Adsorption kinetics and equilibrium study of nitrogen species onto radiata pine (*Pinus radiata*) sawdust
Kadek D. Harmayani and A. H. M. Faisal Anwar

**ABSTRACT**

Nitrogen species (NH$_3$-N, NO$_3$-N, and NO$_2$-N) are found as one of the major dissolved constituents in wastewater or stormwater runoff. In this research, laboratory experiments were conducted to remove these pollutants from the water environment using radiata pine (*Pinus radiata*) sawdust. A series of batch tests was conducted by varying initial concentration, dosage, particle size, pH, and contact time to check the removal performance. Test results confirmed the effectiveness of radiata pine sawdust for removing these contaminants from the aqueous phase (100% removal of NO$_3$-N, and NO$_2$-N; 55% removal of NH$_3$-N). The adsorbent dosage and initial concentration showed a significantly greater effect on the removal process over pH or particle sizes. The optimum dosage for contaminant removal on a laboratory scale was found to be 12 g. Next, the adsorption kinetics were studied using intraparticle diffusion, liquid-film diffusion, and a pseudo-first order and pseudo-second order model. The adsorption of all species followed a pseudo-second order model but NO$_2$-N adsorption followed both models. In addition, the kinetics of NO$_3$-N adsorption showed two-step adsorption following intraparticle diffusion and liquid-film diffusion. The isotherm study showed that NO$_3$-N and NO$_2$-N adsorption fitted slightly better with the Freundlich model but that NH$_3$-N adsorption followed both Freundlich and Langmuir models.

**Key words** | adsorption, nitrogen, radiata pine, sawdust, water

**LIST OF SYMBOLS**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_0$</td>
<td>Initial concentration (mg/L)</td>
</tr>
<tr>
<td>$C_e$</td>
<td>Equilibrium concentration (mg/L)</td>
</tr>
<tr>
<td>$V$</td>
<td>Initial volume of aqueous solution (L)</td>
</tr>
<tr>
<td>$W$</td>
<td>Weight of dry sawdust (g)</td>
</tr>
<tr>
<td>$C_t$</td>
<td>Concentration at any time $t$ (mg/L)</td>
</tr>
<tr>
<td>$q_t$</td>
<td>Amount of adsorption at any time $t$ (mg/g)</td>
</tr>
<tr>
<td>$q_e$</td>
<td>Amount of solid phase concentration at equilibrium (mg/g)</td>
</tr>
<tr>
<td>$q_m$</td>
<td>Maximum capacity constant of adsorbent for adsorbate (mg/g)</td>
</tr>
<tr>
<td>$K_{ads}$</td>
<td>Langmuir constant</td>
</tr>
<tr>
<td>$R_L$</td>
<td>Reliable indicator for adsorption process</td>
</tr>
<tr>
<td>$K$</td>
<td>Freundlich constant for adsorption capacity (mg/g)</td>
</tr>
<tr>
<td>$n$</td>
<td>Freundlich constant for adsorption intensity</td>
</tr>
<tr>
<td>$k_{di}$</td>
<td>Intraparticle diffusion rate constant of stage $i$ (mg/g h$^{1/2}$)</td>
</tr>
<tr>
<td>$M_i$</td>
<td>Intercept of stage $i$ in intraparticle diffusion</td>
</tr>
<tr>
<td>$F$</td>
<td>Fractional attainment of equilibrium in liquid film diffusion model ($F = q_t/q_e$)</td>
</tr>
<tr>
<td>$k_{fd}$</td>
<td>Adsorption rate constant of liquid film diffusion model (1/min)</td>
</tr>
<tr>
<td>$k_1$</td>
<td>Reaction constant of first-order adsorption (1/min)</td>
</tr>
<tr>
<td>$k_2$</td>
<td>Rate constant of second-order adsorption (g/mg h)</td>
</tr>
<tr>
<td>$\Delta q$</td>
<td>Normalized standard deviation (%)</td>
</tr>
<tr>
<td>$N$</td>
<td>Total number of data</td>
</tr>
</tbody>
</table>

**INTRODUCTION**

With rapid development and increased human activities, the increasing problems caused by nitrogen in rivers, lakes, wetlands, and coastal and underground waters is of worldwide concern. The nitrogen species are transported to these receiving water bodies mainly by stormwater runoff or wastewater discharge as a point or non-point source. These compounds are found in the dissolved phase in aqueous solution in the form of ammonia-nitrogen (NH$_3$-N), nitrate-nitrogen (NO$_3$-N) and nitrite-nitrogen (NO$_2$-N). These compounds may result...
from auto-emissions, fluid leaks from vehicles, home use fertilizer and pesticides, refuse, and pet faeces and mixed with stormwater runoff. In wastewater, these are mainly generated from domestic, municipal, or industrial sources. The wastewater or stormwater containing these elements lead to considerable eutrophication and an increase in the frequency of toxic algae blooms (Taylor et al. 2005). The treatment of stormwater/wastewater has now become main focus of attention all over the world, especially for areas where potable water is limited.

