Investigation on the removal of nitrate from water using different types of biosorbents

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Abstract. Eutrophication due to excessive leaching of dissolved nitrogen is a principal cause of water quality degradation. Among different types of removal methods, adsorption is contemporarily deemed favourable due to its simplicity, efficiency and reusability. In this study, six biosorbent candidates, namely rambutan skin (RS), passion fruit skin (PFS), longan seeds (LS), chia seeds (CS), papaya seeds (PS), and luffa (L) were investigated for nitrate removal from water at pH 3.0, room temperature, initial nitrate concentration of 50 mg/L, biosorbent particle size of 425 µm, contact duration of 4 h, shaking speed of 120 rpm, and biosorbent dosage of 0.1 g. Shake flask method was carried out in the adsorption experiments to investigate the effect of heat treatment and acid treatment on the uptake of nitrate from water. The results showed that acid- and heat-treated passion fruit skin biosorbent (biochar, PFSBC) has the best biosorption performance for nitrate uptake of 5.179 mg/g. This biochar possessed high porosity, and abundant surface functional groups for nitrate adsorption.

1. Introduction

Water contamination can be attributed directly from the industrial effluent or indirectly introduced from the atmospheric deposits such as rain water, groundwater systems or soils, which are based on anthropogenic activities, local geology, population boom, fast industrialization, unplanned urbanization, and unqualified usage of natural water resources [1]. Among the contaminants, it is known that the concentration of nitrate rises at tremendous rates, as a result of biological nitrification activities, mining, purification and refining of minerals, and mainly involved in phosphorylation in cellular activities [2]. Such inorganic pollutant is the key limiting nutrient contributing to eutrophication, which disturbs the ecosystem. Besides that, the exposure to high levels of nitrate to human can lead to the inability of oxygen delivery through blood (methemoglobinemia), deterioration of thyroid functions, cancer, and birth defects [3].

Nitrate can be removed using different types of treatment methods. Among the treatment options, the removal methods such as membrane extraction, precipitation, and electrochemical separation often feature some typical drawbacks in operation and maintenance costs, hazardous sludge generation, as well as procedural complexity in stages of treatment [4]. In contrast, adsorption process is proven to be an outstanding alternative to counteract the foreknown downsides. Activated carbons are versatile substances that have prompted much attention owing to their eco-friendliness and have been commercially fabricated as one of the customary adsorbents in adsorption of dissolved pollutants which generally takes place ensuing biological or chemical oxidation treatments in wastewater treatment.
plants, despite with costly maintenance. Nonetheless, restrictions have been mandated due to relatively higher costs, in addition to the adsorbent regeneration capacity or the disposal of the end-of-life sorbent following different strategies than disposal [5].

In conjunction with that, a contingency measure to use low-cost biological and natural adsorbents, namely biosorbents, has been explored for the sorption capability to different types of water pollutants. Biosorption naturally takes place by allowing particular biomass adhere contaminants onto its cellular structure via passive concentration. The physicochemical or metabolically-transmitted pathways of uptake results in accumulation of inorganic constituents from wastewater [6]. Several good candidates of biomaterials for the elimination of nitrate from water mainly consist of algae, bacteria, fungi, agricultural and forestry residues, animal, industrial and municipal wastes, household composts, sludge and other polysaccharide materials [7, 8]. However, to date, as for the adsorbates of interest, cationic contaminants and organic substances such as dyes have substantially prevailed over inorganic anions such as nitrate and phosphate in the depth of investigation [5]. It is also worth noting that there have been also persistent challenges in the evaluation of accessible and affordable biosorbents, such as deficit in publications reporting on derivatives and dry mass, apart from sheer difficulties in direct comparison of data of different sorbents, mainly due to irregularities in the data presentation [9].

This main objective of this research is to investigate the performance of nitrate removal from water using six biosorbent candidates. The effects of heat treatment via partial pyrolysis and acid treatment using 1.0 M HCl solution were evaluated by comparing the adsorption uptake of nitrate between the raw biosorbents and their derivatives after heat treatment (biochar).

2. Methodology

2.1. Materials
All the solvents and reagents used in the preparation of nitrate solutions, biosorbents and standard solutions were of AR grade. The biosorbent candidates, namely the passion fruit skin (PFS), rambutan skin (RS), longan seeds (LS), chia seeds (CS), papaya seeds (PS), as well as loofah (L, dried Luffa aegyptiaca) were collected from the home and market composts, and wholesale suppliers of organic groceries.

