $663\text{ }^\circ\text{C}$ until $876\text{ }^\circ\text{C}$ is the range of temperature for combustion process. Graphite's carbon component could react with air to produce CO and CO_2 , which resulted in a 98% weight loss overall [11]. The temperature increase caused the functionalized carbon to lose weight more quickly than the native carbon.

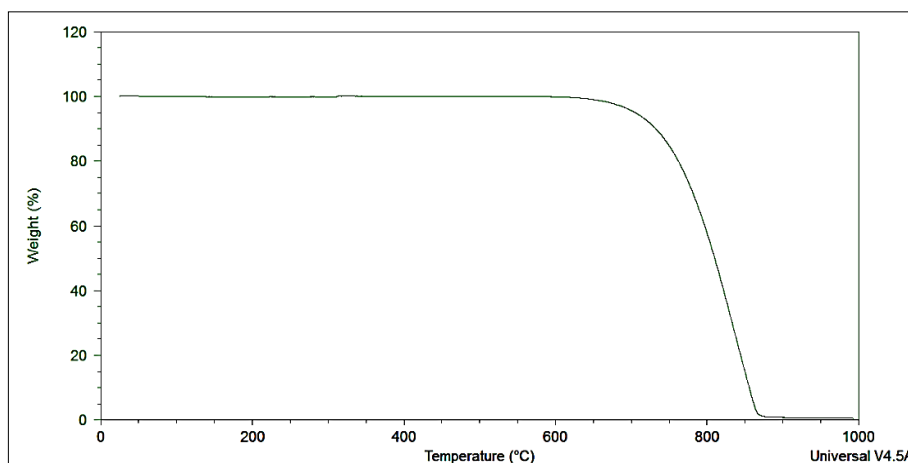


Figure 2: Thermal analysis of graphite adsorbent

3.2 Batch Adsorption Process

3.2.1 Effect of Adsorption Temperature

The effect of temperature on NH_4^+ ions adsorption was studied by varying temperature from 25 to 45 °C. The experiments were conducted at 30 min contact time and 1.5 g of graphite. In Figure 3, it can be observed that the removal of NH_4^+ ions in aqueous solution decreased as the temperature increased. The removal of NH_4^+ ions is 33.21% at room temperature and reduces to 28.98% starting at 35 °C. This might be due to NH_4^+ ions which tend not to escape from the solid phase to the bulk phase of graphite when temperature is increased [13]. The percentage removal becomes constant until 45 °C. This occurs due to the movement capability of molecules of NH_4^+ ions are low towards graphite. Thus, it is observed that as the temperature increased the quantity of ions' adsorbed becomes lower.

