Biosorption of Nitrate by Thermodynamic and Kinetics study using Tamarind Fruit Shells

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Graphical Abstract

Abstract

The majority of nitrate (NO\textsubscript{3}\textsuperscript{−}) pollutants come from a different type of industries. Even if present in low amounts, these nitrates are harmful to humans and aquatic systems. This research investigated the utilisation of Tamarind Fruit shell (TFS) as biosorbent in the removal of Nitrate from aqueous solution. TFS shell was modified by soaking it with distilled water. Many remediation strategies are available, but they are both costly and ineffectual. However, it has been discovered via significant research that waste materials such as tamarind bark, eggshells, and agricultural wastes are well suited to removing nitrate from wastewater using the biosorption process (Panida, et.al., 2010). Biosorption is a nitrate removal process that is both environment friendly and cost-effective. The equilibrium distribution of NO\textsubscript{3}\textsuperscript{−}
onto the surface of the TFS can be best explained by Freundlich isotherm. Based upon the reaction of the thermodynamic study the TFS- \( \text{NO}_3^- \) interaction is an endothermic (Amardeep, et.al., 2013). A substantial chance in the \( \text{NO}_3^- \) - TFS interaction is expected because of the significant gain in the translational entropy by the displaced synchronised water molecules. Then the Chemiluminescence Analysing techniques Spectroscopic studies shows the biosorption capacity of TFS shows a little variation between 1.25 mg/g for 1 mm size and 2.14 mg/g for 0.13 mm size.

**Keywords:** Biosorption, Endothermic, Freundlich isotherm, Entropy, TFS.

**Introduction**

Contamination of ground and surface waters with harmful pollutants such as inorganic anions, metal ions, synthetic xenobiotics, and others has resulted from India's and other countries continued industrial expansion and agricultural development (Sujatha, et. Al., 2022). Biosorption has been shown to be a realistic alternative method for removing heavy metals from wastewater. Several natural and artificial hydrous solids have been investigated as biosorbent of heavy metals. (Panida Sampranpiboon and Pisit Charnkeitkong 2010) Among the umpteen inorganic species, nitrate (\( \text{NO}_3^- \)) is of vital concern on global level, due to its universal in nature regarding human health (Islam and Patel, 2010). \( \text{NO}_3^- \) gains contact in to the environment through various point and/or non-point sources such as agriculture and urban runoff, unsafe disposal of partially and untreated sewage and industrial wastes, leakage from septic tanks, landfill leachate, animal manure, and NOx air stripping waste from air pollution control devices, and others Owing to these effects, the WHO and IS: 10500, 1995 have set the respective maximum permissible limits of 50 and 45 mg/l for \( \text{NO}_3^- \) in drinking water respectively An international environmental concern is the heavy metal pollution of aquatic systems that results from different industrial operations. The majority of industries in developing countries take very few or no steps to clean their wastewater before dumping it.

Since they are not biodegradable and can remain under various environmental circumstances, their presence in water bodies when it exceeds safe levels poses a major risk to people and the ecology (Praveen, et. al., 2021) As a result, it is crucial to rid the aquatic ecosystem of harmful contaminants in order to safeguard the environment and the general people. The focus is on the heavy metals chrome (VI) and iron (III) ions. Chromium is used in wood preservation, textiles, antifouling agents in cooling towers, and chrome plating.

