Article

The Adsorption of Ammonium Nitrogen from Milking Parlor Wastewater Using Pomegranate Peel Powder for Sustainable Water, Resources, and Waste Management

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Abstract: Agricultural wastewater poses serious risks to the environment due to how it is injudiciously used and managed. We investigated the use of pomegranate peel powder (PPP) to adsorb ammonium ions from milking parlor wastewater, which is applied as a nitrogen source for cropland fertilization despite its environmental ramifications. As a valueless by-product of juice and jam industries, PPP shows promising features and characteristics as a potential bio-adsorbent for ammonium nitrogen removal and recovery. The surface characterization of PPP was performed by zeta potential measurement and attenuated total reflectance Fourier transform infrared Spectroscopy (ATR-FTIR) analysis. The adsorption studies were carried out by batch experiments where the initial ammonium nitrogen (NH_4–N) concentration of studied wastewater was 80 mg/L. The effects of different operational parameters, such as pH, adsorbent dose, contact time, stirring speed, and temperature, were investigated. From kinetic studies, the equilibrium time was found to be 120 min, achieving an 81.8% removal synonym of ~2.5 mg/g NH_4–N uptake. The adsorption isotherm data fitted well with Langmuir model with correlation (R^2) > 0.99. Meanwhile, the kinetics followed pseudo-second order model with correlation (R^2) > 0.99.

Keywords: ammonium removal; waste reuse; wastewater recycling; nitrogen recovery; bio-adsorbent

1. Introduction

Milking parlor units consume significant amounts of water for drinking, washing, cleaning, and feed processing, and thus contribute to freshwater resource depletion. These parlor units also produce large volumes of nitrogen-rich wastewater that can be used in agriculture to enhance soil fertility, especially in regions where wastewater treatment services are not available. Because clean water is becoming even more scarce, using this type of wastewater for irrigation will continue to increase. However, this management option is no longer sustainable due to its negative environmental impacts and health risks. Therefore, adequate treatment of this wastewater before its reuse or discharge is necessary to meet effluent quality standards [1].

Ammonium nitrogen (NH_4–N) is one of the main components of milking parlor wastewater [2], and when in excess concentration, its release into bodies of water leads to serious environmental ramifications such as eutrophication, acid deposition, reactive nitrogen emissions, global warming, and over-fertilized soils [3,4]. Nitrogen is often regarded as the most essential and determinant nutrient for plant growth and crop yield [3]; therefore, its recovery is crucial, especially in communities with an increasing food demand and an indiscriminate use of chemical fertilizers [5]. Current wastewater treatment technologies place a heavy burden on dairy farm management, thus illustrating the need for simple, robust, and effective technology that requires low investment and maintenance costs [6]. Many methods, including biological processes, air stripping, and membrane technologies, have been developed to remove and recover NH_4–N from wastewater, though all of these methods have shown many disadvantages [7,8]. However, adsorption technology has proven to have promising features, such as its simplicity, cost effectivity, and potential to recover and reuse ammonium [9].

According to the Food and Agriculture Organization of the United Nations (FAO), more than 1 billion tons of food and agricultural waste are produced annually as a result of expanding agricultural activities and irresponsible food production and consumption [10]. The disposal of this waste into landfills has proven to be responsible for not only social and economic damage, but further for a considerable proportion of greenhouse gas emissions and groundwater contamination by leachate [11]. The traditional method used to mitigate this problem is to recycle this waste into animal feed or compost. Nowadays, there is an increasing interest in using these valueless biomaterials as a renewable resource for low-cost adsorbents in the removal and recovery of pollutants such as ammonium nitrogen [12,13]. These biomaterials contain a large number of functional groups (e.g., –OH, –COH) in their cellulose, hemicellulose, and lignin. Therefore, they hold promising ion-exchange capacities and general adsorptive characteristics [14].

Among food and agricultural wastes tested for pollutant removal, pomegranate peel powder (PPP) showed great efficiency in removing several pollutants from aqueous solutions including chromium, nickel, lead, and copper [15–17]. This efficiency originates to a large extent from functional groups present on the surface of PPP, namely hydroxyl (–OH) and carboxyl (–COOH) groups derived from carboxylic acid, phenols, alcohols, ketone, aldehyde, ethers, and ester components [18]. The global world production of pomegranates is estimated to be more than 1. 5 million tons [19], and since a large portion of this figure is processed for juice, jam, and other products, a huge amount of valueless pomegranate peel is discarded [20].

In this study, we investigated the use of PPP as a bio-adsorbent to remove ammonium nitrogen from milking parlor wastewater in order to establish an ecological water treatment method and to responsibly manage water, nutrients, and solid waste according to the 3R principle (reduce fresh water use and pollution, reuse food and agricultural waste and recycle nitrogen) as shown in Figure 1. Detailed studies on these process mechanisms under real conditions and investigations of the efficiency of nitrogen-loaded adsorbent as fertilizer are still lacking.
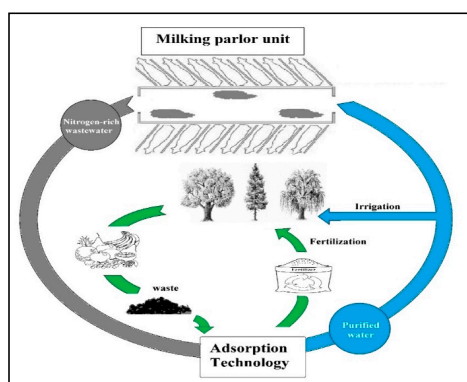

Figure 1. The adsorption process for using food and agricultural waste as bio-adsorbents for milking parlor wastewater purification and management.