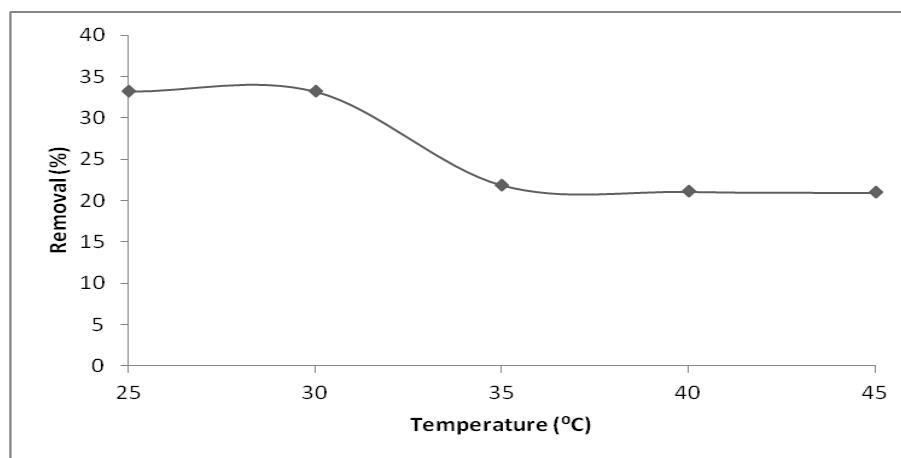


Figure 3: Effect of temperature on the removal of NH_4^+ by graphite adsorbent

3.2.2 Effect of Contact Time

The adsorption rate of NH_4^+ ions on graphite was observed by varying the time from 10 to 100 min. As shown in Figure 4, the removal of NH_4^+ ions were increased from 30 to 50 min which is 35% and 76% accordingly, then it became constant until 90 min. This might be due to the utilization of the adsorption sites of graphite that tend to have a rapid diffusion and achieve fast equilibrium. The adsorption of NH_4^+ ion reached equilibrium at 50 min of contact time. Therefore, 50 min was selected as the optimum time for NH_4^+ ions to be adsorbed onto the graphite surface. The equilibrium condition of graphite happened due to the existing vacant sites which were fully occupied by NH_4^+ ions, either via physical or chemical interaction [14].

3.2.3 Effect of NH_4^+ Ions Initial Concentration

The effect of NH_4^+ ions initial concentration was studied by varying the concentrations from 20, 40, 60, 80, 90 and 100 mg/L, respectively at 25 °C, 50 min time and 1.5 g of graphite. The adsorption of NH_4^+ ions increased with increasing initial concentration as shown in Figure 5. At 100 mg/L the adsorption rate becomes higher compared to the other initial concentrations, hence the initial concentration was optimized at 100 mg/L. At the lowest concentration, the percentage removal is 20.5% and it increased to 52.3% at the highest concentration. Thus, the percentage removal was found to increase with high value of initial concentration of adsorbate

molecule [15]. This can be proved to the fact that high amount of concentration in solution resulted in higher gradient of solute giving the driving force which is necessary for NH_4^+ ions to be adsorbed onto the adsorbent surface [14]. It can be concluded that the initial concentration of NH_4^+ ions play an important role in the adsorption of NH_4^+ ions onto graphite.

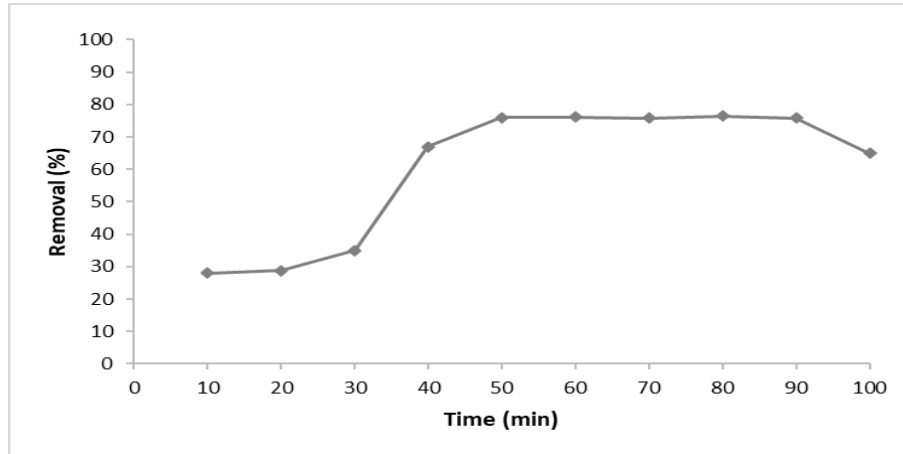


Figure 4: Effect of contact time on the removal of NH_4^+ by graphite adsorbent

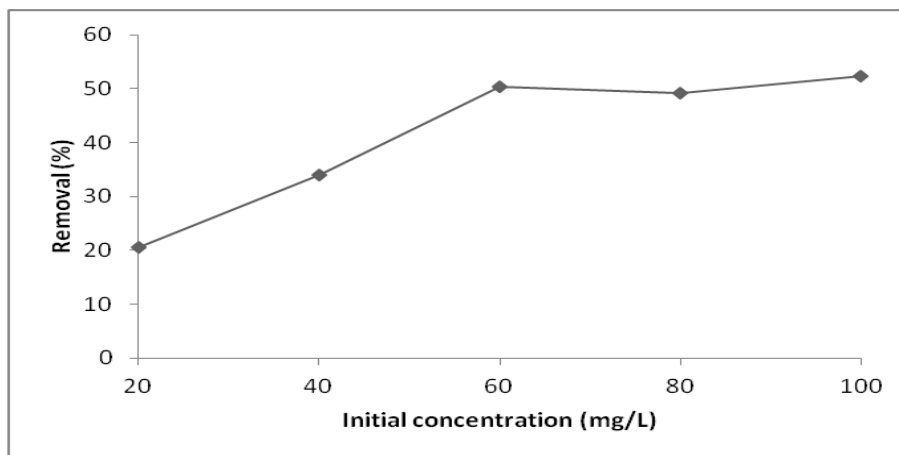


Figure 5: Effect of initial NH_4^+ concentration on the removal of NH_4^+ by graphite adsorbent