According to Hell et al., (1998), BATs were rather costly and also face process in-situ complexity issues when treating groundwater directly. Amith Bhathagar and Milka Sillappar
(2011) conducted a comprehensive analysis of various processes such as ion exchange, reverse osmosis, chemical techniques, and biological methods with respect to adsorption for possible consideration of sorption approach under BATs. Sorption of NO$_3^-$ (concentrations between 1 and 1000 mg/l) from aqueous phase by utilizing powder activated carbon, untreated and/or treated coconut granular activated carbons, coconut shell or coconut husk activated carbon, carbon nanotubes, chitosan beads, sugarcane bagasse, alkaline lignin, cellulose, red mud, and many others have been successfully investigated, during the past one decade (Bhatnagar et al., 2008; Chatterjee and Woo 2009). Due to the presence of suitable functional groups on their pore surfaces, the involvement of agricultural by-products in sorbing various hazardous anions and metal ions was widely established throughout the 1990s (Muhammad Imran Din, et.al., 2013). Simultaneously, the biosorption potential of Tamarind Fruit Shells (TFS) (a waste material after the processing of tamarind fruits) in sorbing Cr$^{6+}$, malachite green, chloropyriphos, NO$_3^-$ and others, from past few years (Arivoli, et.al., 2012). Also, no particular literature concerning the use of TFS in eliminating NO$_3^-$ from the aqueous phase exists as of yet, with the exception of research conducted by Prabhu (2012) in CMBR and FBR systems, respectively. The biosorbent can be characterised by X-ray Fluorescence spectroscopy (XRF) The thermodynamic and equilibrium distribution of NO$_3^-$ onto the TFS, as well as the assessment of the rate-limiting phase, were done in this study (as a continuation of prior investigations) (Appunni, et.al., 2013)

Adsorption has thus become a successful method for cleaning up contaminants. Filtration, precipitation, reverse osmosis, adsorption, coagulation or flocculation, treatment with chlorine or hydrogen peroxide, bacterial cells, membrane systems, and ion exchange adsorption are some more methods used to treat water. As of now, adsorbents such as magnetite supported on cross-linked chitosan, mesoporous biochar, silica-coated magnetite spheres, activated carbon, and clay composites have been created and used. Recently, the adsorption of dyes and metal oxide by nanoparticles (NPs) has drawn considerable attention. Due to their porous architectures and huge specific surface areas, NPs shown potential efficiency.

**Material and Methods**

Biosorbent: Tamarind Fruit Shells (TFS) was procured from the village near Bhavani town, Erode district, Tamil Nadu, India and pulverized to different sizes: i) passing through 1.41mm BIS sieve and retaining on 0.7 mm BIS sieve with a geometric mean size of 1 mm,
ii) passing through 0.7 mm BIS sieve and retaining on 0.5 mm BIS sieve with a geometric mean size of 0.6 mm and, iii) passing through 0.5 mm BIS sieve and retaining on 0.211 mm BIS sieve with a geometric mean size of 0.32 mm, and iv) passing through 0.211 mm BIS sieve and retaining on 0.075 mm BIS sieve with a geometric mean size of 0.13 mm. To enhance the biosorption procedure, apply Response Surface Methodology (RSM). The powder is supposed to absorb the pollutants in its cavities (Biosorption) (Lenin et. al., 2021). The powder is extracted and filtered after being in the contaminated solution under agitation for 3 Hours. It was completely cleaned in distilled water to eliminate inessential contaminants, then oven dried for 10 hours at a temperature below 110°C, cooled in desiccators, and kept in sealed plastic containers (Raja, et. al., 2022). Acidifying causes oxygen surface complexes which supposedly increase adsorption sites. Acidifying also is said to lead to an increase in surface area. All investigations, unless otherwise stated, employed a geometric mean size of 0.13 mm (Gokulan, et.al., 2021).

Chemicals: All chemicals and reagents were purchased from S.d Fine Chemicals Ltd in Mumbai, India, and were of AR grade. 1.6307 g of KNO₃ (owing to its comparatively high solubility in distilled water compared to NaNO₃) was dissolved in pyrogen-free doubly distilled water and then diluted according to the experimental conditions to make a stock solution of NO₃⁻ (1000 mg/l) (Meng Xue Xiong, et.al., 2022) The average pH of the distilled water was 6.6, and the electrical conductivity was less than 10 mho/cm. The chemicals utilised were of the analytical grade and were obtained from Merck (Germany) and the Sigma-Aldrich Company (U.S.A.). MgCl₂.6H₂O, NaOH, ammonium hydroxide (NH₄OH) (28–30%NH₃), iron sulphate hexa-hydrate (FeSO₄.7H₂O), zinc nitrate (Kumar et. al., 2022).