2. Materials and Methods

2.1. Milking Parlor Wastewater

The wastewater used in this study was sampled from a milking parlor unit near the city of Szeged, Hungary. The daily average of the wastewater produced from this unit was estimated to be 10 m^3/day. This wastewater was mainly generated from washing operations including the washing of milk tanks, udders, robotic milking systems, platforms, and milking equipment. This wastewater consisted of water, cleaning chemicals, manure, and urine. Thus, it contained high levels of nutrients such as ammonium (NH_4^+), along with other ions such as potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), and heavy metals [21]. Chemical oxygen demand (COD), biological oxygen demand (BOD$_5$), total nitrogen (TN) and ammonium nitrogen (N–NH$_4^+$) concentrations of wastewater investigated in this study are shown in Table 1.

Table 1. Characteristics of the investigated wastewater.

pH	**7 ± 1**
Chemical oxygen demand (COD) (mg O$_2$/L)	4850 ± 500
Biological oxygen demand (BOD5) (mg O$_2$/L)	1200 ± 300
Total Nitrogen (TN) (mg/L)	120 ± 10
Ammonium nitrogen (N–NH$_4^+$) (mg/L)	80 ± 10

2.2. Adsorbent Preparation

A pomegranate peel was collected, cut into small pieces, and washed with distilled water several times to any remove dust or impurities. It was then oven dried at 105 °C for 2 h. Finally, the dried biomass was crushed and ground down to the desired size (<250 μm) for use in adsorption experiments.

2.3. Adsorbent Characterization

Since the surface area of an adsorbent is a determinant parameter in the adsorption process [22], the specific surface area of the PPP was determined by a Brunauer, Emmett, and Teller (BET) surface analyzer Horiba SA-9600 with liquid N$_2$ at 77 K (−196.15 °C). Results showed that this lignocellulosic material has a low surface area (~0.84 m^2/g). Therefore, a chemical and polar characterization of the PPP surface was mandatory, as they would play a major role in its adsorption capacity, affinity, and selectivity properties through chemical reactions between adsorbate and surface sites [22].

2.3.1. Zeta Potential

The zeta potential is widely used for the quantification of the sign and the magnitude of the electric double layer responsible for electrostatic interactions between the adsorbent and adsorbate. A zetasizer device, the Nano ZS Malvern, was used for zeta potential measurement, where 10 mg of PPP was introduced in 20 mL of ammonium chloride solutions (NH$_4$Cl) at different pH and concentration values.

2.3.2. Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) Analysis

An ATR-FTIR spectroscopy helped to identify the functional groups present on the surface of the adsorbent. A BIO-RAD Digilab Division FTS-65A/896 FTIR spectrophotometer with a 4 cm^{-1} resolution was used to observe the different functional groups present on the PPP's surface. The 4000–400 cm^{-1} wavenumber range was recorded and 256 scans were collected.

2.4. Batch Adsorption Experiments

The initial concentration of ammonium, adsorbent dose, pH, temperature, and contact times were the factors with the most significant impact on the removal of ammonium from the effluents [23].

Therefore, the first series of experiments were carried out to assess the effects of these parameters using the one factor at a time (OFAT) method. For this purpose, an amount of PPP was introduced into a flask containing 60 mL of milking parlor wastewater with an initial NH_4–N concentration of 80 mg L^{-1}. Five values of pH were investigated (3, 4, 5, 6, and 7) by adjusting the initial pH of the different solutions using 0.1 M HCl or 0.1 M NaOH. Three values of adsorbent dose (1, 1.5, and 2 g), temperature (25, 35, and 45 °C) and stirring speed (150, 300, and 450 rpm) were tested. To investigate the effect of contact time, the concentration of NH_4–N in the solution was measured continuously until it became stable (equilibrium state). For measurements, solutions were filtered using 0.45 μm microporous membrane filters and were then analyzed using the Merck spectrophotometer Spectroquant Nova 60. Finally, the NH_4–N removal rate was calculated as shown in Equation (1):

$$\% \text{ Removal} = \frac{c_i - c_f}{c_i} \times 100, \tag{1}$$

where c_i (mg/L) and c_f (mg/L) are the initial and final NH_4–N concentrations, respectively.

For isotherm and kinetics modeling, the adsorbed amount of NH_4–N was calculated as:

$$qe \text{ (mg/g)} = (c_i - c_e)\frac{V}{M}, \tag{2}$$

where c_i (mg/L) and c_e (mg/L) are the initial and equilibrium concentrations of NH_4–N in the solutions, respectively; V (L) represents the solution volume; and M (g) represents the mass of the adsorbent.

Isotherm and kinetic data were fitted to existing models and the best-fit models were selected based on the highest correlation coefficient (R^2).