2.2. Experimental procedures
2.2.1. Preparation of stock solution. Stock solutions for nitrate at a concentration of 50 mg/L nitrate were prepared by dissolving 81.54 mg anhydrous potassium nitrate (KNO₃) in 1 L deionized water. The solutions were well mixed and were stored in sample bottles prior to use. The pH of the solution was adjusted using 1.0 M HCl solution.

2.2.2. Preparation of biosorbents. Each of the biosorbents was cleaned for three times using deionized water under room temperature to get rid of sand, dirt and other coarse impurities. Then, they were dried using a standard laboratory oven at 70°C for 24 h. The dried biosorbents were then pulverized to powder, and was sieved at the mesh size of 425 µm. The grounded powders were then kept in air-tight containers in a desiccator at room temperature prior to use in experiments.

2.2.3. Heat treatment. Each of the biosorbents was cleaned for three times using deionized water under room temperature to get rid of sand, dirt and other coarse impurities. Then, they were dried using a standard laboratory oven at 70°C for 24 h. The biosorbents were then pyrolyzed slowly in a Carbolite Furnace at 500 °C for 4 h, with the heating rate of 10°C/min, to produce biochars. The resultant biochars were then pulverized to powder, sieved at the mesh size of 425 µm. The grounded biochar powders were then kept in air-tight containers in a desiccator at room temperature prior to use in experiments.

2.2.4. Acid treatment of biosorbents and biochars. Acid treatment was carried out using 1.0 M of HCl solution on biosorbent and biochar powders. A volume of 500 ml of 1.0 M HCl solution was added into
1 L beaker that was filled with 100.0 g of biosorbent or biochar powder sample. The mixture was gently heated to 120°C on a hot plate until the boiling virtually took place. The treated biosorbent and biochar powders were washed with deionized water to further displace minute foreign substances and chemical compounds such as trace ions and water-soluble plant pigments until clear filtrates were resulted [10]. All the treated powders were then dried in the standard laboratory oven at 70°C for 24 h, and were kept in air-tight containers in a desiccator at room temperature, prior to use in experiments.

2.2.5. Point of zero charge test. Using the pH drift method as propounded by Noh & Schwarz [11], the initial pH of 0.01 mol/L NaCl aqueous solution (50 ml) was adjusted successively within the range between pH 2.0 and 12.0 by adding 0.1 M HCl and/or 0.1 M NaOH. Next, 0.05 g of each biosorbent or biochar was mixed with 50 mL of solution and stirred for 6 h. The final pH was evaluated and the pH difference (ΔpH) was plotted versus the initial pH. At the point where the initial pH was equivalent final pH, the pH of zero charge was ascertained [12].

2.2.6. Batch adsorption experiment. The ability of six candidates of biosorbents and their biochars on the removal of nitrate from water was investigated using shake flask experiments. In each shake flask experiment, 0.1 g of the biosorbent or biochar powder with particle size of 425 µm was mixed with 100 ml of 50 mg/L nitrate solution for nitrate test at pH 3.0. The mixture was homogenized using an orbital shaker at 120 rpm for 4 h at room temperature. After the experiments, the mixture was filtered through a filter paper and the supernatant was collected for the analysis of nitrate using ion chromatography.

2.3. Analytical method
2.3.1. Detection of nitrate. The supernatants collected from the shake flask experiments were filtered by 0.20 μm syringe filters to obtain the injection samples for ion chromatography analysis. The concentration of nitrate was separately calibrated by ion chromatography (861 Advanced Compact IC, Metrohm, Switzerland), and using Ion Chromatography Column Methrom A supp 5 150/4.0 mm. The chemical reagents used for the chromatography system were ultra-pure water with conductance of less than 0.1 µS/cm, eluent solutions of 3.2 mM Na₂CO₃ and 1 mM NaHCO₃, as well as 0.01 M H₂SO₄ as regenerant solution. The anionic concentrations were evaluated by comparing the chromatogram peaks, elution times, and areas of samples to standard solutions. Then, the adsorption uptake of nitrate, \( q_t \) (mg/g) was calculated using equation (1).

\[
q_t = \frac{V}{m} \times (C_i - C_f)
\]

where \( C_i \) indicates the initial nitrate concentration in the solution (mg/L), \( C_f \) indicates the final nitrate concentration in the solution (mg/L), \( V \) indicates the volume of the aqueous solutions (L), and \( m \) indicates the mass of biosorbent or biochar used (g).

