Peanut Biochar as a Stable Adsorbent for Removing NH₄-N from Wastewater: A Preliminary Study

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ABSTRACT

The removal of ammonium ions from synthetic wastewater by a novel adsorbent, the peanut hull biochar (PHB) powder, was investigated. The pore analyses, specific surface area, scanning electron microscopy (SEM) images and FTIR spectra were used to characterize the surface and reactivity of PHB. The mathematical models were used to analyze the adsorption isotherms. Adsorption isotherm of ammonium ions using batch technique showed that, at equilibrium conditions, the removal rate was increased linearly with increasing the initial concentration of ammonium ions in water (2.0 – 20.0 gm⁻³). After 24 hr of reactions, the average amounts of NH₄⁺ removed by PHB represented 66.3% regardless the type of associated anions (Cl⁻ or SO₄²⁻). Concentrations of ammonium ions recovered from PHB surfaces represented 0.2–0.39% of the total removed NH₄⁺-N and reflected a strong sorption forces owned by PHB surfaces. The characteristics of pore volume, area and size distribution of PHB and tendency to increase the percents of small nano-pores as shown by SEM images may strengthen the removal results. The adsorption equilibrium fitted well to both the Langmuir and Freundlich models. The obtained results introduce the peanut hull biochar materials as an inexpensive adsorbent which has high adsorption capacities and recalcitrant nature.

Key words: ammonium ion; peanut hull biochar; adsorption isotherm; wastewater treatment

Introduction

The extent of water contamination has risen due to the large quantities of industrial and domestic waste discharges to the environment. Increased nitrogen concentrations in domestic waters are becoming significant among the pollutants. The removal of various nitrogen compounds from wastewater is receiving wide attention because the discharge of these contaminants is obvious in the growth of algae and aquatic plants. Unless steps are taken to manage the discharge of these contaminants, over fertilization will continue to increase, especially with the multiple reuse of water. Nutrient compounds such as ammonium (NH₄-N), nitrite (NO₂⁻) and nitrate (NO₃⁻) often present in different types of wastewater, can end up in lakes, rivers and drinking water reservoirs with effluent discharges. The ammonia and ammonium ions are the most commonly encountered nitrogenous compounds in wastewaters. They also cause undesired odors and several diseases.

Several investigators studied ammonium ion removal using adsorbents such as natural and synthetic zeolite, silicate clay minerals including sepiolite. Aguilar et al. [1] investigated physicochemical removal of NH₄-N using activated silica, powdered activated carbon and precipitated calcium carbonate. They found very low ammonia removal of around 3–17% but protein-N removal was appreciable (74-89%). Ion exchange usually employs organic resins, which are very selective but expensive. However, there are cheaper alternative natural and waste materials that can be used to replace high cost materials. Various researchers have studied the effectiveness of a variety of low cost materials for ammonia removal such as clay and zeolite [29,27,8,13], limestone [4], natural and waste materials such as waste paper, refuse cement and concrete [3] and sepiolite and activated sepiolite [26,5].

Biochar is a by-product of biomass pyrolysis (residues of crops, wood trees, turfgrass, animal manure, etc) which is undertaken to generate energy.

Its incorporation into soil is currently being promoted as one of the tools that could be deployed to combat anthropogenically induced increases in atmospheric CO₂ concentrations [19,24]. To date, the beneficial effects of adding biochar to soil include increasing soil moisture retention, improving soil structure, increasing nutrient retention, decreasing N₂O and CH₄ emissions, reductions in leaching of inorganic N, adsorption of anthropogenic chemicals such as steroid hormones, pesticides and heavy metals [22,28,32,33,2,9].

Recent studies showed that application of biochar to soil altered N leaching rates [11,28,31] and support its potentiality to absorb ammonia (NH₄⁺-N). On the other hand, the observed reduction in the N₂O emissions from ruminant urine affected soil was attributed to adsorption of NH₃ and reducing the N pool available for soil microbes [34].

Peanut hulls are abundant agricultural by-products in the south-western Nile Delta of Egypt. They are plentiful, inexpensive, and renewable resources. According to the statistics of Egyptian Ministry of Agriculture and Land Reclamation (2006), the total yield of peanut produced was 199,346 metric ton and the peanut hulls represented about 29% of total yield (57,810 ton) based on oven-dried weight. Therefore, reuse of these waste materials – in the pyrolized form – in removing NH₄⁺-N from municipal wastewater will be valuable and economy wise.