3. Results and Discussion

3.1. Adsorbent Characterization

3.1.1. Zeta Potential

The results of the zeta potential measurement showed that the PPP's surface was negatively charged in all studied pH and solution concentrations. When the pH increased, the value of the zeta potential decreased. Therefore, the PPP's surface became highly negatively charged, as shown in Figure 2a. The PPP's surface thus contributed to the ability of functional groups to adsorb ammonium ions through electrostatic interaction [24]. However, the zeta potential increased by increasing the NH_4Cl concentration, as shown in Figure 2b, due to the charge screening of electrolytes and the saturation of available negatively charged surface sites [25].
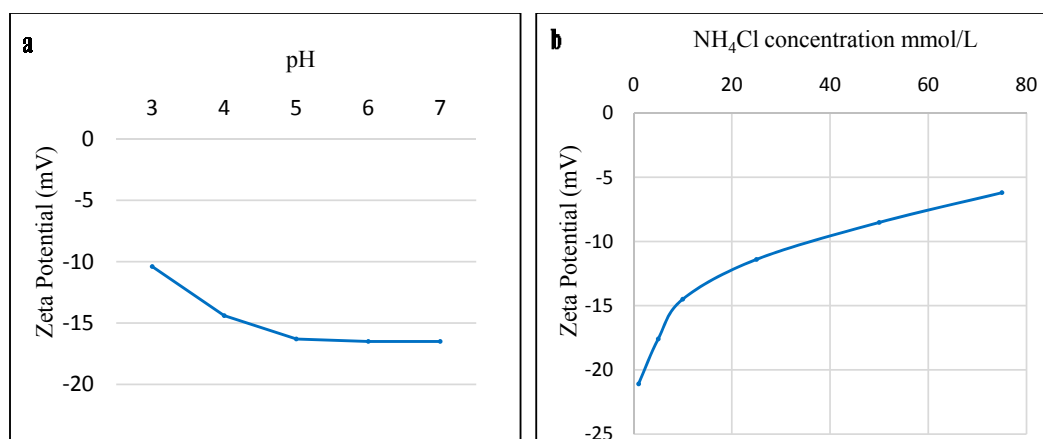

Figure 2. (**a**) The zeta potential of pomegranate peel powder (PPP) as a function of pH in an (10 mmol/L) NH_4Cl solution; (**b**) the zeta potential of PPP as a function of an NH_4Cl concentration.

3.1.2. ATR-FTIR Analysis

Figure 3 presents the FTIR-ATR analysis of PPP, where the absorption bands can be attributed to the functional groups by using data from literature [26].
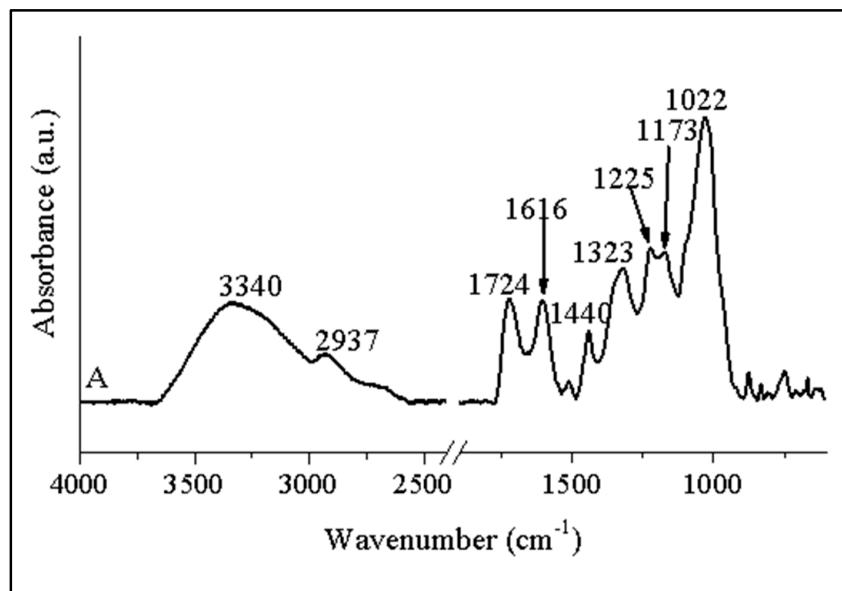

Figure 3. Attenuated total reflectance Fourier transform infrared Spectroscopy (ATR-FTIR) of PPP.

The bands at approximately 3340 cm^{-1} were assigned to the stretching vibration bond of hydroxyl groups, such as carboxylic acid, phenol or alcohols. The band observed at about 2937 cm^{-1} was assigned to the stretching vibration bond of aliphatic C–H groups. The peak around 1724 cm^{-1} represented C=O groups (carboxylic acid, acetate groups COO, ketone, and aldehyde). The band at 1616 cm^{-1} was assigned to the stretching vibration bond of C=O and C=C. The peaks at 1616, 1323, and 1022 cm^{-1} were assigned to C–O groups of carboxylic acid, alcoholic, phenolic, ether, and ester groups. These abundant carboxyl and hydroxyl groups in the PPP's surface may function as proton donors; hence, the deprotonated groups could have bound ammonium ions. These results agreed with results of the zeta potential measurement and proved that PPP is rich in functional groups.

