EVALUATION OF AMMONIUM (NH_4^+) ADSORPTION CAPACITY IN AQUEOUS SOLUTION BY HYDROCHAR DERIVED FROM PAPER SLUDGE

Hoang Le Phuong
TNU - University of Technology

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ABSTRACT

The purpose of the study is to recover paper sludge to create adsorbent material used for removing ammonium (NH_4^+) from aqueous solution. Paper sludge in Hoang Van Thu paper joint stock company was recycled and used for hydrochar production (HBG) through hydrothermal carbonization with supporting of an HCl solution at a carbonization temperature of 250 ^oC for ammonium adsorption. Batch adsorption experiments were carried out to investigate and evaluate the effects of some factors on ammonium (NH_4^+) adsorption of HBG materials. The results indicate that the optimal conditions for ammonium adsorption onto HBG accurate at pH of 8, contact time of 120 min, initial ammonium concentration of 50 mg/L, and a maximum adsorption capacity calculated based on Langmuir isotherm model of 5.22 mg/g. The experiment data fitted well with the Langmuir model and the pseudo-second-order model with the R^2 of 0.98 and 0.99, respectively. Hydrochar derived from paper sludge exhibited a significant adsorption capacity of ammonium in aqueous solution, making it a promising adsorbent for removal of ammonium in wastewater.

ĐÁNH GIÁ KHẢ NĂNG HẤP PHỤ AMMONIUM (NH_4^+) TRONG NƯỚC BẰNG VẬT LIỆU THAN SINH HỌC NGUỒN GỐC TỪ BÙN GIẤY

Hoàng Lê Phương
Trường Đại học Kỹ thuật Công nghiệp – ĐH Thái Nguyên

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TỪ KHÓA

Hấp phụ
Bùn giấy
Than sinh học
Ammonium
Hấp phụ ammonium

TÓM TẮT

Mục đích của nghiên cứu là thu hồi bùn giấy tạo ra vật liệu hấp phụ ứng dụng để loại bỏ thành phần ammonium (NH_4^+) trong dung dịch nước. Bùn giấy thải từ công ty cổ phần Giấy Hoàng Văn Thụ được tái chế và sử dụng để chế tạo vật liệu than sinh học hydrochar (HBG) thông qua quá trình cacbon hoá thuỷ nhiệt trong dung dịch HCl ở 250 ^0C. Vật liệu HBG được sử dụng để hấp phụ ammonium trong nước. Hàng loạt các thí nghiệm theo mẻ đã được tiến hành để nghiên cứu đánh giá ảnh hưởng của một số yếu tố đến quá trình hấp phụ ammonium của vật liệu HBG. Kết quả cho thấy điều kiện thích hợp cho quá trình hấp phụ ammonium của vật liệu HBG ở pH dung dịch bằng 3, thời gian hấp phụ 120 phút, nồng độ ammonium ban đầu 50 mg/L và dung lượng hấp phụ cực đại tính theo mô hình Langmuir là 5,22 mg/L. Dữ liệu thí nghiệm phù hợp với mô hình đẳng nhiệt Langmuir và mô hình động học bậc 2 với các giá trị tương quan R^2 lần lượt là 0,98 và 0,99. Than sinh học hydrochar chế tạo từ bùn giấy đã cho thấy khả năng hấp phụ đáng kể ammonium trong dung dịch nước và có thể trở thành chất hấp phụ đầy tiềm năng để loại bỏ ammonium trong nước thải.

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Email: phuongqtn@tnut.edu.vn

1. Introduction

Ammonium (NH_4^+) is one of the pollutants which has found in various wastewater sources such as urban and industrial wastewater, agricultural waste, leachate and other sources. Discharging ammonium pollutants directly into water bodies such as rivers, lakes, and seas is the cause of eutrophication and consequently one of the factors contributing to the degradation of underwater ecosystems. This process reduces water's self-purification ability and has serious implications for both drinking water and human health [1]. Therefore, removing ammonium from wastewater before releasing it into the environment is crucial.