2.3.2. Characterization study. The morphologies of the prepared biomaterials before and after the shake flask experiments were analyzed using Scanning Electron Microscopy-Energy Dispersive X-Ray Analyzer (SEM-EDX), Fourier-transform infrared spectroscopy (FTIR) and X-Ray Diffraction (XRD).

3. Results and discussion
Figure 1a shows that, in general, all the biosorbent candidates in this study are not suitable to be used for nitrate removal in their raw states without acid and heat treatments, as negative adsorption uptake were obtained. This observation generally suggests that the nitrate contained inside the biosorbents was leached out when they were contacted with the aqueous solution. Nevertheless, it is also observed that adsorption ability of the biosorbents are improved when heat treatment is applied to convert the biosorbents into biochars, especially together with acid treatment, as shown in Figures 1a and 1b.
3.1. Effect of acid treatment

In general, the leaching of nitrate is observed during the experiments for raw biosorbents, and this process is found to be worsened when the biosorbents underwent acid treatment with HCl before the adsorption process, as shown in figures 1a and 1b. The leaching of nitrate from both the acid-treated and raw biosorbent candidates can be explained by the nitrate oversaturation at the free adsorption sites on the surfaces, while higher extent of saturation is presumed after acid treatment [13]. For the pre-sorption raw biosorbent samples, acid washing and subsequent deionized water washing are ineffective in removing the intact N-containing compounds as well as nitrate from the surface [14]. As postulated by Freundlich, when the surface saturation increases, the binding energy reduces exponentially, which in turn causes the initially existing surface nitrate to detach from the pre-sorption raw biosorbent samples, and thereby leach into the bulk phase [15].

Besides, nitrate leaching is aggravated by the increase in acidity and decrease in point of zero charge (pH\text{PZC}) of all the raw biosorbent candidates following the acid treatment. The pH of zero charge is crucial for indicating the acidity-basicity and the net surface charge of the biosorbents and biochars in the aqueous solution [12]. Fundamentally, any pH value higher than pH\text{PZC} complies with the prevalence of surface basic groups. As shown in figure 2, acid treatment reduces the pH\text{PZC} of all the raw biosorbent candidates from the range of 2.68 to 2.99, to 2.23 to 2.61, which are all increasingly lower than the pH of nitrate solution at 3.0. At pH 3.0, with more negative net surface charge of acid-treated biosorbents than raw biosorbents, the possible main mechanism that worsens the nitrate leaching is the repulsive forces between the surface portions with the negatively charged functional group and the nitrate ions in the aqueous solution [12]. It could be also coincided with the hydrogen bonding between some existent
surface –OH groups and protons of the acid-treated colloidal biosorbent particles in the aqueous solution that outweighs the effect of ion exchange between surface hydroxide and aqueous nitrate [16].

![Figure 2. Point of zero charge (pH\textsubscript{PZC}) study on all biosorbent candidates (raw, acid- and heat-treated).](image)

3.2. Effect of heat treatment

Figures 1a deduces that the use of heat treatment to convert the biosorbents into biochars was found to reduce the leaching of nitrate into the aqueous solution during the adsorption. The results are concurrent with the EDX analysis of the biosorbents and biochars as shown in table 1. It was found that the N content on the pre-sorption adsorbent surface was found to drop slightly upon the application of heat treatment for all types of biosorbents in this study. The decrease in N composition could have been attributed to the disintegration of weaker bonds during heat treatment, where a small amount of nitrogen in biomass was released as nitrogen-containing volatile gases through reduction of oxygen-containing polar functional groups, such as nitro compounds on the biochar surface, while the remaining nitrogen was retained in the biochar [17, 18].