3.2. Influencing Parameters

3.2.1. Effects of Adsorbent Dose

The effect of the adsorbent dose was studied by using different doses of PPP: 1 g (~16 g/L), 1.5 g (~25 g/L). and 2g (~33 g/L). Generally, the percentage of adsorption increased with increasing adsorbent dose. However, the amount of molecules adsorbed per unit mass of adsorbent decreased [13]. As illustrated in Figure 4, the removal rate of ammonium ions by the PPP increased significantly (from 53.9% to 88.7%) when the PPP dose was increased from one to two grams due to the increase in surface area available in the solution, as more free binding sites were available for the sorption of ammonium ions [27]. However, the calculation of NH$_4$–N uptake q$_e$ by Equation (2) showed that 1.5 g of the PPP achieved a 2.49 mg/g of NH$_4$–N uptake, whereas this value was only 2.02 mg/g for 2 g of the PPP. Therefore, 1.5 g of the PPP was used for the following experiments.
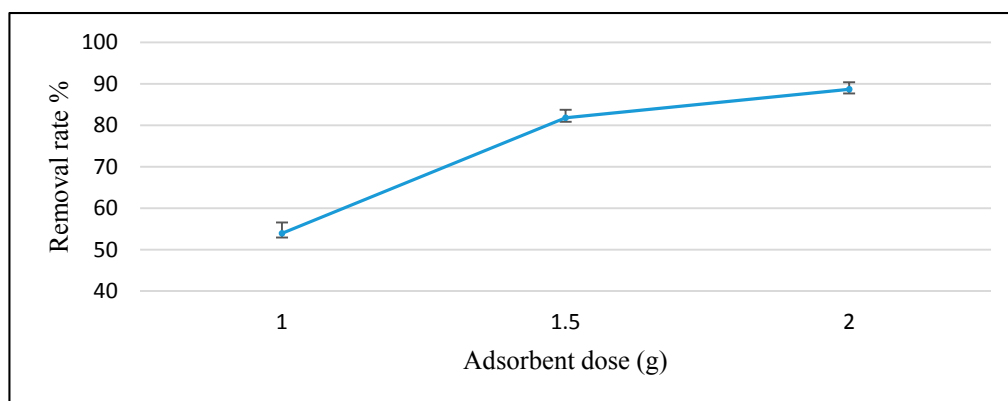
Figure 4. Effect of PPP doses on ammonium nitrogen removal from milking parlor wastewater (pH = 6, stirring speed = 300 rpm, temperature (T°) = 25 °C, time (t) = 120 min).

3.2.2. Effects of pH Solutions

Initial pH levels of a solution play a critical role in the adsorption process, as its main effect is related to the protonation/deprotonation of the adsorbate and the adsorbent surface [22]. The optimum removal of ammonium ions by the PPP was around 81% at pH 6, as shown in Figure 5. This removal decreased with the decreasing pH because of the presence of more protons H^+ in acidic solutions. These protons competed effectively with ammonium cations and led to the protonation of the PPP's surface. Therefore, the uptake of ammonium ions by electrostatic forces decreased. However, the slight decrease in the removal rate at pH 7 could be attributed to the deprotonation of ammonium ions.
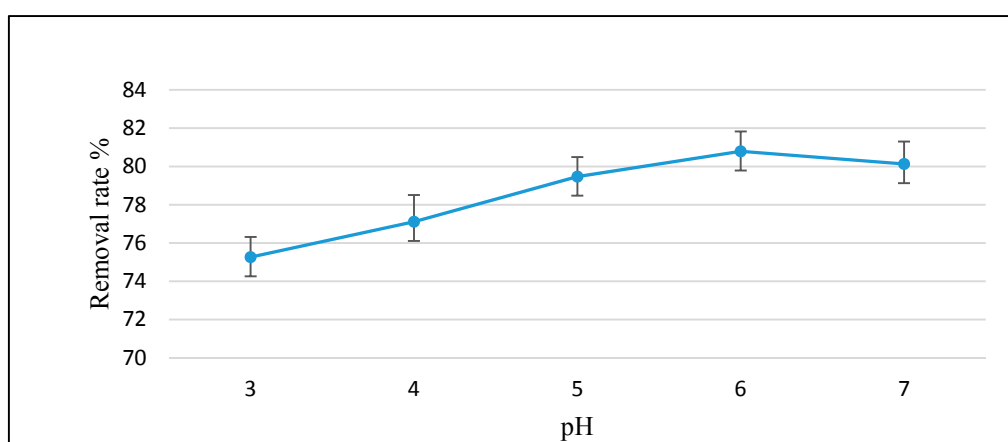

Figure 5. Effects of pH on ammonium nitrogen removal from milking parlor wastewater by PPP. (Adsorbent dose = 1.5 g, stirring speed = 300 rpm, T° = 25 °C, t = 120 min.)

3.2.3. Effects of Stirring Speeds

Stirring speed is a parameter influencing the process of examining PPP's adsorption abilities, as it is the physical driving force of the adsorption process. The removal of ammonium ions by the PPP varied with different stirring speeds, the optimal of which was at a stirring speed of 300 rpm, as it achieved the peak removal rate, as shown in Figure 6. The increase in this speed led to a decrease in the removal rate because it created turbulence that perturbs the ammonium ion uptake. Likewise, a lower speed was not enough for the ammonium ions to encounter available active sites, which resulted in a low ammonium ion uptake as well [28]. Therefore, a moderate stirring speed is required to improve the diffusion of ammonium ions toward the active sites present on the surface of PPP.
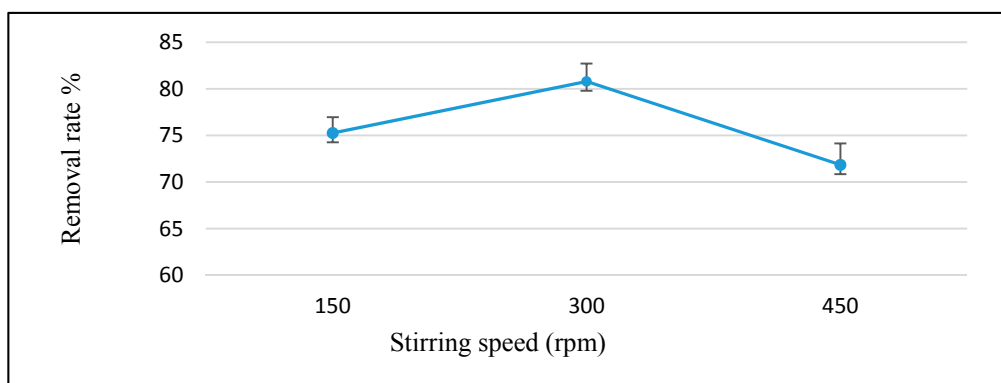
Figure 6. The effects of varying stirring speeds on ammonium nitrogen removal from milking parlor wastewater by PPP (adsorbent dose = 1.5 g, pH = 6, T° = 25 °C, t = 120 min).