Nitrogen compounds can be removed from the aqueous phase either by biological processes (e.g., nitrification or denitrification) or by physical adsorption using sorption media. In the nitrification process, ammonia is oxidized to nitrite and then nitrite to nitrate. In the denitrification process, the nitrate is reduced to nitric oxide or nitrogen gas in the presence of a carbon sources as an electron donor (Xuan et al. 2010). Current methods available for the removal of nitrogen species from aqueous solution include reverse osmosis, electrodialysis, activated carbon adsorption, adsorption by green media and ion exchange with synthetic resins (Wanieli & Chang 2008). Among these methods, adsorption was found to be the most effective mechanism for its operational simplicity and economic viability (Hameed et al. 2008; Koner et al. 2013). Initially, activated carbon was widely used as an effective medium due to its high adsorptive capacity, but its cost is relatively high. To date, a substantial amount of research has been undertaken into removing nitrogen species from water using different sorption media (Lee et al. 2002; Kim et al. 2003; Öztürk & Beka 2004; Hsieh & Davis 2005; Karamdag et al. 2006; Ray et al. 2006; Sari et al. 2007; Xuan et al. 2010; Liu et al. 2013). Different types of low-cost and green sorption media such as tree bark, wood chips, wheat straw, tire crumbs, sawdust, alfalfa, mulch compost, paper (newspaper), cotton, and sulfur/limestone have been described in Xuan et al. (2010) and Kim et al. (2003). Alfalfa and newspaper demonstrated 100% nitrate removal efficiency but mulch compost could remove only 60% of the nitrate (Kim et al. 2003). Although sawdust, wheat straw, and wood chips showed good nitrate removal efficiency (>95%), wood chips performed better than sawdust. However, both of these sorption media are known to be good carbon sources that can act as electron donors in the denitrification process. But increasing the hydraulic retention time may provide higher removal efficiency (Kim et al. 2003).

It has been reported that sawdust may be a promising low-cost adsorbent option for removing unwanted materials including heavy metals, basic dyes, and toxic salts (Shukla et al. 2002) because of its ready availability and low price. Basically wood sawdust is a waste material from wood industries that can be reused for contaminant removal from water. The sawdust of radiata pine (Pinus radiata) may be considered as a potential low-cost adsorbent in Oceania as it is grown on a large scale in Australia and New Zealand where it is the basis of the pulp and paper industries (Uprichard 2002). Radiata pine is also widely used in engineering applications, construction industries and for decorative purposes, and as a result, large volumes of waste wood and sawdust are left over. The major wood components of radiata pine include cellulose, lignin, and tannins, but it may also contain some other phenolic compounds. These elements are active ion exchange compounds (Shukla et al. 2002). Lignin is a hydrophobic polymer, builds up from the phenylpropane nucleus and is generally recognized as the principal wood sorbent (Shukla et al. 2002; Boving & Neary 2007). The detailed properties of radiata pine wood can be found on the website of the Department of Agriculture and Fisheries, Queensland Government, Australia (DAF 2016). In our earlier study (Harmayani & Anwar 2012), the sawdust of radiata pine was shown to be a cost-effective medium for removing pollutants from stormwater where the effects of initial concentration and dosage were investigated. In this study, data were checked only for adsorption isotherms but no adsorption kinetics were investigated. Although many studies have been conducted on adsorption isotherms and kinetics, few studies have dealt with the different stages of adsorption (Choi et al. 2007; Argun et al. 2007). The adsorption actually occurs rapidly in the interior faces of the pores that have easy initial access for the adsorption process. Next, the adsorption process slows down because of the limitation of available surface areas. This causes adsorption to occur in different stages. In this study, adsorption kinetics are investigated for different stages of the adsorption process using intraparticle diffusion and liquid-film diffusion models followed by pseudo-first order and pseudo-second order models. The equilibrium adsorptions are also investigated to fit the Freundlich and Langmuir isotherm. For this, the data were collected in batches with varying initial concentration, dosage, particle size, pH, and contact time.

**MATERIALS AND METHODS**

**Materials**

The raw sawdust of radiata pine (Pinus radiata) was collected from a wood processor and supplier (Stokic...
Nominees) in Maddington, Western Australia. The supplier usually produces huge amounts of sawdust everyday as waste material and confirmed that the collected sawdust was not chemically treated. The sawdust was sieved into five particle sizes of <300 μm, 300–600 μm, 600 μm–1.18 mm, 1.18–2.36 mm, and >2.36 mm, respectively. The average grain diameter ($d_{50}$) and the uniformity coefficient of the sawdust were found to be 0.93 mm and 1.75, respectively. The texture of radiata pine wood is fine but uneven (Radiata Pine 2016). The chemical properties of radiata pine sawdust (cellulose = 50%, hemicellulose = 18.5% and lignin = 24.8%) can be found in Aguilera & Martin (1985). This composition of sawdust slightly varies with radiata pine wood because the chemical compositions are estimated for inner wood (ring 1–10) and outer wood (ring 16–25) separately (Uprichard 2002). However, the sawdust used in this study was from both inner and outer wood mixed together. At first, the sawdust was washed with distilled water to remove any possible pollutants. After each washing, 2 mL of washed water was analyzed to check for any possible nitrogen residues coming from the sawdust. After 6–7 washes, the nitrogen content in the washed water was found to be negligible. The washed sawdust of different particle sizes was placed in different metal trays and oven dried at 105 °C for 24 hours. The dried sawdust was then placed in an airtight container at room temperature (22 ± 2 °C).