Methods

Analysis of NO₃⁻: The NO₃⁻ was analysed by double beam UV-VIS Spectrophotometer with 10 mm path length high quality quartz cuvettes at a wavelength of 220 nmλ. The concentration of NO₃⁻ in the aqueous phase was assessed by using the standard graph (linear plot of absorbance versus concentration of NO₃⁻) as shown in Figure 1. Also as per Prabhu (2012), the interference caused by leaching of organic matter from TFS at 220 nmλ was appropriately taken into account by measuring its absorbance at 275 nmλ. The experimental errors were below 4%.

Characterisation of Biosorbent: The physicochemical characteristics of the TFS were determined as per the standard methods followed by Stadler et al., 2008 and are shown in
Table 1. Also, the specific surface area (m$^2$/g) and BET surface area (m$^2$/g) are measured by Filtrasorb-II:2300 and the pH of zero point charge (pH$_{zpc}$) was analyzed by the instrumental method and standard titrimetric method (Gokulan, et.al., 2019). With the Non-Local Density Functional Theory (NLDF) and the assumption of a cyclindrical pore shape, the pore size distribution was determined from the adsorption branch. (Gokulan et al., 2014) These results are shown in Table 2. Although the TFS' precise properties and functional groups have been published elsewhere (Popuri et al., 2007), the SEM and FTIR findings are still being tested targeting for lead contamination in industrial wastewater (India), and therefore want to prepare synthetic lead nitrate solution accordingly.

![Calibration Curve for NO$_3^-$ Analysis](image.png)

**Fig 1. Calibration Curve for NO$_3^-$ Analysis**

**Table 1 Physiochemical Characteristics of the TFS**

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Parameter</th>
<th>Result (average of triplicate results)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pH</td>
<td>3.98</td>
</tr>
<tr>
<td>2</td>
<td>Specific gravity</td>
<td>1.25</td>
</tr>
<tr>
<td>3</td>
<td>Bulk density, kg/m$^3$</td>
<td>0.54 – 0.58</td>
</tr>
<tr>
<td>4</td>
<td>Porosity (mechanical)</td>
<td>0.25 – 0.30</td>
</tr>
<tr>
<td>5</td>
<td>Loss of weight after washed with 4 l (200 ml x 20) of distilled water, %</td>
<td>3</td>
</tr>
<tr>
<td>6</td>
<td>Dissolved organic matter from TFS, %</td>
<td>1.1</td>
</tr>
</tbody>
</table>
Biosorption Studies: All biosorption experiments were carried out in a CMBR system using either distilled or tap water at room temperature. The biosorption of NO$_3^-$ was assessed using a jar test device with 6 flat blade stirrers (each 7.6 x 2.5 cm$^2$) operated by a 0.05 HP motor with an induced speed range of 10 to 400 rpm (Figure 2). All of the studies were conducted in 1L Borosil glass beakers holding 300 mL of prepared NO$_3^-$ solution equating to a liquid depth of 3.5 cm and a preset dosage of biosorbent.

Kinetics Studies: For the assessment of equilibrium time in CMBR, the biosorption kinetics were individually studied for each dosage of TFS (2, 4, 6, 8, and 10 g/l) of geometric mean size of 0.13mm; for an initial concentration of 70mg/l, at a pH of 5, and under an agitation speed of 100 rpm. (Jegan et al., 2020). The Brunauer-Emmett-Teller (BET) theory seeks to explain how molecules physically adhere to a solid surface. Similarly, separate kinetics tests were carried out for different diameters of TFS (1, 0.6, 0.32, and 0.13mm) as well as varied starting concentrations of 100, 70, 40, and 10 g/l.