3.2.4. Effects of Temperature

The removal of ammonium nitrogen by PPP increased slightly from 81.8% to 87.2% when the temperature was raised from 25 to 45 °C, as illustrated in Figure 7. Generally, increasing the temperature improves the mobility of ammonium ions and the availability of active sites; thus, it facilitates the diffusion of ammonium ions from the solution to the surface's active sites. However, the effect of increasing the temperature in this study was not of high significance, and in the case of adsorption from an aqueous phase, the effect of the temperature strongly depends on the nature of the adsorbent surface (energetically heterogeneous or homogeneous). Therefore, temperature could potentially have a variable effect on the adsorption process. Furthermore, high temperatures are not always beneficial for the process [22]. This was further proven in a similar study that assumed an ammonium adsorption equilibrium by lignocellulosic material to be a thermo-dependent process [29].
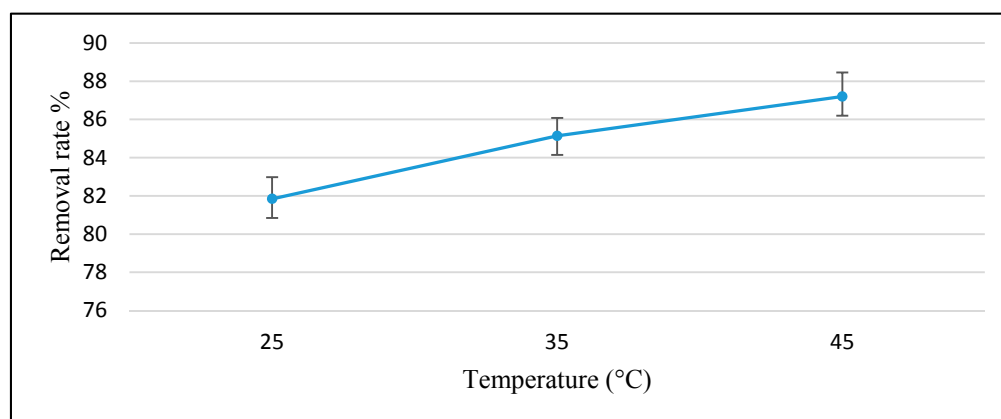

Figure 7. The effect of temperatures on ammonium nitrogen removal from milking parlor wastewater by PPP (adsorbent dose = 1.5 g, pH = 6, stirring speed = 300 rpm, t = 120 min).

3.2.5. Effects of Contact Time

The adsorption of contaminants from a liquid solution by a solid surface is usually divided into three phases [14]. Figure 8 shows that the adsorption of ammonium ions by PPP started with a rapid initial phase. This was characterized by a high removal rate (71% within 5 min) due to the initially large and available active sites in the surface of the PPP that mainly comprised of carboxyl (–COOH) and hydroxyl (–OH) groups. Then, as the contact time increased, the removal rate slowed due to the slow diffusion of ammonium ions into the internal structure of the PPP. This phase is known as the intermediate phase. Finally, the removal rate achieved a constant value (81.8% within 120 min) where no further ammonium ions were removed from the solution due to the saturation of free active sites as the system reached equilibrium.
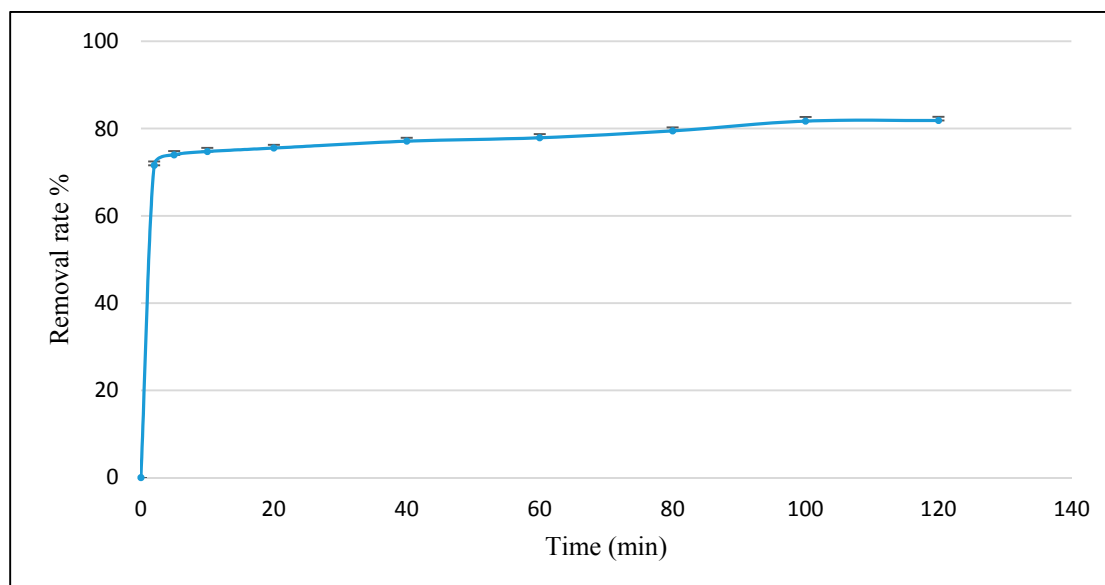
Figure 8. The effect of contact time on ammonium nitrogen removal from milking parlor wastewater by PPP (adsorbent dose = 1.5 g, pH = 6, stirring speed = 300 rpm, T° = 25 °C).