All analytical grade chemicals used in the experiments were purchased from Thermo Fisher Scientific, Sydney, Australia. All nitrogenous solutions were prepared using deionised (DI) water. The stock solutions of ammonia-nitrogen (NH$_3$-N), nitrate-nitrogen (NO$_3$-N), and nitrite-nitrogen (NO$_2$-N) were prepared from NH$_4$Cl, NaNO$_3$, and NaNO$_2$, respectively. To avoid any possible deterioration in concentration or any other possible contamination, new solutions were prepared by diluting the standard solution with DI water before each experiment. The pH of the solution was adjusted with small amounts of 1 mol/L NaOH and HCl, respectively. The pH was measured by a HACH pH meter (±0.1). The concentrations of different nitrogen species (NH$_3$-N, NO$_3$-N, and NO$_2$-N) were measured following standard methods given in APHA (1998) using an AQUAKEM 200 water analyzer (Labmedics Analytical Solutions) (±0.015–0.02).

**Adsorption experiments**

**Batch equilibrium studies**

Batch experiments were conducted with varying initial concentrations (0.5–5 mg/l), dosages (2–20 g), particle sizes (<300 μm, 300–600 μm, 600 μm–1.18 mm, 1.18–2.36 mm, and >2.36 mm), pH (4–9), and contact times until it reached equilibrium. In each experiment, sawdust of selected dosage and particle sizes was placed in an Erlenmeyer flask and 200 ml of aqueous solution of selected concentration were added. For all tests, pH was adjusted to 6.5 (±0.5), except for pH-dependent tests where pH was varied between 4 and 9. To eliminate any possible evaporation, the flask was closed by wrapping the top of the flask in parafilm. The flasks were shaken at 100 rpm on a shaking platform of 16-flask capacity (Innova 2100, New Brunswick Scientific) at room temperature (22 ± 2 °C). Two ml samples were collected from the flask at predetermined time intervals until it reached equilibrium. The samples were filtered in a filter syringe of 0.45 μm and analyzed for pollutant concentrations. Duplicate experiments were conducted three times under identical conditions and the mean values of concentrations were used in the analysis. If the standard error was greater than 0.01, the experiment was repeated to minimize the errors. However, the equilibrium adsorption, $q_e$ (mg/g) may be calculated as:

$$q_e = \frac{(C_0 - C_e)}{W} \times V$$

where $C_0$ and $C_e$ are the initial and equilibrium concentrations (mg/L), $V$ is the initial volume of aqueous solution (L), and $W$ is the weight of dry sawdust (g). The percentage of adsorption was calculated by:

$$\text{Removal} \% = \left(\frac{C_0 - C_e}{C_0}\right) \times 100$$

**Batch kinetic studies**

The procedure for batch kinetic experiments was similar to that of the equilibrium tests. The aqueous samples collected at different time intervals, $t$ during batch experiments were measured using the same analytical technique. The amount of adsorption at any time $t$, $q_t$ (mg/g) may be calculated by:

$$q_t = \frac{(C_0 - C_t)}{W} \times V$$

where $C_0$ and $C_t$ (mg/L) are the initial concentration and a concentration at any time $t$ respectively, $V$ is the initial volume of solution (L), and $W$ is the weight of dry sawdust (g).
Adsorption theory

Adsorption isotherms

Adsorption isotherms explain the relation between the amount of solute adsorbed and the concentration of solute in the fluid phase, at a given temperature. They indicate how the adsorbed molecules are distributed in solid and liquid phases when the adsorption process reaches equilibrium. The adsorption isotherm can be found by fitting the experimental data with equilibrium isotherm models. The Two most well-known isotherm models are the Langmuir and the Freundlich isotherm.


\[
\frac{1}{q_e} = \frac{1}{q_m K_{ads}} \left( \frac{1}{C_e} \right) + \frac{1}{q_m}
\]

where \( q_e \) (mg/g) is the solid phase concentration at equilibrium; \( q_m \) (mg/g) is the maximum capacity constant of adsorbent for adsorbate; and \( K_{ads} \) is the measure of affinity of adsorbate with adsorbent known as the Langmuir constant (unitless). The Langmuir isotherm can be obtained by plotting a graph of \( 1/q_e \) versus \( 1/C_e \). The major characteristics of the Langmuir isotherm can be described by the dimensionless constant separation factor or adsorption intensity, \( R_L \) (Sari et al. 2007):

\[
R_L = \frac{1}{1 + K_{ads} C_0}
\]

The parameter \( R_L \) is considered to be a reliable indicator for adsorption processes. The nature of the adsorption process and the shape of the isotherm can be represented by the value of \( R_L \):

- \( R_L = 0 \) indicates irreversible
- \( 0 < R_L < 1 \) indicates favorable
- \( R_L = 1 \) indicates linear
- \( R_L > 1 \) indicates unfavorable

Freundlich isotherm. The linear form of the Freundlich isotherm may be written as (Febrianto et al. 2009; Hossain et al. 2009):

\[
\log q_e = \log K + \frac{1}{n} \log C_e
\]

where \( K \) (mg/g) and \( n \) are the constants for adsorption capacity and intensity, respectively. These constants can be found from the linear plot between \( \log q_e \) and \( \log C_e \).