In addition, the results are in agreement with the work of Chen et al. [19] and Liu et al. [20], whereby the carbon and cellulose structures in the biosorbent were reported to be highly broken down, resulting in formation of fresh surfaces, new honeycombed pores and tubular channels at high temperature of pyrolysis. It further provided better mass transfer opportunity. On the contrary, without heat treatment, the deficiency in the necessary available area on the surfaces of all raw biosorbents, as well as the non-specificity of the adsorption sites prohibits the nitrate adsorption from the aqueous solution. This propensity is similar with the results generated by Berkessa et al. [21], where low percentage removal of nitrate was reported at high initial concentration of nitrate.
Table 1. EDX Results for the nitrogen (N) and chloride (Cl) contents (wt %) for pre-sorption and post-sorption biosorbents and biochars in acid-treated and raw forms.

| Biosorbent / Biochar | Heat treatment | Acid treatment | N (wt %) | Cl (wt %) |
|----------------------|----------------|----------------|---------|-----------|
| RS                   | No             | No             | 2.85    | 1.48      | 0.19    | 0.41    |
|                      | Yes            | No             | 1.74    | 0.04      | 2.06    | 2.18    |
|                      | Yes            | Yes            | 2.07    | 1.78      | 0.18    | 0.05    |
|                      | Yes            | Yes            | 0.08    | 10.12     | 1.64    | 1.86    |
| PFS                  | No             | No             | 1.77    | 1.54      | 0.61    | 0.10    |
|                      | Yes            | No             | 0.86    | 4.50      | 2.10    | 1.92    |
|                      | Yes            | Yes            | 1.82    | 1.63      | 1.07    | 0.52    |
|                      | Yes            | Yes            | 0.02    | 10.99     | 4.36    | 2.90    |
| LS                   | No             | No             | 3.16    | 1.38      | 0.17    | 0.41    |
|                      | Yes            | No             | 2.12    | 2.79      | 4.07    | 3.41    |
|                      | Yes            | No             | 2.47    | 0.95      | 0.29    | 0.27    |
|                      | Yes            | Yes            | 1.96    | 5.37      | 2.96    | 3.00    |
| CS                   | No             | No             | 6.06    | 4.68      | 0.27    | 0.58    |
|                      | Yes            | No             | 2.44    | 4.30      | 2.63    | 1.67    |
|                      | Yes            | No             | 3.59    | 3.68      | 0.33    | 0.25    |
|                      | Yes            | Yes            | 1.49    | 4.73      | 1.65    | 1.64    |
|                      | Yes            | Yes            | 1.49    | 4.73      | 1.65    | 1.64    |
| PS                   | No             | No             | 5.33    | 4.30      | 0.35    | 0.40    |
|                      | Yes            | No             | 3.00    | 6.36      | 2.69    | 2.68    |
|                      | Yes            | No             | 4.33    | 2.52      | 1.23    | 1.10    |
|                      | Yes            | Yes            | 2.00    | 5.53      | 3.15    | 1.98    |
|                      | Yes            | No             | 2.68    | 1.43      | 0.40    | 0.38    |
|                      | Yes            | No             | 5.01    | 0.13      | 2.31    | 1.72    |
|                      | Yes            | No             | 1.77    | 1.41      | 0.43    | 0.52    |
|                      | Yes            | Yes            | 2.46    | 2.15      | 1.11    | 1.47    |

3.3. Effect of Acid Treatment and Heat Treatment

Significant improvement in nitrate removal is observed when both acid and heat treatments are applied together, as shown in figures 1a and 1b. This was notable for both raw PFS and RS, whereby the adsorption uptake of nitrate increased from -1.006 mg NO₃/g (raw RS) to 4.637 mg NO₃/g (acid treated RSBC), whereas for PFS, the adsorption uptake increased from -2.164 mg/g (raw PFS) to 5.179 mg NO₃/g (acid-treated PFSBC). This is also supported by the results as shown in table 1 where highest increase in N content after adsorption for these acid-treated biochar samples are observed in comparison to other types of biochars.

The demineralization process throughout the acid washing and subsequently deionized water washing got rid of ash and traces of miscellaneous metal salts from biochars, therefore little or no bioavailable nitrate from the ash and other inhibitory ions and molecules were added to the solutions [22]. This potentially created more sorption sites on the biochar surface and facilitated greater extent of nitrate sorption [23]. This resulted in lessened release of nitrate from acid-treated biosorbents and biochars than the raw form, with greater amount of available ion-exchange sites, where in table 1, for the pre-sorption samples, the N contents were mostly lower in acid-treated biochars than in raw biochars.