Currently, various methods, including biological, chemical, physical, or their combinations, have been developed to treat ammonium in water. Some specific methods include ion exchange, chemical precipitation, biological nitrification – denitrification process and adsorption [2]. Among these, adsorption is one of the most favored methods due to its simple operational processes, low cost, high removal efficiency and environmental safety [1], [2]. For ammonium adsorption, numerous materials have been researched such as zeolite [3], bentonite [4], activated carbon [5], biochar [6] and natural soil minerals [2].

In recent years, some types of sludge such as wastewater treatment sludge and paper sludge, have also been investigated for their potential use as adsorbents. Sludge from wastewater treatment systems has been reclaimed to produce biochar for ammonium adsorption in the study conducted by Yin et al [7]. The results showed that the ammonium adsorption capacity of the adsorbent could reach 22.85 mg/g higher than that of some other materials. Sewage sludge also was studied to create $FeCl_3$- activated carbon, which was used to remove As(III) and Cr(VI) from wastewater, exhibiting good adsorption behaviors [8]. Yaras and Arslanoğlu [9] investigated the adsorption capacity of Cu^{2+} in water using paper waste sludge. Despite the use of untreated raw sludge, the material exhibited a maximum adsorption capacity of Cu^{2+} of 114.42 mg/g higher than activated carbon adsorbent synthesized from coconut shells.

In Vietnam, the recovery of paper sludge as an adsorbent for pollution in water has not yet received significant attention in research. Therefore, conducting an indepth study on utilizing this waste material as an adsorbent for treating wastewater containing NH_4^+ holds substantial economic and environmental significance in solving waste by waste. The objectives of this research include: (1) create hyrochar material from paper waste sludge; (2) investigate the effect of various factors on NH_4^+ adsorption capacity of the synthesized hydrochar.

2. Materials and methods

2.1. Hydrochar preparation

The paper sludge was collected from the first settling tank within the wastewater treatment system of Hoang Van Thu Paper Factory Joint Stock Company, Thai Nguyen city, Thai Nguyen province. The collected paper sludge, then, was air-dried under sunlight for 3 days and followed by further drying at 100 ℃ for 48 h. In the next step, the dried sludge was transformed into hydrochar by hydrothermal carbonization. Specifically, 10 g of dried paper sludge was placed in a 300 mL Teflon flask containing 40 mL of 0.1 M *HCl* solution. Then, the Teflon flask was heated at a rate of 10°C/min in an electric furnace at 250 °C for 24 h. Subsequently, the Teflon flask was allowed to cool to the ambient temperature. The obtained mixture was filtered with a 0.45 μm membrane filter to remove liquid. The solid fraction was washed several times with distilled water and dried at 105 °C for 2 h. Finally, the hydrochar was crushed and sieved to obtain particles with a diameter smaller than 0.5 mm. The hydrochar was labeled as HBG and stored in glass vial for use in subsequent studies.

The fundamental physicochemical properties of HBG, including specific surface area and pore volume, were determined by the BET method (Micromeritics TriStar 3000 V6.07A); the elemental composition was determined by X-ray scattering (EDX, Hitachi S-4800 equipment).

2.2. Batch adsorption experiment

A series of batch experiments were conducted to evaluate the influencing factors on the adsorption process of NH_4^+ by HBG including pH, initial NH_4^+ concentration and contact time.

The experiments on the pH effect were conduct in 50 mL triangular flask containing 0.1 g of HBG and 25 mL of *NH₄Cl* with a concentration of 20 mg/L. The pH of the solution was adjusted within the range of 3 to 11 by adding 0.1M *HCl* or 0.1M *NaOH*. The mixture was stirred for 60 minutes. The impact of contact time was studied at various time intervals ranging from 5 to 240 min, with an initial NH_4^+ concentration of 20 mg/L, an adsorbent dosage of 0.1 g and the initial pH of the solution set at the optimal pH obtained from the previous experiment. The influence of the initial NH_4^+ concentration was investigated across concentrations from 10 to 100 mg/L, with an adsorbent dosage of 0.1 g in 25 mL of *NH₄Cl* solution. The pH of the solution and contact time were based on the values obtained from the above experiments. Each experiment was replicated at least three times.