3.2.4 Effect of Graphite Adsorbent Dosage

The percentage removal of NH_4^+ ions as a function of adsorbent dosage between 0.5 to 3.0 g at 100 mg/L initial NH_4^+ ions concentration, at 25 °C and 50 min time is shown in Figure 6. The percentage removal is 66.69% at 0.5 g and decreased to 15.89% at 3.0 g. The results indicated that the removal of NH_4^+ ions decreased with increasing amount of adsorbent. This might have happened due to the adsorption sites of the adsorbent are in excess [2]. Thus, it needs less amount of graphite for NH_4^+ ions removal. Graphite was investigated based on its potential to adsorb NH_4^+ ions because of its layer and planar structure.

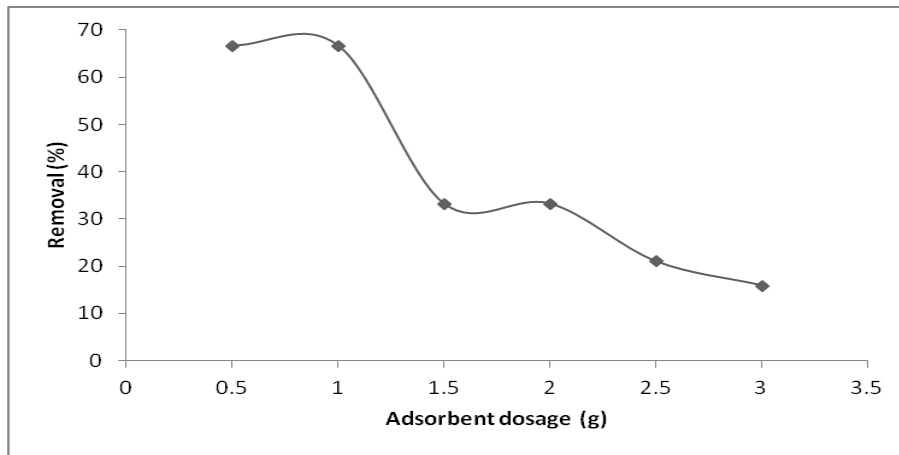


Figure 6: Effect of adsorbent dosage on the NH_4^+ removal by graphite adsorbent

3.3 Adsorption Isotherms analysis

The relationship between the amount of adsorbate that adsorbed onto the adsorbent and the concentration of dissolved adsorbate in liquid at equilibrium was studied using isotherms models of adsorption. Adsorption isotherm, also known as equilibrium data, is crucial for the design of the adsorption process. The best correlation coefficient must be produced in the equilibrium data curve in order to optimise the design of the equilibrium adsorption [15]. The adsorption of NH_4^+ ions onto graphite was fitted by using Langmuir and Freundlich isotherm equations to assess their mechanistic insights. Figure 7 and Figure 8 show the fitted line for linear equations of Langmuir and Freundlich isotherms, respectively.