The objectives of the current work aimed to introduce the peanut biochar as a cost effective adsorbent material to efficiently remove NH₄-N ions from wastewaters depending on its own surface characteristics and reactivity.

Materials and Methods

2.1. Preparation of feedstock:

The peanut hull used in this study was collected from a local market. The collected biomaterial was extensively washed with tap water to remove soil and dust. Washing process was repeated with distilled water then dried in an oven at 70 °C for 24 h. Dry feedstock was splitted into two parts, one part was crushed into powder and sieved by 0.5mm polypropylene sieve then preserved in the desiccators for use. The other part was used for preparing the biochar and activated carbon materials.

2.2. Preparation of biochar:

The dried feedstock of peanut hull was transferred into flexible aluminum dishes and sealed by aluminum foil then transferred into muffle furnace and pyrolized at the temperature of 450 °C for 15 min under limited O₂ conditions. After cooling to ambient temperature, the produced biochar was crushed and sieved using 0.5mm polypropylene sieve then stored in plastic jars. Total carbon (Walkley-Black wet digestion method; Nelson and Sommers, [23]) and nitrogen (digested and determined according to Bremner and Mulvaney, 1982) contents of the resulted biochar were 55.0% and 1.9%, respectively, and pH (determined according to Warncke, [35]) was 9.28.

2.3. Surface characterization of biochar:

Analysis of pore area, volume and size as well as specific surface area of peanut hull feedstock (PHF) and peanut hull biochar (PHB) were determined using N₂ sorption isotherms run on Beckman Coulter SA(TM) 3100 Surface Area and Pore Size Analyzer. The Brunauer-Emmett-Teller (BET) method was used to determine mesopore-enclosed surfaces. On the other hand, SEM analysis was carried out for both samples using a Joel 6360 OLA.

2.4. Adsorption Isotherm:

In a batch adsorption experiment, four grams of PHB were transferred into one-liter double jacketed reaction vessels and stirred (at a rate of 300 rpm) with distilled water for 24 h before the addition of ammonium chloride (NH₄Cl) or ammonium sulfate ((NH₄)₂SO₄) by final concentration 2000, 10000, 20000 or 100000 ppm NH₄-N. The adsorption isotherm was conducted at 30 °C for 24 h then the suspension samples were withdrawn by syringe needle and filtered using 0.45μm Gelman membrane filter. Concentration of NH₄-N in the supernatants was determined by Kjeldahl automatic distillation and titration (AutoKjeldahl Unit K-370). The amounts of adsorbed NH₄-N by PHB were calculated according to the following equation:

\[ q = \frac{(C_o - C_i) \times V}{1000 \times m} \]  \hspace{1cm} (1)

Where C₀ is the initial concentration of ammonium (mg L⁻¹), Cᵢ the ammonium concentration after adsorption (mg L⁻¹), V is the volume of simulated wastewater (ml) and m is the biochar mass (g).

To estimate the maximum adsorption capacity and evaluate the adsorption intensity of ammonium onto PHB, Langmuir and Freundlich models were used to fit the experimental data.

2.5. Ammonium Desorption experiment:

The desorption was done using 2.0 M KCl solution to extract the absorbed ammonium from the biochar. The biochar weights were dry matter weights. The used biochar was shaken with KCl solution for 2 h then filtered as in the original tests using filter paper to remove the solids. It was then tested for available ammonium using the same above mentioned procedure.
Results and Discussion

3.1. Pore analysis and specific surface area:

Biomass feedstock and the processing conditions of pyrolysis are the main factors determining pore size distribution in biochar, and therefore its total surface area. According to the results of pores analysis and specific surface area (Table 1), pyrolysis of PHB increased the percent of small pore volumes (< 20 nm), about 42.5% compared to the PHF. Also, the data of pore area distribution analysis showed that pyrolysis process increased the pore area percent of small pores (<20 nm) from 68.04% in PHF to 79.18% of the total pore area in PHB. On the other hand, the total pore size of PHB increased about 8.3% more than those of PHF (Table 1). As can be seen from the table, pyrolysis of PHF approximately doubled the value of specific surface area of PHB.