After the adsorption process, the mixture was filtered through a filter paper with a size of 11 μm. The remaining concentration of NH_4^+ in the solution was determined through colorimetric method using UV/Vis spectrophotometer at a wavelength of 640 nm.

The adsorption capacity of NH_4^+ by HBG at time *t* (q_t, *mg/g)* and at equilibrium (q_e,*mg/g)* was determined using equations (1) and (2), respectively. The adsorption efficiency *H (%)* was calculated using equation (3):

$$q_t = \frac{(C_o - C_t)V}{m} \quad (1)$$

$$q_e = \frac{(C_o - C_e)V}{m} \quad (2)$$

$$H = \frac{(C_o - C_e)x100\%}{C_o} \quad (3)$$

Where, C_o, C_t and C_e are NH_4^+ concentrations (*mg/L*) in the solution at beginning time, any time *t*, and equilibrium, respectively. *V (L)* is the volume of solution and *m (g)* is the dry weight of used adsorbent.

2.3. Adsorption kinetic and isotherm models

In this study, the kinetics of adsorption process NH_4^+ onto HBG was analysed by using the pseudo-first-order and pseudo-second-order models, given by Eqs (4) and (5), respectively:

$$q_t = q_e(1 - e^{k_1 t}) \quad (4)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (5)$$

Two typical isotherm models including Langmuir and Freundlich models were used to describe the adsorption isotherm of ammonium onto HBG. The equations of two models are given by Eqs (4) and (5), respectively:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (6)$$

$$q_e = K_F C_e^{\frac{1}{n}} \quad (7)$$

Where, q_m *(mg/g)*, q_t *(mg/g)* and q_e *(mg/g)* are the maximum adsorption capacity, adsorption capacity at time *t* and equilibrium, respectively; k_1 *(min^{-1})* and k_2 *(g.mg^{-1}.min^{-1})* are the first-order and second-order rate constants, respectively; K_L *(L/mg)* is the Langmuir constant; K_F *(mg/g)* is the Freundlich constant; *n* the adsorption intensity.

3. Results and discussion

3.1. Characteristics of HBG

The HBG material was determined for its specific surface area, pore volume, and elemental composition. The results are revealed in Figure 1. It can be seen that specific surface area and

pore volume of HBG were measured at 2.24 m^2/g and 0.0105 cm^3/g, respectively. The elemental composition of the HBG material includes C (45.02%), O (38.12%), Ca (10.38%), Al (2.46%), Si (2.08%), and Na (1.94%). The presence of metal components in HBG may play a certain role in adsorbing pollutants.