Adsorption kinetics

The adsorption kinetics are studied using the batch data set collected at different time intervals. The adsorption kinetics are observed in two phases including a rapid adsorption followed by a slow process before reaching equilibrium. The adsorption process can follow either or both kinetic sorption and diffusion models. The regression coefficient between experimental and theoretical data is the indicator of an appropriate model. The different models used are described next.

Intraparticle diffusion model. The intraparticle diffusion model was used to check the diffusion mechanism (Weber & Morris 1964). This model is empirically derived and has an established functional relationship that can be used for most adsorption processes. In this model, uptake varies almost proportionally with \( t^{1/2} \) instead of the contact time \( t \) itself.

\[
q_t = k_{di} t^{1/2} + M_i
\]

where \( k_{di} \) (mg/g h\(^{1/2}\)) is the intraparticle diffusion rate constant of stage \( i \) which can be obtained from the linear plot between \( q_i \) and \( t^{1/2} \). The \( M_i \) is the intercept of stage \( i \) and provides an idea about the thickness of the boundary layer. A larger intercept indicates a higher boundary layer effect. Zero intercept of this plot means that the process is only due to intraparticle diffusion. Otherwise, some other mechanism may take place such as liquid film diffusion.

Liquid film diffusion model. The liquid film diffusion model is applicable when the flow of reactant from bulk liquid to surface of adsorbent determines the rate constant, which is expressed by (Boyd et al. 1947):

\[
\ln(1 - F) = -k_{fd} t
\]

where \( F \) is the fractional attainment of equilibrium \( (F = q_t/q_m) \), and \( k_{fd} \) is the adsorption rate constant of the liquid film diffusion model (1/min). A linear plot of \(-\ln(1 - F)\) versus \( t \) with zero intercept would suggest that the adsorption occurs in the thin film of liquid surrounding the solid surface.

Pseudo-first order kinetic model. This model assumes that there is an attraction of physical forces between the molecules of adsorbate and adsorbent. The non-linear form of the pseudo-first order reaction model is generally
expressed as (Ho et al. 2000):
\[
\frac{dq}{dt} = k_1(q_e - q_t)
\]  
(9)

The integrated form of this differential equation becomes:
\[
\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303}
\]  
(10)
where \( k_1 \) (1/min) is the reaction constant of first-order adsorption, which can be obtained from the linear plot between \( \log(q_e - q_t) \) and \( t \).

**Pseudo-second order kinetic model.** The pseudo-second order rate model assumes binding of ions with adsorbent molecules by a chemisorption mechanism. The pseudo-second order rate model is expressed as (Ho & Mckay 1998):
\[
\frac{dq_t}{dt} = k_2(q_e - q_t)^2
\]  
(11)

Integrating Equation (11) with boundary condition \( q = 0 \) to \( q = q_t \) at \( t = 0 \) to \( t = t \):
\[
\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{1}{q_e} t
\]  
(12)

where \( k_2 \) (g/mg h) is the rate constant of second-order adsorption, which can be calculated from the linear plot between \( t/q_t \) and \( t \) (Dursun et al. 2005).

**Validity of kinetic models.** The validity of kinetic models for the adsorption process were checked by normalized standard deviation \( \Delta q \) (%):
\[
\Delta q(\%) = 100 \sqrt{\frac{\sum [(q_e(\text{exp}) - q_e(\text{cal}))^2]}{N - 1}}
\]  
(13)
where \( N \) is the total number of data, and \( q_e(\text{exp}) \) and \( q_e(\text{cal}) \) (mg/g) are the adsorption capacity found from experiments and calculation, respectively.

**RESULTS AND DISCUSSION**

**The effect of concentration**

A series of batch tests was conducted at different initial concentrations of 0.5–5 mg/L at constant pH (6.5 ± 0.5) and dosage (20 g of sawdust of 300–600 μm). The effect of concentration on the removal process is shown in Figure 1(a)–1(c). The maximum removal of NO\textsubscript{3}-N and NO\textsubscript{2}-N was found to
be 99–100% but about 55% of NH3-N was removed. The ionized ammonia from the aqueous phase may be adsorbed onto the solid phase by a cation exchange process (Vymazal 2007). The adsorbed ammonia species are usually attached loosely and can desorb easily if the water chemistry conditions of the aqueous phase change.

For a given NH3-N concentration in aqueous solution, a fixed amount of NH3-N is adsorbed onto the sawdust in Table 1.