Table 2 Size, Surface Areas and pH$_{zpc}$ of TFS

<table>
<thead>
<tr>
<th>S.No</th>
<th>TFS size, mm</th>
<th>Geometric mean size</th>
<th>Approximate No. of particles per 10 mg$^2$</th>
<th>Specific Surface area*, m$^2$/g</th>
<th>BET surface area*, mg/g</th>
<th>pH$_{zpc}$*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Spherical equivalent</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.13</td>
<td>0.16</td>
<td>2445 ± 10</td>
<td>34.1</td>
<td>76.4</td>
<td>4.62</td>
</tr>
<tr>
<td>2</td>
<td>0.32</td>
<td>0.38</td>
<td>405 ± 8</td>
<td>26.3</td>
<td>74.6</td>
<td>4.63</td>
</tr>
<tr>
<td>3</td>
<td>0.6</td>
<td>0.72</td>
<td>85 ± 3</td>
<td>24.6</td>
<td>69.1</td>
<td>4.61</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>1.2</td>
<td>25 ± 1</td>
<td>20.8</td>
<td>62.9</td>
<td>4.65</td>
</tr>
</tbody>
</table>

Interruption test: The rate-limiting stage of the biosorption process was assessed using the multiple interruption test established by (Shankhamala et al., 2021). The TFS was removed from the reaction mixtures one or more times and then reintroduced after a 5-minute interruption interval. NO$_3^-$ was measured at the conclusion of each response time period (Gokulan, et al., 2019).

Equilibria Studies: The goal of the biosorption equilibrium investigation was to learn more about the nature of the NO$_3^-$ equilibrium distribution on the biosorbent and in the liquid.
phase. The general equilibria experiments were carried out for different diameters (1, 0.6, 0.32, and 0.13 mm) in the concentration range of 10 to 100 mg/l of NO$_3^-$, at a TFS dosage of 10 g/l, agitation speed of 100 rpm, pH of 5, contact period of 3 h, and at room temperatures. For the thermodynamic relationship between NO$_3^-$ and TFS, equilibria studies were conducted for five temperatures: 20, 30, 40, 50, and 60° C, at a TFS dose of 10 g/l, pH of 5, contact time of 3 h, agitation speed of 150 rpm (Orbital Shaker- cum- Incubator, Neolab, India), and NO3 concentrations ranging from 10 to 100 mg/l.

Fig 2 - Photograph Showing the Orbital Shaker used for Equilibria and Thermodynamic Studies

Results and Discussion

Reliability of TFS in Removing NO$_3^-$

Although the biosorption of numerous anionic hazardous species is mostly dependent on the biomaterial's properties, its dependability should also be examined in light of the marginal differences that might exist between materials gathered in different places. TFS is widely available in various regions of Tamilnadu (as indicated in literature), and it was gathered for this study in a place other than those mentioned in prior studies (Rao and Puttanna, 2000; Demiral et al., 2010; Prabhu, 2012). As a result, a TFS biosorption of NO3 reliability investigation was carried out. According to Cengeloglu et al., (2006) reliability study, the biosorption capacity of TFS is highly dependent on the source or origin of TFS. In addition, there was a 10% difference between the Perundurai-based TFS and the Bhavani-based TFS in this study. This is because to the minor morphological differences that the
various TFSs may have exhibited. However, targeting for lead contamination in industrial wastewater (India), and therefore want to prepare synthetic lead nitrate solution accordingly across the numerous TFSs collected in different regions of Tamilnadu, a 10-15% variance in NO$_3^-$ biosorption might be predicted.