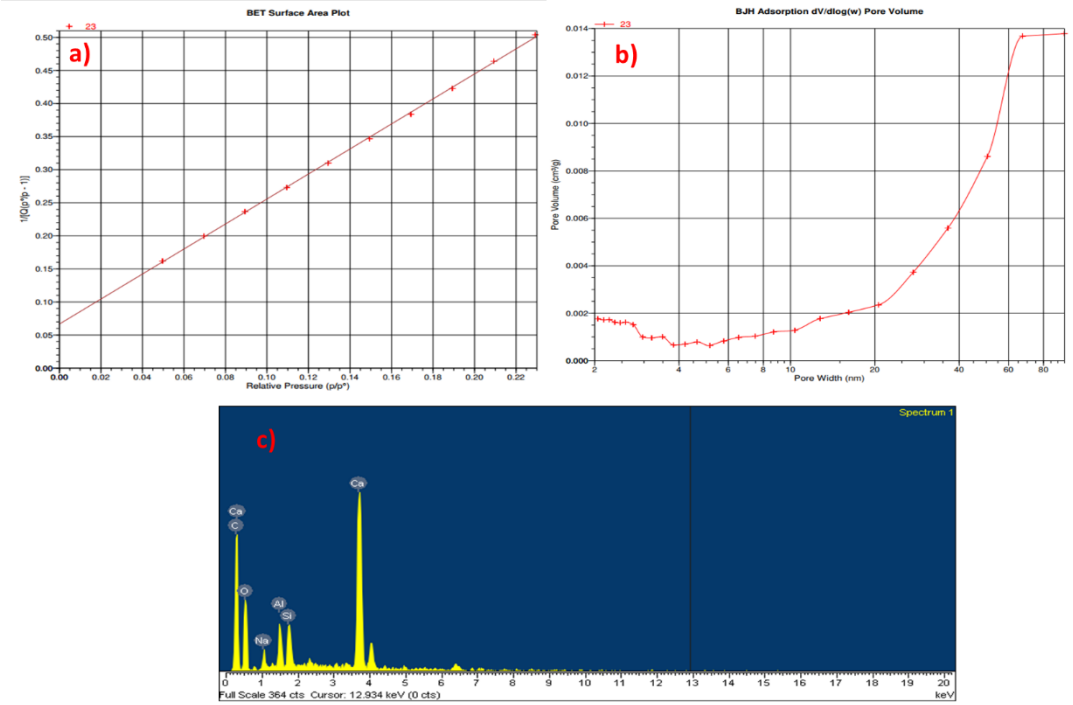

Figure 1. *The fundamental physicochemical properties of HBG (a) BET surface area (b) Pore volume and (c) EDX spectra*

3.2. Effect of solution pH

The pH value of the aqueous solution is one of the important factors influencing the adsorption capacity. Investigating the impact of pH on the adsorption capacity of NH_4^+ onto HBG in aqueous solution aims to identify the optimal pH value for the adsorption process. The results are presented in Figure 2a.

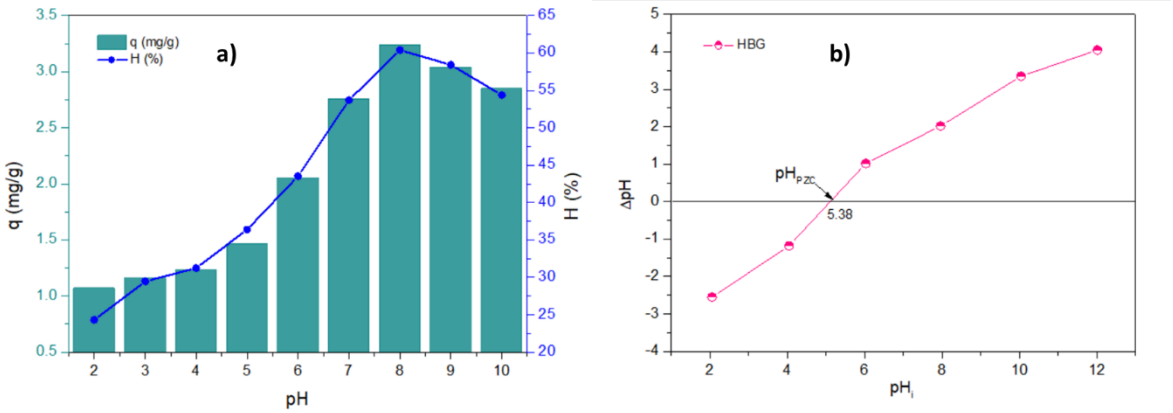

Figure 2. *(a) Effect of solution pH on the ammonium adsorption by HBG; (b) pH_{PZC} of HBG*

As shown in Figure 2a, it can be observed that pH significantly influenced the ammonium adsorption capability of HBG. The adsorption capacity and efficiency increased as the solution pH rose from 2 to 8. Specifically, the adsorption capacity rose from 1.07 mg/g to 3.24 mg/g, and the adsorption efficiency increased from 24.31% to 60.38%. However, as the pH value continued to increase from 8 to 10, both adsorption capacity and efficiency decreased.