The SEM images (Fig. 1) indicated that PHB has different macromolecular structure than the PHF. The SEM analyses of PHF and PHB showed the porous characteristic of biochar surfaces and the development of voids compared with the PHF.

3.2. FTIR analysis:

As a biomass, the peanut hull is a complex material consisted of polyphenol such as catechol, pyrogallic acid and m-trihydroxybenzene, mineral, lipid, and cellulose, etc. Chemical sorption can occur by the polar functional groups of these constitutes, which include carboxyl groups and phenolic hydroxyl as chemical bonding agents [36]. FTIR spectrum of the PHB in the range of 4000–500 cm$^{-1}$ is shown in Fig. (2), it could be seen, the band at 3398 cm$^{-1}$ was ascribed to the mixed stretching vibration absorption band of amino and hydroxyl groups. The small band obtained at 1591 cm$^{-1}$ was assigned to the carboxyl group stretching vibration or assigned to C=C in plane aromatic vibrations from lignin formations [15]. The peak at 1402 cm$^{-1}$ was caused by the phenolic O-H bending. The peak at 1122 cm$^{-1}$ is indicative of the OH in-plane bending cellulose. The small bands at 781 and 615 cm$^{-1}$ represent C-H aromatic and alkayl bend, respectively. Comparable FTIR results were obtained for chemically pyrolyzed peanut hull by Ozer et al., [25].

<table>
<thead>
<tr>
<th>Properties</th>
<th>PHF</th>
<th>PHB</th>
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<tbody>
<tr>
<td>BJH pore volume distribution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt; 20.0 nm</td>
<td>24.520</td>
<td>34.950</td>
</tr>
<tr>
<td>20 - 80 nm</td>
<td>45.250</td>
<td>41.010</td>
</tr>
<tr>
<td>&gt; 80.0 nm</td>
<td>30.270</td>
<td>24.060</td>
</tr>
<tr>
<td>BJH pore area distribution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt; 20.0 nm</td>
<td>68.040</td>
<td>79.180</td>
</tr>
<tr>
<td>20 - 80 nm</td>
<td>24.980</td>
<td>16.900</td>
</tr>
<tr>
<td>&gt; 80.0 nm</td>
<td>7.000</td>
<td>3.920</td>
</tr>
<tr>
<td>BJH total pore size (ml g$^{-1}$)</td>
<td>0.012</td>
<td>0.013</td>
</tr>
<tr>
<td>BET specific surface area (m$^{2}$ g$^{-1}$)</td>
<td>1.001</td>
<td>1.900</td>
</tr>
</tbody>
</table>

Fig. 1: SEM Micrographs of PHF (A and C) and PHB (Band D) showing pores and cavities in the surfaces at different magnifications.
3.3. Adsorption Isotherm of Ammonium onto Biochar:

The results of NH\textsubscript{4}-N removal by PHB showed a high adsorption capacity throughout the tested range of ammonium concentrations (Fig. 3). PHB removed about 66.14, 66.25, 67.75 and 55.68% of NH\textsubscript{4}\textsuperscript{+} from the solutions containing 2, 10, 20 and 100 g kg\textsuperscript{-1} biochar, respectively. There were no significant differences in the removed ions according to their accompanied anions (Cl\textsuperscript{-} or SO\textsubscript{4}\textsuperscript{2-}). The amounts of removed NH\textsubscript{4}-N ions showed a high efficiency of PHB in removing process comparing with other available sorbents. Using a mixture of lime stone and granular activated carbon by ratio 25:15, about 58% of NH\textsubscript{4}-N was removed in a batch adsorption experiment with shaking time of 150 min and settling time of 120 min with initial concentration of 2.5 mg/L NH\textsubscript{4}-N and the removal percent was 39% for initial concentration 100 mg/L NH\textsubscript{4}-N. In another study, the percents of removed NH\textsubscript{4}-N by activated silica, powdered activated carbon and precipitated calcium carbonate was very low (3-17%) according to the results shown by Aguilar \textit{et al.} [1].