3.3. Adsorption Isotherm

Isotherm modeling was used to investigate the adsorption rate quantitatively through a curve relating to the adsorbed amount of solute (q_e) to its equilibrium concentration in solution (c_e), as shown in Figure 9. Fitting isotherm data to mathematic functions of existing models helps to understand the interactions adsorbents and adsorbates have in their processes and offer details about the chemistry of binding [30]. An isotherm of the amount of ammonium ions adsorbed by PPP was evaluated through a series of batch adsorption experiments using different doses of PPP and a constant initial NH_4–N concentration and temperature.

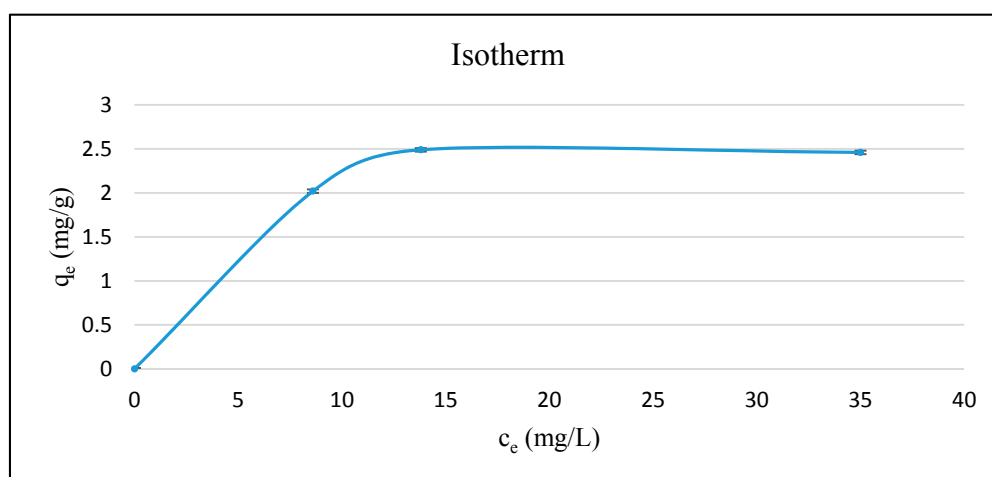**Figure 9.** An isotherm of the adsorption of ammonium nitrogen from milking parlor wastewater by PPP (pH = 6, stirring speed = 300 rpm, T° = 25 °C, t = 120 min).

Among models tested to describe the adsorption of ammonium ions from milking parlor wastewater by PPP, the Langmuir isotherm offered the best fit to experimental adsorption data according to the value of the correlation coefficient ($R^2 > 0.99$), as shown in Figure 10.
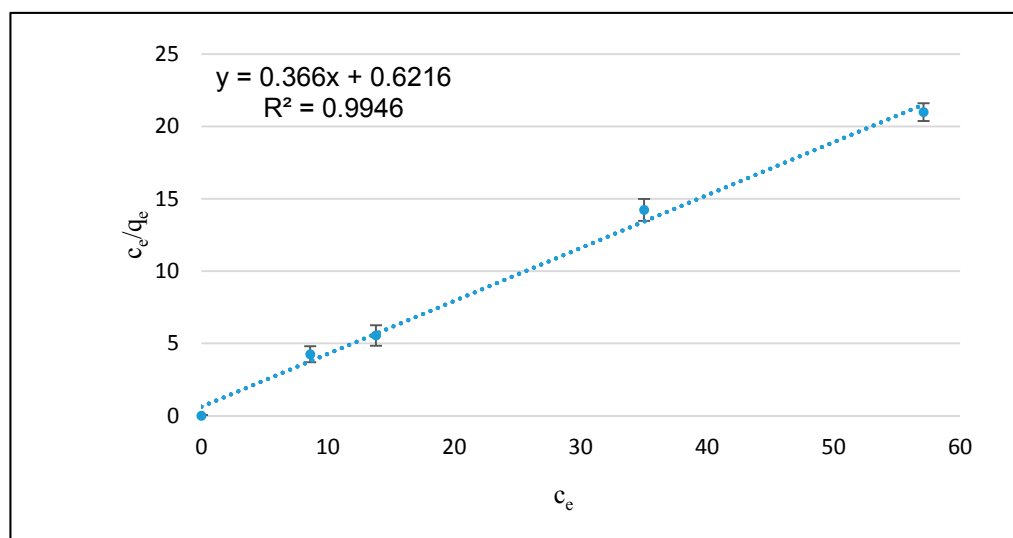
Figure 10. The Langmuir isotherm of adsorption of NH_4-N from milking parlor wastewater by PPP (pH = 6, stirring speed = 300 rpm, T° = 25 °C, t = 120 min).