In a strongly acidic environment (solution pH from 2 to 5), the ammonium adsorption of HBG was relatively low. This is because of the competition between H^+ ions and NH_4^+ ions for adsorption sites on the HBG adsorbent during this pH range. Additionally, the surface of HBG became positively charged due to the solution pH being lower than the point of zero charge (pH_{PZC}) of HBG. pH_{PZC} of HBG was found to be 5.38 (Figure 2b). This created a repulsive force between the HBG surface and the positively charged ammonium ions in the solution [10]. In the pH range from 6 to 8, the adsorption capacity increased significantly, reaching its maximum at pH = 8. At this point, the solution pH was greater than the pH_{PZC} of the adsorbent, resulting in a negatively charged surface, the adsorption process occurred strongly through electrostatic attraction mechanisms. When the solution pH increased more than 9, NH_4^+ ions in the solution transformed into NH_3, which cannot be adsorbed by electrostatic attraction [11].

This experimental result indicated that the optimal pH for the ammonium adsorption process onto HBG was 8. This pH value was chosen for subsequent experiments.

3.3. Effect of contact time and adsorption kinetics

The effect of contact time on the adsorption of ammonium onto HBG was studied at a solution pH of 8, initial NH_4^+ ammonium concentration of 20 mg/L, adsorbent dose of 0.1 g/25 mL NH_4^+ and contact time ranging from 5 to 240 minutes. The results are presented in Figure 3a.

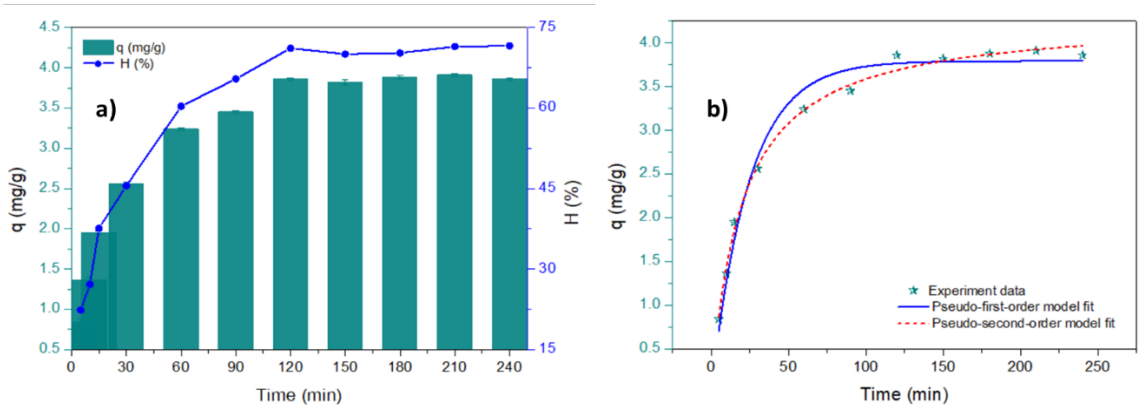

Figure 3. *(a) Effect of contact time on NH_4^+ adsorption by HBG; (b) Kinetic models of NH_4^+ adsorption onto HBG*

From the results in Figure 3a, it can be observed that both the adsorption capacity and adsorption efficiency of NH_4^+ onto HBG increased rapidly for the first 60 min and slowed down gradually with the contact time from 60 to 120 min and reaching their maximum values at 120 minutes, with respective values of 3.86 mg/g and 71.14%. From 120 to 240 min, the adsorption process reached saturation. This was attributed to a significant number of active sites on the surface of HBG being available during the initial stage, facilitating a rapid adsorption process. Over time, these active sites became saturated with NH_4^+ ions, leading to a slower and more stable adsorption process [12]. Based on the study, the equilibrium adsorption time was determined to be 120 min, and this time was chosen for further investigations.