**Assessment of Sorption Equilibrium Time in CMBR**

Solute absorption in the CMBR is quick initially, then slows down as it approaches saturation. The sorption rate is larger than the desorption rate during quick stage sorption, and as time passes, the disparity between the rates gradually narrows until they appear to be equal (Hariprasad and Geresh, 2009). Equilibrium time is defined as the point at which the sorption and desorption rates appear to be equal. The fluctuation of sorbate removal with respect to elapsed time is predicted to follow a curvilinear pattern in CMBR, and the equilibrium time can range from a few minutes to many days. Because operating the system for a long period is difficult and cumbersome, the equilibrium time is chosen so that no significant occurs beyond this time, i.e., the curve (removal vs time) is nearly asymptotic to the time axis (Priya, et. al 2020). The choice of the equilibrium period, on the other hand, is largely determined by system factors such as the initial sorbate concentration, sorbent dosage, and sorbent size. To further understand the influence of these factors on equilibrium time, kinetic experiments were done.

**Evaluation of Biosorption Equilibrium Time**

![Biosorption Kinetics Profiles of NO$_3^-$ by TFS.](image)
Fig. 4 Effect of Biosorbent Size on Biosorption of $\text{NO}_3^-$ by TFS

Figures 3-8 demonstrate the fluctuations in $\text{NO}_3^-$ concentrations over time for various factors. The $\text{NO}_3^-$ removal efficiencies (percent) at various periods were computed using these charts. However, after looking at the graphs, any figure between 2.5 and 4 h for the equilibrium time might be proposed. To get over this issue, a logical technique based on two separate criteria (Bhargava and Kelledar, 1991) was used to calculate a precise equilibrium period. The criteria are: i) based on the arbitrary cutoff value of the slope (3%) of the variation curve and ii) based on the arbitrary termination point of 95% of maximum removal, for chosen variable. The equilibrium time (from criterion I) was estimated, for each of the variable.
Fig. 5 Effect of Biosorbent Dose on Biosorption of NO$_3^-$ by TFS

Fig. 6 Variation of NO$_3^-$ Removal with respect to L for $t_8$ and $t_{180}$

Fig. 7 Variation of Equilibrium Time vs D/C$_o$
Determination of Rate Limiting Step

There are essentially three consecutive mass transport steps associated with the sorption of solutes from the solution by porous sorbents. Figure 9 shows a schematic representation of them. Film transport is the second stage, which involves solute diffusion across a hypothetical "film" or hydrodynamic boundary layer. Except for a small amount of sorption that occurs on the exterior surface of the sorbent during the third and final step, the solute then must diffuse within the pore volume of the sorbent and/or along pore-wall surfaces to an active sorbent sizes (pore diffusion) (Crittender and Weber, 1978). Because they act in series, the slower of the two steps will be rate limiting (Benefield et al., 1982).

Interruption Test

The kinetics profiles of both interruption and non-interrupted tests are shown in Figure 10. Pore diffusion is the rate-limiting phase in both rapid and slow biosorption zones,
according to the multiple interrupted testing curve (i.e., because of the substantial deviations between the uninterrupted and interrupted kinetics profiles, as per Zogorseki et al., 1976).

Fig. 10 Kinetics Profiles of NO3⁻ Biosorption by TFS – Interruption and Uninterruption Tests

Effects of Temperature and Thermodynamic Parameters

The Freundlich sorption isotherms at various temperatures are given in Figure 11. Although Kf values rose as the temperature of the solution increased, the degree of attachment (reduction in 1/n values) fluctuated as the temperature of the solution grew. Further, the effect of temperature can be illustrated by using thermodynamic parameters like, changes in the energy (ΔG⁰), enthalpy (ΔH⁰), entropy (ΔS⁰).