The Langmuir equation, the linearized form, and constant parameters of the Langmuir isotherm are presented in Table 2.

Table 2. Equations and parameters of the Langmuir isotherm.

Equation	Linearized Form	Qm	B	RL
$Q = \frac{Qm\ b\ ce}{1+\ bce}$	$\frac{ce}{qe} = \frac{ce}{Qm} + \frac{1}{Qm\ b}$	2.49	0.42	0.02

Note: Qm (mg/g) is the maximum NH_4–N uptake, b (L/mg) is the Langmuir adsorption constant, q_e (mg/g) is the equilibrium NH_4–N uptake, and c_e (mg/L) is the equilibrium concentration.

The constant b can be obtained from the slope and intercept of the graph (c_e/q_e) against (c_e), whereas the parameter (R_L) is the separation factor, which can be calculated as:

$$R_L = 1/(1 + bci). \tag{3}$$

The value of R_L obtained (0.02) was very low, which indicated that the amount of adsorption of ammonium ions from milking parlor wastewater by PPP was favorable [31].

This isotherm model assumes that the adsorption process is localized and controlled by a monolayer coverage of adsorbent surfaces and all adsorption sites possess an equal affinity for the adsorbate. Furthermore, no interaction occurred between the adsorbed molecules on neighboring sites and the intermolecular forces decreased rapidly with distance [32].

3.4. Adsorption Kinetics

Adsorption kinetics present the progression of time in the adsorption process, thus determining the time required to reach the state of equilibrium and the mass transfer of ammonium ions from milking parlor wastewater to the adsorption sites present in the PPP surface, as shown in Figure 11. Understanding adsorption kinetics arises from identifying governing mass transfer mechanisms and their unique parameters [22].
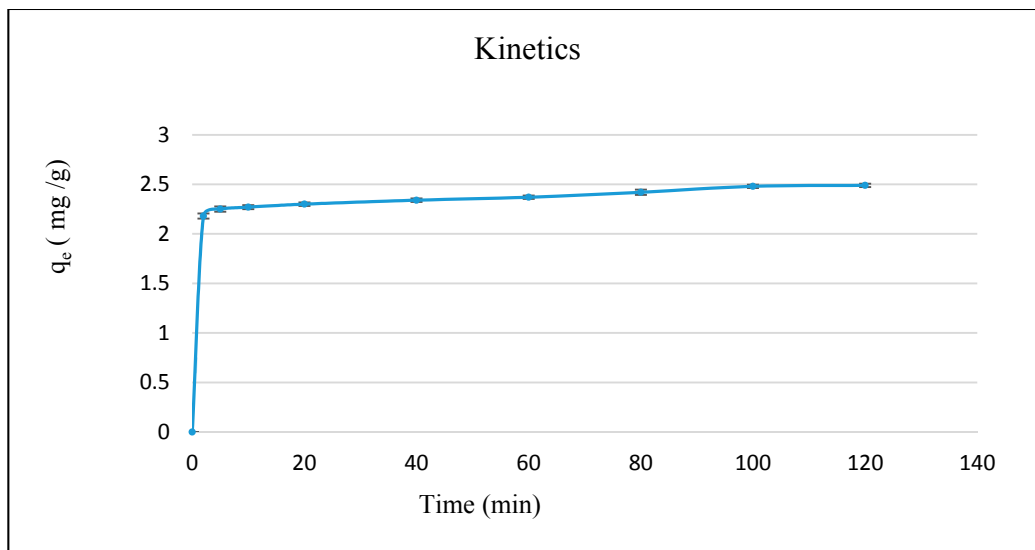
Figure 11. The kinetics of the adsorption of ammonium nitrogen from milking parlor wastewater by PPP (adsorbent dose = 1.5 g, pH = 6, stirring speed = 300 rpm, T° = 25 °C).

3.4.1. The Pseudo-Second Order Kinetic Model

Among existent kinetics models, the pseudo-second order kinetic model, a plot of (t/qt) against (t), fits well with adsorption kinetic data according to the value of the correlation coefficient ($R^2 > 0.99$), as shown in Figure 12.
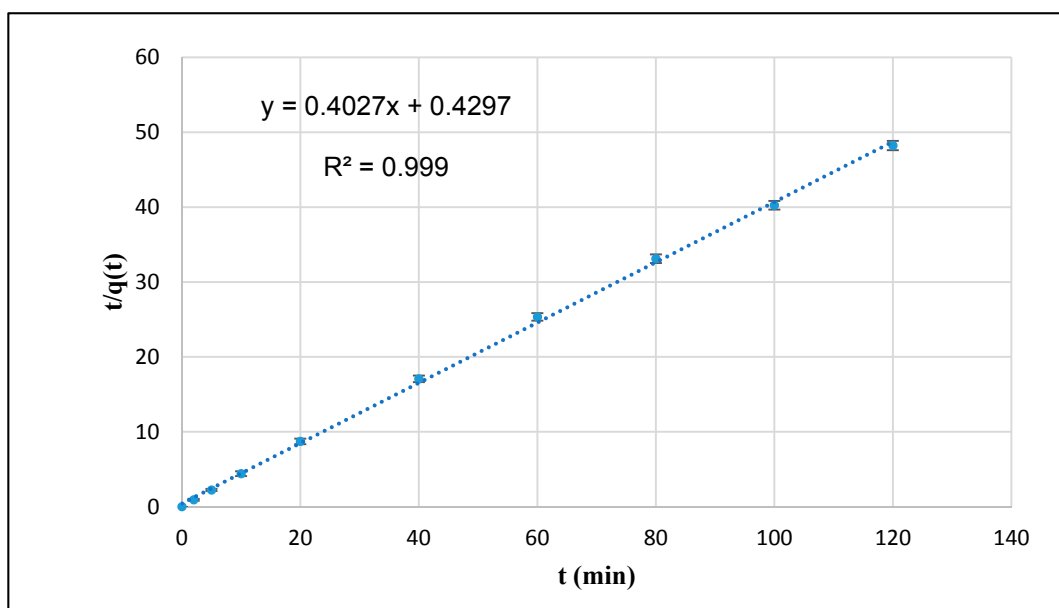