Langmuir and Freundlich isotherms are used to represent adsorption of components from liquid phase on to a solid phase. The two models were used to estimate the maximum adsorption capacity and to evaluate the adsorption intensity of ammonium onto PHB. The two models’ linear forms are:

\[
\frac{C_e}{q_e} = \frac{1}{ab} + \frac{C_e}{b} \quad \text{(Langmuir model)}
\]

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \text{(Freundlich model)}
\]

where \(C_e\) (mg/L) is the equilibrium concentration in the solution, \(q_e\) (mg/g) the ammonium adsorbed at equilibrium, \(b\) (mg/g) the maximum adsorption capacity, \(n\) Freundlich constant related to adsorption intensity, and \(a\) (L/mg) and \(K_F\) ((mg/g)(L/mg)\(^{1/n}\)) are the adsorption constants for Langmuir and Freundlich models, respectively. Adsorption follows both Langmuir and Freundlich isotherms (Fig. 4 A and B). However, the values of regression coefficients indicated that the equilibrium data fitted well with the Langmuir (\(R^2 = 0.999\) for chloride and sulfate forms of ammonium solution) and Freundlich (\(R^2 = 0.997\) for both salts) adsorption isotherms. Therefore, the adsorption of ammonium ions onto the peanut biochar could be attributed to monolayer adsorption as well as multilayer adsorption and also describing the heterogeneous nature of PHB surfaces.

3.4. Ammonium Desorption:

Shaking of PHB with extraction solution (2.0 M KCl) did not release the sorbed ions of ammonium where about 0.2% and 0.39% of the total sorbed NH\textsubscript{4}\textsuperscript{+}-N were released from biochar treated with (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} and NH\textsubscript{4}Cl solutions. These results reflected a strong sorption forces owned by PHB surfaces toward ammonium ions.

During thermal decomposition of peanut hull biomass, mass loss occurs mostly in the form of organic volatiles, leaving behind voids, which form an extensive pore network. The PHB structure shown by SEM images indicated the occurrence of micro-cavities which seem to work as irreversible sinks in which NH\textsubscript{4}\textsuperscript{+} ions were assumed to be strongly bonded by the internal - or hidden - functional groups of biochar. This envisioned structure could play a role in irreversibility of the adsorbed NH\textsubscript{4}\textsuperscript{+} when recovered by the salt solutions such as 2.0 M KCl. Therefore, the recalcitrant nature of biochar will help in long-lasting this phenomenon and may support some thoughts that can be pursued to explain...
ammonium trapping or may so called NH₄⁺-fixation by biochar. On the other hand, the non-recoverable, trapped, NH₄⁺ may need other extractants or extraction methods rather than the mentioned ordinary extractant used to release exchangeable NH₄⁺. Also, it is speculated that the value of measured surface area did not reflect the actual exchange sites and the internal surfaces may be the major player in sorption process. The porous property of PHB may be another factor which may play as compartments in which NH₄⁺ ions strongly retained.

Fig. 3: Adsorbed NH₄-N on PHB after 24 hours as a function of ammonium salt and initial ammonium concentration.

Langmuir (A)          Freundlich (B)

<table>
<thead>
<tr>
<th>Salt</th>
<th>Equation</th>
<th>R²</th>
</tr>
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<tbody>
<tr>
<td>NH₄Cl</td>
<td>y = 0.1363x - 8E-07</td>
<td>0.9999</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>y = 0.1355x - 5E-06</td>
<td>0.999</td>
</tr>
</tbody>
</table>

Fig. 4: Adsorption isotherm of ammonium ions onto peanut hull biochar fitted by Langmuir (A) and Freundlich (B) models.

4. Conclusion:

From the current work, we can conclude that PHB can be used as a cost effective sorbent material in removing processes of wastewater contaminants. PHB showed a high efficiency in removing NH₄-N from water and the removed amounts increased with increasing the initial concentrations of NH₄-N in water. The porous network and active functional groups owned by biochar surfaces helped in the irreversible strong retention of NH₄⁻ ions. Both Langmuir and Freundlich models were fitted in description of adsorption isotherms of NH₄⁻ onto PHB and reflected the heterogeneous properties of the surfaces. Further investigations are needed to explore the retention mechanisms of wastewater...
contaminants by biochar as a new inexpensive recalcitrant material.

References