<table>
<thead>
<tr>
<th>Wood origin</th>
<th>Treated or untreated</th>
<th>Experimental method</th>
<th>Adsorbate</th>
<th>Result</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Pinus radiata</em>, Western Australia</td>
<td>Untreated</td>
<td>Batch</td>
<td>NH3-N</td>
<td>Maximum removal</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>NO3-N</td>
<td>NH3-N = 55%</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>NO2-N</td>
<td>NO3-N = 100%</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>NO2-N = 100%</td>
<td></td>
</tr>
<tr>
<td>Poplar tree (Samsun clone), Turkey</td>
<td>Untreated and treated with 1N H2SO4 (activated sawdust)</td>
<td>Batch</td>
<td>Cu(II)</td>
<td>Adsorption capacity: 5.432 mg/g (untreated)</td>
<td>Acar &amp; Eren (2006)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>13.495 mg/g (treated)</td>
<td></td>
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<tr>
<td>Cedar wood from Annaba, Algeria</td>
<td>Untreated</td>
<td>Fixed-bed</td>
<td>Methylene blue</td>
<td>Adsorption capacity: 142.36 mg/g</td>
<td>Hamdaoui (2006)</td>
</tr>
<tr>
<td>Beech tree from Greece</td>
<td>Untreated and treated with salts (CaCl2, ZnCl2, MgCl2, NaCl)</td>
<td>Batch and Fixed-bed</td>
<td>Methylene blue (basic dye)</td>
<td>Adsorption capacity of treated sawdust increased up to 98% (CaCl2), 87% (ZnCl2), 90% (MgCl2), 100% (NaCl) compared with untreated sawdust</td>
<td>Batzias &amp; Sidiras (2007)</td>
</tr>
<tr>
<td><em>Cedrus deodara</em> from Hyderabad, Sindh, Pakistan</td>
<td>Untreated and treated with NaOH</td>
<td>Batch</td>
<td>Cd(II)</td>
<td>Cd(II) uptake: 0.6 mg/g for untreated and 1.9 mg/g for treated sawdust</td>
<td>Memon et al. (2007)</td>
</tr>
<tr>
<td>Oak tree (<em>Quercus coccifera</em>), Turkey</td>
<td>Treated with HCl</td>
<td>Batch</td>
<td>Cu</td>
<td>Removal:</td>
<td>Argun et al. (2007)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ni</td>
<td>93% for Cu(II) at pH 4</td>
<td></td>
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<td></td>
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<td></td>
<td>Cr</td>
<td>82% for Ni(II) at pH 8</td>
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<td></td>
<td></td>
<td>84% for Cr(VI) at pH 3</td>
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<tr>
<td>Walnut tree from Turkey</td>
<td>Untreated</td>
<td>Batch</td>
<td>Pb</td>
<td>Removal:</td>
<td>Yasemin &amp; Zeki (2007)</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>Cd</td>
<td>75% for Pb</td>
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<td>Ni</td>
<td>60% for Cd</td>
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<td></td>
<td>30% for Ni</td>
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<tr>
<td>Meranti wood from tropical countries (Malaysia or Indonesia)</td>
<td>Treated with HCl</td>
<td>Batch</td>
<td>Methylene blue (basic dye)</td>
<td>Adsorption capacity: 120.48, 117.64, 149.25, and 158.73 mg/g at pH 3</td>
<td>Ahmad et al. (2009)</td>
</tr>
<tr>
<td>Brazilian sawdust (<em>Caryocar spp.</em>, <em>Manilkara spp.</em>, <em>Tabebuia spp.</em>) from Brazilian Santarem city</td>
<td>Untreated</td>
<td>Batch</td>
<td>Pb</td>
<td>Adsorption: 89.10 ± 8.28; 145.04 ± 12.43; 95.31 ± 8.28 mg/g for <em>Caryocar spp.</em>, <em>Manilkara spp.</em>, <em>Tabebuia spp.</em>, respectively</td>
<td>Prado et al. (2010)</td>
</tr>
<tr>
<td><em>Eucalyptus globulus</em> from Beja, north-west of Tunisia</td>
<td>Untreated</td>
<td>Batch</td>
<td>Ammonium (NH4+)</td>
<td>Adsorption capacity: 1.25 mg/g</td>
<td>Wahab et al. (2010)</td>
</tr>
<tr>
<td>Finland wood</td>
<td>Treated with 1N H2SO4</td>
<td>Batch</td>
<td>Phenol</td>
<td>Adsorption capacity: 1.477 mg/g at pH 4.13</td>
<td>Larous &amp; Meniai (2012)</td>
</tr>
<tr>
<td>Mango wood (<em>Mangifera indica</em>) from India</td>
<td>Treated with 0.1N NaOH followed by 0.1N H2SO4</td>
<td>Batch</td>
<td>Cr(VI)</td>
<td>Adsorption capacity: 10.86 mg/g</td>
<td>Kapur &amp; Mondal (2013)</td>
</tr>
</tbody>
</table>
order to saturate the available sorption sites. But NH$_3$-N concentration in the aqueous phase may be reduced as a result of the nitrification process. As a result, some NH$_3$-N will desorb to regain its equilibrium and the aqueous phase will have a new concentration. This is why the NH$_3$-N adsorption was found to be lower in this study. However, the maximum removal for NH$_3$-N and NO$_3$-N was obtained within 15–30 minutes for the concentration range 0.5–2.5 mg/L. The removal rate with initial concentration above 2.5 mg/L was found to be much lower for NH$_3$-N and NO$_3$-N adsorption. The effect of concentration on NO$_2$-N removal was smaller but it took longer (45 hours) to reach maximum removal. The adsorption capacity (μg/g) with different initial concentrations is shown in Figure 1(d). Results revealed that the adsorption capacity increases linearly with increasing initial concentration because of higher availability of nutrient ions in the solution. It provides an important driving force to overcome the mass transfer resistance of nutrient ions between the aqueous and solid phase. Higher concentrations contain a greater number of nitrogenous ions which provides a higher probability of collision between the ions and the sawdust surface. Similar results were found for adsorption of chromium(VI) on pomace (Malkoc et al. 2006); methylene blue on wheat shells (Bulut & Aydin 2006); and basic dye on banana stalk waste (Hameed et al. 2008). A list of studies (including this study) is given in Table 1 that have used sawdust of different wood origin for removing different adsorbates such as heavy metals (Cu, Cd, Cu, Ni, Cr, Pb), phenol and nitrogenous species. Other than this study, only Wahab et al. (2010) was found in the literature to use Eucalyptus globulus sawdust to remove NH$_4^+$ from aqueous solution.