The experimental data in this study was analyzed using the pseudo-first-order and pseudo-second-order models to describe the kinetics of the adsorption process. The results are presented in Figure 3b and Table 1.

Table 1. *Calculated parameters of the kinetic models for ammonium adsorption onto HBG*

Pseudo-first-order			Pseudo-second-order			$q_{e,tn}$ (mg/g)
q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	k_2 ($g.mg^{-1}.min^{-1}$)	R^2	
3.79	0.0411	0.97	4.29	0.0117	0.99	3.86

From the results in Figure 3b and Table 1, it can be observed that the adsorption process of NH_4^+ onto HBG fitted well to both first-order kinetic and second-order kinetic models. However, the correlation coefficient (R^2) obtained from the second-order model at 0.99 that was slightly higher than that of the first-order model (0.97). Additionally, the maximum adsorption capacity determined from the second-order kinetic and first-order kinetic models (4.29 mg/g and 3.79 mg/g) were very close to the experimental adsorption capacity (3.86 mg/g). This indicates that both models were suitable for description of the ammonium adsorption process onto HBG. The chemical reaction between NH_4^+ ions and functional groups on the surface of HBG dominated the adsorption process [13]. These findings are consistent with the results of other studies, such as Boopathy et al [5] and Khalil et al [14]. Boopathy's study focused on ammonium adsorption onto activated carbon derived from coconut shells [5], while Khalil's study investigated ammonium adsorption onto biochar derived from rice husk [14]. Both studies also found better agreement with the second-order kinetic model compared to the first-order model.

3.4. Influence of initial ammonium concentration and adsorption isotherm study

The initial concentration of ammonium is one of the important factors influencing the adsorption process. These experiments were conducted at initial concentrations of NH_4^+ varied from 10 mg/L to 80 mg/L, pH of 8, contact time of 120 min and the HBG dosage of 0.1 g/25 mL. The results illustrating the impact of the initial ammonium concentration on the adsorption process by HBG are presented in Figure 4a.

The results indicated that as the initial concentration of ammonium solution increased from 5 mg/L to 50 mg/L, the adsorption capacity rose from 1.94 mg/g to 4.57 mg/g. However, when the initial NH_4^+ concentration rose from 60 mg/L to 80 mg/L, the adsorption capacity remained nearly unchanged and reached a stable state. This can be attributed to the fact that increasing the concentration of NH_4^+ solution enhanced the concentration gradient between the solution and the adsorbent's surface, leading to increase adsorption capacity. Nevertheless, with a constant amount of HBG adsorbent, a constant number of active sites became saturated during the adsorption process, resulting in a plateau in adsorption capacity as the solution concentration continued to rise [15].

Additionally, as the concentration of NH_4^+ solution increased from 5 mg/L to 80 mg/L, the adsorption efficiency gradually decreased from 82.1% to 48.4%. This reduction in efficiency was also attributed to the limited number of active sites on the adsorbent due to the constant amount of adsorbent used [16].

To further understand the adsorption mechanism of NH_4^+ ions on HBG, the experiment data was fitted with the Langmuir and Freundlich models to analyze the adsorption isotherm. The results are illustrated in Figure 4b and Table 2.

It can be seen that, the correlation coefficient R^2 value of the the Langmuir model (0.98) was higher than that of the Freundlich model (0.89). Furthermore, the calculated adsorption capacity from the Langmuir isotherm model was 5.22 mg/g, which was quite close to the experimental data (4.57 mg/g). This affirms that the single-layer Langmuir isotherm model was appropriate for explaining the NH_4^+ adsorption process onto HBG [16]. Additionally, the value of *1/n* obtained

from the Freundlich model was 0.269 smaller than 1, indicating a favorable adsorption process for ammonium onto HBG. Therefore, HBG adsorbent can be effectively utilized for ammonium ion adsorption [2]. These results were consistent with other studies; for instance, the research by Alshameri et al. [2] and Fidel et al. [17] both demonstrated that the ammonium adsorption process in water follows the Langmuir isotherm model.