On the other hand, as shown in figures 1a and 1b, acid treatment enhances the sorption ability of all biochars to nitrate in aqueous solutions, except LBC, with their acidities decrease and points of zero charge increase. With higher basicity on the LBC surface than the aqueous solution, this observation infers that, at pH 3.0, which is higher than the point of zero charge of acid-treated LBC, nitrate
adsorption becomes more prohibitory after acid treatment due to the net negative surface charge, which induces the electronic repulsion between the surface and nitrate anions [24, 25]. Also, upon HCl acid activation, the biochar surfaces were bound with chloride and hydroxide ions from the aqueous solution to be exchanged for the negatively charged nitrate anions. In table 1, for the same biosorbent candidate, the acid-treated biochars have relatively higher Cl contents than the non-treated samples. Meanwhile, some protonated surface regions tended to neutralize the solution at the solid-liquid interface and allowed the adsorption of nitrate onto the surface via electrostatic attraction [26–28]. Only acid-treated PFSBC, RSBC, PSBC, CSBC and LSBC have the pH$_{PZC}$ exceeding the pH of nitrate solution at 3.0 to possess the net positive surface charge that favours nitrate adsorption.

3.4. Characterization study
The surface morphologies of acid-treated PFS, PFSBC, RS and RSBC are shown in figure 3. In general, higher porosity was illustrated on the surfaces of biochars (PFSBC and RSBC) than biosorbents (PFS and RS). In addition, the pores with wider range of size are also seen in biochars (between ≈ 5 μm and ≥ 40 μm) than in biosorbents (≈ 30 μm), which gives rise to greater exposed effective surface area of contact for biosorption [29].

![Figure 3. SEM Analyses of Acid-Treated Biosorbent Candidates and their Biochars: (a) PFS, (b) RS.](image)

The ability of the acid treated RSBC and acid treated PFSBC to adsorb nitrate from water can be justified from the FTIR analysis (figure 4a and 4b). The detection of surface chloride group is validated by the C-Cl stretching between 600 and 750 cm$^{-1}$. Also, under the heat treatment condition, the functional groups of aliphatic and aromatic carboxyl, as well as hydroxyl were produced and exposed on the surfaces of biochars during the thermal destruction of cellulose and lignin in biomass pyrolysis [24, 30]. This is indicated by the C=O stretching at around 1,055 cm$^{-1}$, and aromatic C=O between 1,600 and 1,700 cm$^{-1}$, as well as hydroxyl group shown with the broad moderate peaks between 3,000 and 3,700 cm$^{-1}$ in the pre-sorption samples [31–33].

In addition, the nitrate adsorbed on the surface of RSBC and PFSBC samples was identified in the forms of attached nitrate group and with the formation of nitrogen-containing functional groups, as shown in the detection of C-N stretching and C=O stretching vibrations in −CONH in amides and aromatic amines around 1,150 cm$^{-1}$, N=O stretching in nitro compound and bending vibration of −NH$_2$ near by 1,600 cm$^{-1}$, and special vibration of nitrate groups around 800 cm$^{-1}$ and 1,400 cm$^{-1}$ [31, 34, 35].
Figure 4. FTIR Spectra of (a) Acid-Treated Passion Fruit Skin Biochar (PFSBC), (b) Acid-Treated Rambutan Skin Biochar (RSBC).

4. Conclusions
A range of biosorbent and biochar powders derived from six raw biosorbent candidates via acid and heat treatments were compared as regards their biosorption performances with the untreated biosorbents. Among them, acid-treated PFSBC has the best biosorption performance for nitrate removal from aqueous solution with the adsorption uptake of 5.179 mg/g. The adsorption of nitrate were predominantly affected by the relatively higher porosity and wider pore size range in biochars than biosorbents, as well as protonated surface functional groups of amide, aromatic amine, carboxyl, chloride and hydroxide that served as ion-exchange sites.

Acknowledgments
This work was financially supported by Universiti Tunku Abdul Rahman (UTAR) under UTARRF Funding of IPSR/RMC/UTARRF/2018-C1/002 and IPSR/RMC/UTARRF/2019-C2/N01.
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