The effect of dosage

The removal of nitrogen compounds with various dosages (2–20 g dry sawdust of 300–600 μm diameter) was investigated with a constant initial concentration of 1 mg/L and the results are shown in Figure 2(a)–2(c). Increasing dosage increases overall surface area and so improves the removal process. But for all compounds, it appears that removal efficiency increases until it reaches a dosage of 12 g of sawdust. Beyond this limit, removal was found to be insignificant. The adsorption capacity (μg/g) showed a decreasing trend with increasing dosage (Figure 2(d)) because of the availability of fewer nitrogen ions per unit mass of sawdust when the initial concentration remains the same. The adsorption capacity was reduced by 55% for NH$_3$-N, 78% for NO$_3$-N, and 64% for NO$_2$-N, respectively, with a sawdust dosage increasing from 2 to 5 g. Similar findings were also obtained for adsorption of Cr(VI) on activated neem leaves (Babu & Gupta 2008), methylene blue on wheat shells (Bulut & Aydin 2006), and Ni(II) on clays (Gupta & Bhattacharyya 2006).

Figure 2 | (a)–(c) The effect of dosage of sawdust and contact time on nitrogen removal, (d) nitrogen adsorption capacity (μg/g) with sawdust dosage.
The effect of particle sizes and pH

The effect of particle sizes of sawdust (<300 μm, 300–600 μm, 600 μm–1.18 mm, 1.18–2.36 mm, and >2.36 mm) was investigated in batches with constant pH (6.5 ± 0.5). The effect of pH (4–9) of solution was investigated with constant particle sizes <300 μm. In both cases, 10 g of dry sawdust and an initial concentration of 0.5 mg/L were used. The results shown in Figure 3 revealed that these parameters have an insignificant effect on the removal process. This was also confirmed by Student’s t-test ($P > 0.05$) of removal percentage where the null hypothesis supports that the mean removal is not significantly different from that of the removal of individual particle sizes. However, the NH$_3$-N removal varies from 35 to 40%, NO$_3$-N removal varies from 85 to 91% and maximum removal of NO$_2$-N was 98% for all particle sizes. When the sorbent mass is saturated, solute diffusion may occur at the center of solid particles (Jansson-Charrier et al. 1996). This is why the sorption capacity was found to be independent of the particle size of sawdust. Moreover, adsorption/desorption might be controlled by ion exchange capacity, which involves the replacement of ions (Hossain et al. 2009). The sawdust might have high porosity and a large quantity of light metals (Ca, K, Mg, and Na), which makes it more vulnerable to being exchanged (Ragland & Aerts 1997). This result

Figure 3 | The effect of particle sizes of sawdust (a)–(c) and pH of solution (d)–(f) on nitrogen removal.
supports the findings of chromium(III) biosorption on orange (Citrus sinensis) waste (Marin et al. 2009).

**Adsorption kinetics**

There is an appropriate quantitative approach to distinguishing between the kinetic and the diffusion rate control. It is a straight line plot of slope $k_{diff}$ yielded by plotting the amount of adsorption ($q_t$) against the square root of contact time ($t^{1/2}$), according to Equation (7). If the straight line passes through the origin, it indicates intraparticle diffusion control (Ho et al. 2000). Therefore, the intraparticle diffusion model will be analyzed first, followed by the pseudo-first order and pseudo-second order kinetic models.

The adsorption data for all three species were fitted for the intraparticle diffusion model ($q_t$ versus $t^{1/2}$) (Figure 4) and a low $R^2$ value was found for NH$_3$-N (0.005–0.611) and NO$_3$-N (0.153–0.800) adsorption, respectively. This indicates that the NH$_3$-N and NO$_3$-N adsorption are not diffusion controlled. On the other hand, NO$_2$-N adsorption showed intraparticle diffusion with two-stage adsorption ($R^2 = 0.953–0.994$ for stage 1 and $R^2 = 0.726–0.960$ for stage 2). The first step represents the adsorption of NO$_2$-N onto the sawdust surface and the second step concerns the diffusion of NO$_2$-N to the adsorption site (Kalavathy et al. 2005; Gupta et al. 2012). A surface adsorption mechanism took place in the first 25 hours of contact time for a NO$_2$-N concentration of 0.5–2.5 mg/L, and 36 hours of contact time for a concentration range of 3.0–5.0 mg/L. After these time periods, diffusion became rate controlling. The slope of the second linear portion yields the intraparticle diffusion rate constant $k_{d2}$ (Table 2). Results show that a higher initial concentration leads to a higher diffusion rate. This is due to higher concentrations remaining in the solution phase after surface adsorption, resulting in an increase of driving force and therefore increasing the diffusion rate. The values of rate constant were found to be 0.179–4.772 μg/g hours$^{0.5}$ for a NO$_2$-N concentration range of 0.5–5 mg/L.