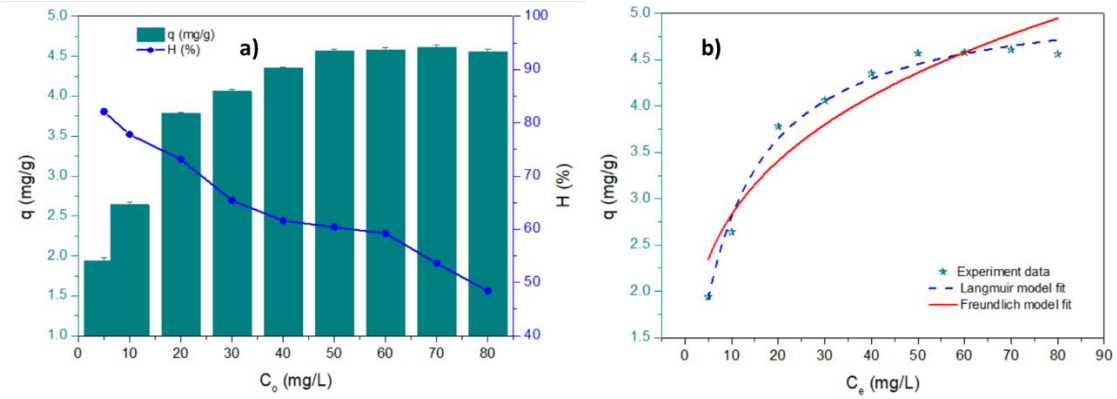

Figure 4. *(a) Influence of initial NH_4^+ concentration on adsorption process by HBG (b) Adsorption isotherm models of NH_4^+ onto HBG*

Table 2. *Calculated parameters of the isotherm models for ammonium adsorption onto HBG*

Langmuir			Freundlich			$q_{e,tn}$ (mg/g)
q_e (mg/g)	K_L (L/mg)	R^2	1/n	K_F (mg/g)	R^2	
5.22	0.116	0.98	0.269	1.52	0.89	4.57

To assess ammonium adsorption, the results from this study were compared with those of other adsorbents. The findings for ammonium adsorption with some other types of adsorbents are presented in Table 3. The data in Table 3 shows that ammonium adsorption capacity of HBG was lower than that of corn straw biochar and acidified magnetic sludge biochar. However, the adsorption capacity of HBG for ammonium was higher than that of digested sludge biochar and magnetic excess sludge. This suggested that HBG could be an effective and low-cost adsorbent for removing ammonium from aqueous solutions.

Table 3. *Comparison of HBG with other adsorbents for ammonium adsorption capacity*

Absorbent	Equilibrium ammonium concentration range (mg/L)	Langmuir maximum adsorption capacity (mg/g)	References
HBG	0 - 80	5.22	This study
Corn straw biochar	0 - 200	10.05	[18]
Digested sludge biochar	2 - 80	1.4	[19]
Acidified magnetic sludge-biochar	-	9.67	[20]
Magnetic excess sludge	45	1.79	[21]

4. Conclusions

In this study, hydrochar derived from paper waste sludge (HBG) was used for the ammonium adsorption from water. The ammonium adsorption capacity of HBG was the maximum at initial solution pH, contact time and initial ammonium concentration of 8, 120 min and 50 mg/L, respectively. The Langmuir and pseudo-second-order models fitted best with experimental data to describe ammonium adsorption onto HBG. The calculated maximum adsorption capacity based on the Langmuir isotherm model is 5.22 mg/g. This value may not be exceptionally high.

Therefore, further research is needed to modify the paper sludge material to enhance surface functional groups and specific surface area, aiming to improve adsorption efficiency. Moreover, to gain a better understanding of the adsorption mechanism, further research into the underlying mechanisms of the ammonium adsorption process by HBG is essential.

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