Figure 12. The pseudo-second order kinetic model of the adsorption of ammonium nitrogen from milking parlor wastewater by PPP (adsorbent dose = 1.5 g, pH = 6, stirring speed = 300 rpm, T° = 25 °C).

Equations (4) and (5) are equations and linearized forms of the pseudo-second order model, respectively.

$$\frac{dQt}{dt} = k2(Qe - Qt)2, \tag{4}$$

$$\frac{t}{Qt} = \left(\frac{1}{k2Qe2}\right) + \left(\frac{1}{Qe}\right)t. \tag{5}$$

This kinetic model assumes that the adsorption process is governed by chemical sorption with a sharing and exchanging of electrons between adsorbent and adsorbate through valence forces. This is a result of the large number of functional groups in the adsorbent surface [29].

3.4.2. Weber–Morris Model

This model is called also intra-particle diffusion model and it is a linear plot of qt versus √t, which is employed to identify the governing step in the adsorption process. The equation of this model and its linearized form are the same and they are expressed in Equation (6).

$$qt = k3 \sqrt{t} \tag{6}$$

As illustrated in Figure 13, the linear plots at all studied concentrations do not pass through the origin with a low value of R^2, indicating that intra-particle diffusion is not the rate-limiting step. Furthermore, more than one phase is involved in the adsorption of ammonium ions from milking parlor wastewater by PPP (e.g., external diffusion, adsorption). Similar results were found for the adsorption of ammonium ions from aqueous solutions onto Posidonia oceanic fibers [31].
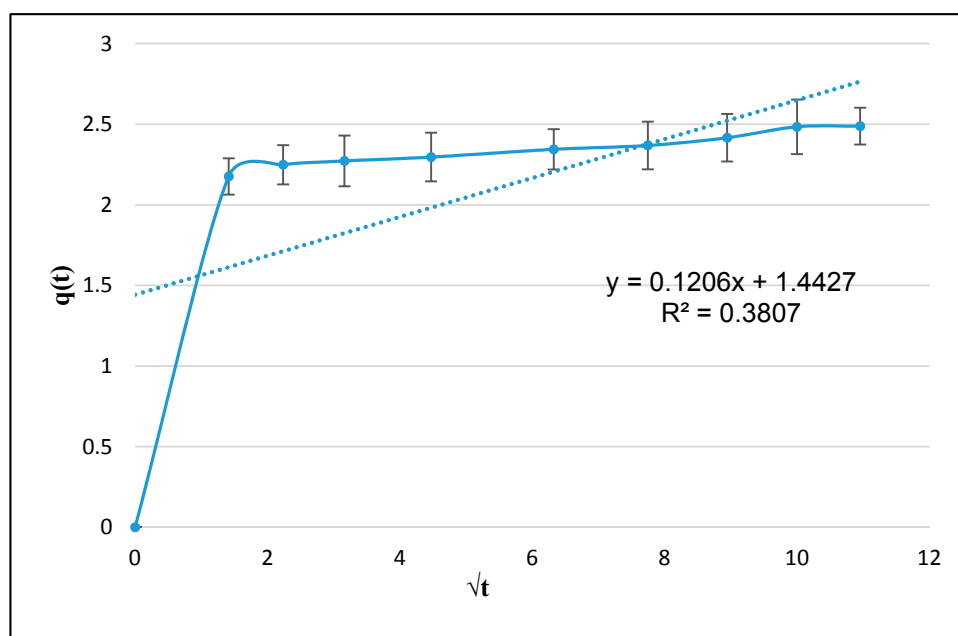

Figure 13. The Weber–Morris model of the ammonium nitrogen adsorption from milking parlor wastewater by PPP (adsorbent dose =1.5 g, pH = 6, stirring speed = 300 rpm, T° = 25°C).

4. Conclusions

This study showed that using PPP for the adsorption of ammonium nitrogen from milking parlor wastewater can achieve an 81.8% removal through a ~2.5 mg/g NH_4–N uptake in 120 min. The factor with the highest impact on the removal efficiency was the adsorbent dose, while the effects of other factors, such as the pH, stirring speed, and temperature, were nearly negligible. Therefore, PPP provides the advantage of working in a wide range of pH levels, temperatures, and stirring speeds. The ammonium adsorption capacity of PPP can increase should one suitably pretreat the wastewater targeted, since this study was performed using untreated wastewater rich in suspensions that potentially limited the adsorption of ammonium ions.

Lastly, the use of PPP for the adsorption of ammonium from wastewater is an eco-friendly treatment method that would not only mitigate the stress on freshwater resources in the agricultural sector, but would also provide a sustainable management system of nutrients and solid waste. However,

investigations on the reuse of ammonium-loaded PPP as a fertilizer are still lacking and present a pivotal issue.

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