However, the plots in Figure 4 do not show zero intercepts but show two intercepts $M_1$ and $M_2$. In this adsorption process, the higher concentration of solution results in a higher intercept, indicating that intraparticle diffusion may not be the sole dominating factor controlling the mechanism of the adsorption process (Bhattacharyya & Gupta 2006). This may be explained by the liquid film diffusion model. When a thin liquid film surrounding the solid phase plays a significant role, the liquid film diffusion model may be used (Equation (8)). The plot of $-\ln (1-F)$ versus $t$ (figure not shown) has a positive linearity with $R^2 = 0.929–0.995$ with intercepts close to zero (–0.046 to 0.081) (Table 2). This reveals that the interaction process might be diffusion controlled in a liquid film (Bhattacharyya & Gupta 2006). The film diffusion rate coefficient for NO$_2$-N adsorption was found to be 0.051–0.093 min$^{-1}$ for initial concentrations in the range 0.5–5 mg/L. The mass transfer of NO$_2$-N adsorption involves diffusion through the fluid film around sawdust particles and also through the pores of the internal sites of sawdust. Initially, the concentration slope between the film and solid surface was large, and as a result, the transfer of solute onto the solid surface was faster. The solute takes longer to transfer from the solid...
The effect of initial concentration and contact time data were used to study the pseudo-first order and pseudo-second order adsorption kinetics and the model parameters are

Table 2 | Parameters of intraparticle diffusion and liquid film diffusion models for NO2-N adsorption onto sawdust

<table>
<thead>
<tr>
<th>C0 (mg/L)</th>
<th>M1</th>
<th>kdi (μg/g hours2/3)</th>
<th>R2</th>
<th>M2</th>
<th>kdt (μg/g hours2/3)</th>
<th>R2</th>
</tr>
</thead>
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<tr>
<td>0.5</td>
<td>0.488</td>
<td>0.819</td>
<td>0.953</td>
<td>3.564</td>
<td>0.179</td>
<td>0.867</td>
</tr>
<tr>
<td>1.0</td>
<td>0.709</td>
<td>1.675</td>
<td>0.976</td>
<td>7.025</td>
<td>0.383</td>
<td>0.904</td>
</tr>
<tr>
<td>1.5</td>
<td>−1.354</td>
<td>2.915</td>
<td>0.976</td>
<td>10.374</td>
<td>0.581</td>
<td>0.726</td>
</tr>
<tr>
<td>2.0</td>
<td>−1.965</td>
<td>3.755</td>
<td>0.989</td>
<td>12.233</td>
<td>0.973</td>
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<td>−2.437</td>
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<td>0.981</td>
<td>12.986</td>
<td>1.494</td>
<td>0.828</td>
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<td>3.0</td>
<td>3.645</td>
<td>3.777</td>
<td>0.994</td>
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<td>0.958</td>
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<td>4.0</td>
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<tr>
<td>5.0</td>
<td>7.484</td>
<td>4.415</td>
<td>0.957</td>
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</table>

<table>
<thead>
<tr>
<th>Nutrient</th>
<th>C0 (mg/L)</th>
<th>qe (exp) (μg/g)</th>
<th>qe (cal) (μg/g)</th>
<th>k1 (1/min)</th>
<th>R2</th>
<th>Δq (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH3-N</td>
<td>0.5</td>
<td>5.783</td>
<td>0.052</td>
<td>0.864</td>
<td>0.81</td>
<td>2.627</td>
</tr>
<tr>
<td>NO2-N</td>
<td>0.5</td>
<td>4.613</td>
<td>0.083</td>
<td>0.963</td>
<td>0.03</td>
<td>5.308</td>
</tr>
<tr>
<td>NO3-N</td>
<td>0.5</td>
<td>5.161</td>
<td>0.065</td>
<td>0.813</td>
<td>4.86</td>
<td>13.85</td>
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<tr>
<td>NO2-N</td>
<td>1.0</td>
<td>10.386</td>
<td>0.09</td>
<td>0.938</td>
<td>0.01</td>
<td>10.672</td>
</tr>
<tr>
<td>NO2-N</td>
<td>1.5</td>
<td>15.699</td>
<td>0.085</td>
<td>0.995</td>
<td>0.01</td>
<td>16.949</td>
</tr>
<tr>
<td>NO3-N</td>
<td>2.0</td>
<td>22.134</td>
<td>0.08</td>
<td>0.987</td>
<td>0.05</td>
<td>23.041</td>
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<tr>
<td>NO2-N</td>
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<td>0.968</td>
<td>0.06</td>
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<td>0.97</td>
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<td>NO2-N</td>
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<td>0.958</td>
<td>0.21</td>
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<td>55.197</td>
<td>0.051</td>
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<td>0.06</td>
<td>57.143</td>
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</table>

The effect of initial concentration and contact time data were used to study the pseudo-first order and pseudo-second order adsorption kinetics and the model parameters are
presented in Table 3. The higher value of $R^2$ and lower value of $\Delta q$ provide better goodness of fit. The results revealed that the pseudo-second order model is more appropriate to explain the kinetic behavior of adsorption onto radiata pine sawdust for all three compounds. But NO$_2$-N adsorption also followed a pseudo-first order model. The linear relationship between $t/q_t$ and $t$ shown in Figure 5 reveals the applicability of second-order kinetics. The values of $q_e$ and $k_2$ were determined from the slope and intercept of this plot. This procedure shows the adsorption behavior over the whole range of experimental condition (Hameed et al. 2007). The good relationship between $t/q_t$ versus $t$ in Figure 5 provides strong agreement between experimental and calculated $q_e$ values (Table 3).