Fig. 11 Freundlich Sorption Isotherm for Different Temperatures
Fig. 12 Plot of ln(q_e/C_e) vs q_e at Different Temperatures for Removal of NO₃⁻ by TFS

Where, K₀ is a thermodynamic equilibrium constant for biosorption process, determined from the plot of lnq_e/C_e vs q_e (Figure 12) and extrapolating to zero q_e, as per the graphical procedure explained elsewhere (Khan and Singh, 1987). A linear plot of ln K₀ vs 1/T (Figure 13) was obtained and ΔH₀ (59.32 kJ/ mol) and ΔS₀ (201.95 J/K mol) were determined. The endothermic nature of NO₃⁻ biosorption was reflected by (i) the positive values of ΔH₀ and (ii) the decreasing values of ΔG₀ with increasing temperature. The high randomness at the solid/solution and greater affinity of NO₃⁻ to TFS, during biosorption, is revealed by high values of ΔS₀. Also, the increased randomness in the NO₃⁻ - TFS interaction was due to significant gain in the translational entropy by the displaced coordinated water molecule than is lost by NO₃⁻ species (Unninathan and Anirudhan, 2001).

For this purpose, the equilibrium concentration (C_e) at constant amount of sorbed NO₃⁻ was obtained from the sorption isotherm data at different temperatures (Figure 14). From the plot of ln C_e vs 1/T (Figure 14), ΔHₓ were calculated for different amount of NO₃⁻. These values are respectively 61.09, 60.12, 54.64, 59.23, and 59 kJ/mol for the loadings of 5, 10, 20, 25, and 30 mg/g surface loadings. In the experiments, we obtain equilibrium concentration for any initial concentration after the equilibrium time (c_e). then ascertain qe's value. Plotting C_e/qe on the y-axis and C_e on the x-axis then allows the Langmuir isotherm model to be solved. The variation of ΔHₓ with the surface loading is shown in Figure 15, which indicates that TFS possess heterogeneous surface with effective lateral interaction between sorbed NO₃⁻ species.
Fig. 13 Plot of \( \ln (K_0) \) vs \( 1/T \)

Fig. 14 Plots of \( \ln C_e \) vs \( 1/T \) for Constant Biosorption of \( \text{NO}_3^- \)
Conclusion

The Tamarind Fruit Shells, a waste material from natural environment, was converted into a biosorbent, which show good sorption for the elements studied. This material can be used for the removal of these essentials from the liquid effluent after optimisation of different physico-chemical parameters of the effluent. Based on the investigation pertaining to “Thermodynamic and Equilibrium Biosorption of NO$_3^-$ by Tamarind Fruit Shells”, the following conclusions are drawn. The TFS is a good biosorbent in eliminating NO$_3^-$ from aqueous phase. The TFS is highly suitable in CMBR system. The TFS dose and initial NO$_3^-$ concentration will highly influence the attainment of equilibrium time when compared to the size of TFS. The rational approach is most appropriate than the rough judgement, for the assessment of equilibrium in CMBR. Based on the interruption tests, pore diffusion is the rate limiting in the entire biosorption kinetics. The equilibrium distribution of NO$_3^-$ onto the surface of the TFS can be best explained by Freundlich isotherm, due to the fact that the experimental data's R$^2$ value fits the Freundlich Isotherm appropriately. The natural log of the negative intercept instead of the Freundlich constant k (lnk). It's acceptable to be unfavorable. Calculate exp(-0.7585) to find k, and you'll receive a consistent positive Freundlich capacity constant. Also, the biosorptive capacity of TFS shows a little variation between 1.25 mg/g for 1 mm size and 2.14 mg/g for 0.13 mm size. The TFS - NO$_3^-$ interaction is an endothermic process. Based on the cost analysis and the absorption period, the biosorption process is also evaluated. A high randomness at the solid/solution and greater affinity of NO$_3^-$ to TFS is expected during biosorption. Using the Brunauer-Emmett-Teller (BET) theory, the adsorption property can be ascertained. A substantial randomness in the NO$_3^-$ - TFS interaction is
expected because of the significant gain in the translational entropy by the displaced coordinated water molecules.

**Declarations**

**Ethical approval:** Not applicable

**Consent to participate:** Not applicable

**Consent for publication:** Not applicable

**Funding:** Not applicable

**Competing interests:** The authors declare no competing interests.

**Availability of data and materials:** All data generated or analyzed during this study are included in this published article.

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