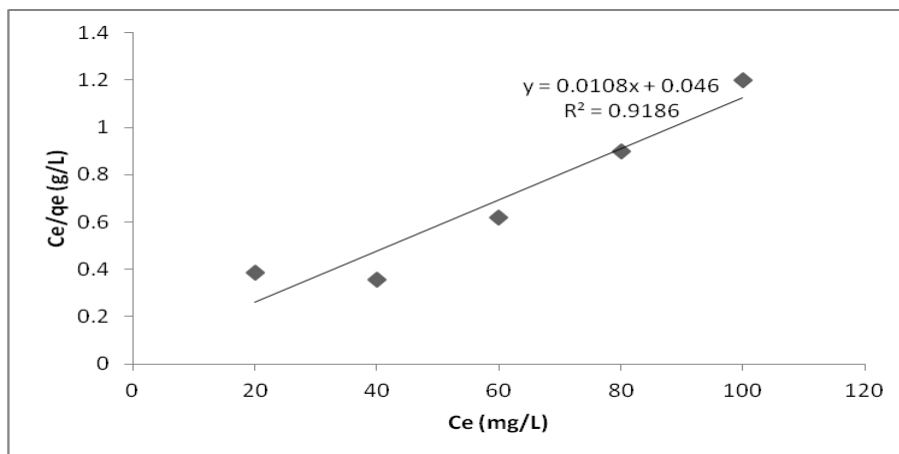


Figure 7: Langmuir isotherm of NH_4^+ adsorption onto graphite adsorbent

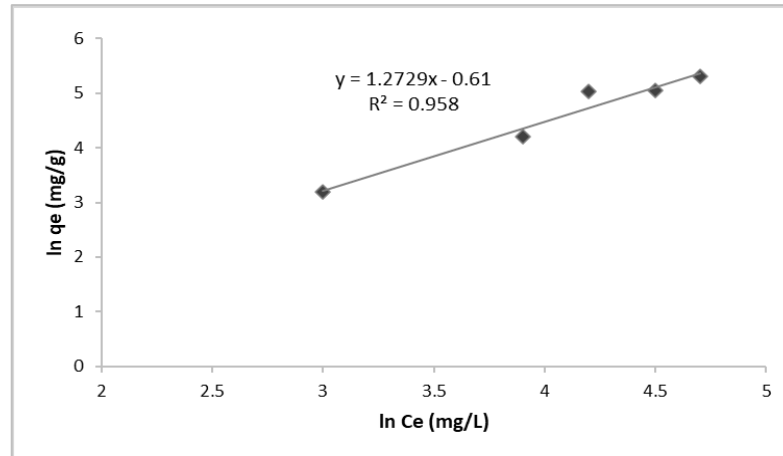


Figure 8: Freundlich isotherm of NH₄⁺ adsorption onto graphite adsorbent

The values of correlation coefficient (R^2) for both isotherms were 0.9186 for Langmuir and 0.958 for Freundlich isotherms. The best fitting was given by Freundlich isotherm, which explains a multilayer adsorption of NH₄⁺ ions onto heterogeneous surface of graphite adsorbent [16]. The Freundlich isotherm was applicable for non-ideal adsorption on heterogeneous surface as well as multilayer adsorption. Table 1 shows the summary for the equilibrium data for both isotherms model.

Table 1: Equilibrium studies data for Langmuir and Freundlich

Isotherm model	Equation	Condition
Langmuir	$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$	q _m : 158 mg/g K _L : 0.0098 L/g R ² : 0.9186
Freundlich	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	n = 1.651 K _F = 10.78 L/mg R ² : 0.9580

The values of maximum monolayer adsorption capacity (q_m), Langmuir constant (K_L), correlation coefficient (R^2), and Freundlich constant (K_F) were calculated. All parameters were obtained by slope and intercept of the plot from the isotherms. The values of maximum monolayer adsorption capacity and Langmuir constant, were 158 mg/g of q_m and 0.0098 L/g of K_L. Freundlich constant calculated was 10.7 L/mg, with n value of 1.651. High value of n which is more than 1 indicating a strong bond between the adsorbent and adsorbate [17].

3. CONCLUSIONS

In this study, batch adsorption experiments of NH₄⁺ ions were carried out by using graphite adsorbent. The results indicated that, graphite is one of the potential media for reactive adsorption in an aqueous condition and there is a possibility to utilize its layered structure to capture the NH₄⁺ ions. The effect of various operating parameters such as contact time, adsorption temperature, NH₄⁺ ions initial concentration, and adsorbent dosage were conducted. The best operating conditions were found to be 50 min of contact time, 25 °C of adsorption temperature, and 100 mg/L of initial NH₄⁺ ions concentration. The adsorption data were described well by Freundlich isotherm model, which best represents the multilayer adsorption.

ACKNOWLEDGEMENT

The completion of this work was supported by facilities and laboratories provided by Universiti Teknologi Mara Cawangan Pulau Pinang, Malaysia.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest which involves other organization or entity (with a financial or non-financial) which has no financial bearing in the subject matter of materials discussed in this manuscript.

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