**Adsorption isotherm**

The Langmuir and Freundlich models using Equations (4) and (6) were fitted with experimental data and are shown in Table 4. The Langmuir model makes assumptions of monolayer coverage and constant adsorption energy while the Freundlich model assumes a heterogeneous surface adsorption (Bulut & Aydin 2006). The maximum Langmuir adsorption capacity ($q_m$) varies from 0.021 to 0.048 mg/g for different species. The values of $K_{ads}$ in the Langmuir model were found to be very high ($K_{ads} > 1$) except for NH$_3$-N, which indicates that NO$_3$-N and NO$_2$-N adsorption is high. The values of $K$ and $n$ in the Freundlich isotherm (Table 4) were calculated from the intercept and slope of the linear plot (Equation (6)). In general, increasing $K$ means an increase in the adsorption capacity of sawdust. The $K$ values show that sawdust is more effective for removing NO$_2$-N. The $n$ value indicates the favorability of sorption. Generally, $n$ values in the range of 2–10 represent good, 1–2 moderately difficult, and less than 1 indicates poor adsorption characteristics (Aksu 2005). Also the closer the $n$ value of Freundlich to zero, the more heterogeneous the system is (Hameed et al. 2008). The results revealed that sawdust is a good adsorbent for NO$_3$-N and NO$_2$-N ($n > 2$) removal. However, the $n$ value is lower than 2 for NH$_3$-N, which shows a complex adsorption characteristic. The value of the regression coefficient ($R^2$) of the Langmuir and Freundlich isotherms revealed that the Freundlich model fits slightly better for NO$_3$-N and NO$_2$-N adsorption but NH$_3$-N adsorption fits fairly well with both models.

The adsorption intensity ($R_L$) with initial concentration of aqueous solution is plotted in Figure 6. From these results, one can observe that the adsorption is more favorable at higher concentrations. Also the value of $R_L$ in the range $0 < R_L < 1$ at all initial concentrations confirms the favorable adsorption (Babu & Gupta 2008). These results revealed that

**Table 4 | Parameters of the Langmuir and Freundlich isotherms**

<table>
<thead>
<tr>
<th>Species</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_m$ (mg/g)</td>
<td>$K_{ads}$</td>
</tr>
<tr>
<td>NH$_3$-N</td>
<td>0.048</td>
<td>0.228</td>
</tr>
<tr>
<td>NO$_3$-N</td>
<td>0.021</td>
<td>99.201</td>
</tr>
<tr>
<td>NO$_2$-N</td>
<td>0.042</td>
<td>294.615</td>
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</table>

Figure 5 | Pseudo-second order plots of nitrogen adsorption.
the radiata pine sawdust may be used as an effective medium for removing nitrogen species from aqueous solution and hence, it can be used for stormwater/wastewater treatment. However, the pore size distribution and soil–fluid interfacial area plays an important role in the adsorption process. The solid walls of sawdust that provide this interfacial area are mainly composed of cellulose and lignin and other hydroxyl groups, such as tannins or other phenolic compounds. Lignin is a polymer material and is built up from the phenylpropane nucleus, which is an aromatic ring with three-carbon side chain. Tannins are water soluble but they are complex polyhydric phenols. Pore size and pore distribution can be better understood by scanning electron microscope (SEM) microphotograph. According to the International Union of Pure and Applied Chemistry, pores are classified as micropores (pore diameter <20 Å), mesopores (20 Å <d< 500 Å), and macropores (d> 500 Å) (Ahmad et al. 2009). It has been shown in Ahmad et al. (2009) that the average pore diameter of meranti sawdust is mesopores (363.4 Å). In this research, SEM analysis was not done but further research is now underway to understand the actual pore size and solid-fluid interfacial area for adsorption in radiata pine sawdust.

CONCLUSIONS

The adsorption capability of radiata pine sawdust was investigated in batches and examined for removal of selected nitrogen species (NH3-N, NO3-N, and NO2-N) from aqueous solution. The results show that sawdust is an effective adsorbent for removing these species from the water environment, especially at lower concentrations. The amount of sawdust dosage showed significant effects on the removal process but the effect of pH and particle size was negligible. The optimum sawdust dosage for maximum removal was found to be 12 g, beyond which the removal was insignificant. For NO3-N and NO2-N 100% removals were obtained, but only 55% removal was found for NH3-N. The maximum removal of NO3-N and NH3-N was obtained within a shorter period of contact time, while it took longer to reach maximum removal for NO2-N. The adsorption kinetics was studied using intraparticle diffusion, liquid-film diffusion, and pseudo-first order and pseudo-second order models. The adsorption of all species followed the pseudo-second order model but NO2-N adsorption followed both pseudo-first and pseudo-second order. The kinetics of NO2-N adsorption also showed two-step adsorption following intraparticle diffusion and liquid-film diffusion. The isotherm study shows that NO3-N and NO2-N adsorption follow the Freundlich model slightly better than the Langmuir, but NH3-N adsorption follows both models. Radiata pine trees are abundant and their sawdust can be used as a low-cost adsorbent for the treatment of stormwater and/or wastewater.

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