Applications and limits of theoretical adsorption models for predicting the adsorption properties of adsorbents

Hyun Ju Park, Duc Canh Nguyen, Choon-Ki Na and Chung-il Kim

ABSTRACT

The objective of this study is to evaluate the applicability of adsorption models for predicting the properties of adsorbents. The kinetics of the adsorption of NO₃⁻/CO₃²⁻ ions on a PP-g-AA-Am non-woven fabric have been investigated under equilibrium conditions in both batch and fixed bed column processes. The adsorption equilibrium experiments in the batch process were carried out under different adsorbate concentration and adsorbent dosage conditions and the results were analyzed using adsorption isotherm models, energy models, and kinetic models. The results of the analysis indicate that the adsorption occurring at a fixed adsorbate concentration with a varying adsorbent dosage occur more easily compared to those under a fixed adsorbent dosage with a varying adsorbate concentration. In the second part of the study, the experimental data obtained using fixed bed columns were fit to Bed Depth Service Time, Bohart–Adams, Clark, and Wolborska models, to predict the breakthrough curves and determine the column kinetic parameters. The adsorption properties of the NO₃⁻ ions on the PP-g-AA-Am non-woven fabric were differently described by different models for both the batch and fixed bed column process. Therefore, it appears reasonable to assume that the adsorption properties were dominated by multiple mechanisms, depending on the experimental conditions.

Key words | nitrate nitrogen, PP-g-AA-Am non-woven fabric, sorption isotherms, sorption mechanism

INTRODUCTION

Currently, many efforts are being made to develop hybrid systems for waste treatment that integrate electrolytic analysis, membrane separation, chemical flocculation, the ion exchange method (the adsorption method), etc., with conventional biological treatment processes (Park & Kim 2000). In particular, in the ion exchange and the adsorption methods, the simultaneous removal of ionic substances such as N, P, and heavy metals is possible, and the treatment efficiency is relatively consistent regardless of the climate and density. Furthermore, not only are there no toxic by-products from such processes, but also the operation of the treatment processes and control and maintenance, are simple and easy. Therefore, the ion exchange method is becoming the simplest and safest unit process in building a hybrid advanced treatment system, combining existing biological treatment processes.

As a result, the range of applications for the current ion exchange method is expanding from water purification systems to systems for the removal of heavy metals, ammoniac nitrogen, nitrate nitrogen (NO₃⁻-N), phosphoric acid, and volatile organic compounds from sewage and wastewater. Therefore, a systematic understanding of the adsorption mechanism is needed in order to design and operate effective processes and optimize the efficiency, economic viability, and ease of operation.

Typically, an adsorbent’s efficiency is estimated from its adsorption isotherm, constructed based on the adsorption equilibrium. The adsorption isotherm demonstrates the relationship between the adsorbate’s equilibrium concentration and the adsorbent’s equilibrium adsorption capacity per unit mass at a given temperature. Many models, including the isotherms of Langmuir, Freundlich, Elovich, Sips, Dubinin-Radushkevich, and Temkin, use this information to understand the adsorption mechanism and are indispensable tools for investigating the performance of an adsorbent or an adsorbate and the adsorption mechanism. In researching the adsorption of Ag on activated carbon, Hahn et al. (2006)
investigated the effects of the concentration of the adsorbate on the adsorption characteristics and the results were applied to the Langmuir and Freundlich isotherms. Ok et al. (2002) altered the adsorbent’s dosage (weight) and studied the adsorption characteristics of Cu, Zn, and Cd ions on activated carbon. They concluded that the experimental results could be applied well to the Freundlich isotherm. In summary, various experimental methods and adsorption models have been used to investigate the adsorbent’s maximum adsorption and its adsorption characteristics.

While the adsorption process is being used in fields such as water treatment, mixed gas separation, and the treatment of organic pollutants, theoretical research on the process remains incomplete compared to the degree of commercialization. This is primarily because an adsorption isotherm that adequately describes the adsorption equilibrium relationship between an adsorbate and an adsorbent has not been proposed yet. Furthermore, the absorbed molecules tend to be non-ideal in most adsorption systems (Kim 2006). For the ion exchange or the adsorption methods to be more widely used in the water purification and wastewater treatment processes, an adsorption model and its application method needs to be provided, so that the adsorption equilibrium relationship, as well as the adsorption characteristics of the adsorbate and the adsorbent, can be clearly investigated.

In our previous papers, we have reported the preparation method for the PP-g-AA-Am non-woven fabric starting from PP-g-AA-Am, using the photo-induced graft polymerization of acrylic acid (AA) onto polypropylene (PP) non-woven fabric followed by the amination of the grafted AA via its reaction with diethylenetriamine (DETA) (Park & Na 2006). The effect of the PP-g-AA-AM non-woven fabric on the removal of NO3-N has also been investigated using a fixed bed column test with groundwater (Park et al. 2013). In this study, we have evaluated the adsorption of NO3-N on the anion exchanger, in both batch and fixed bed columns. The effect of various variables such as the adsorbate concentration, adsorbent dosage, flow rate, and bed height has been experimentally explored.

**MATERIALS AND METHODS**

**Materials and reagents**

The PP non-woven fabric was washed with a neutral detergent solution before being used as the substrate polymer for grafting. Acrylic acid (AA, Daejung Chemical Co., Korea), benzophenone (BP, Yakuri Pure Chemical Co., Japan), H2SO4, and FeSO4.7H2O were used as the monomer, photoinitiation, graft accelerator, and the homopolymer inhibitor, respectively. Methanol and diethylenetriamine (DETA, Daejung Chemical Co., Korea) were used as the homopolymer removal solvent and the amination reagent for converting the PP-g-AA non-woven groups to the amine groups, respectively; AlCl3 was used as the reaction catalyst. Extra pure KNO3 and NaCl were used to prepare the anion solution and regenerate the adsorbent in the column.

**Preparation of PP-g-AA-Am fabric**

The PP-g-AA-Am fabric was prepared by grafting AA onto the PP non-woven fabric and subsequently converting the carboxyl (–COOH) group in the grafted AA to an amine (Am) group via a reaction with DETA. Detailed descriptions of the preparation of the PP-g-AA-Am fabric are available in the literature (Park & Na 2006; Park et al. 2013).

**Batch experiments**

The adsorption equilibrium and adsorption rate experiments were conducted to evaluate the adsorption characteristics of NO3-N from artificial wastewater on the PP-g-AA-Am fabric. The adsorption equilibrium experiments were conducted in batch mode using a rotary constant temperature shaker. Two types of experiments were conducted, namely: adsorption isothermal experiments under equipotent conditions, where the amount of adsorbent was fixed and the concentration of the adsorbate was varied; and isothermal experiments under equimolal conditions, where the concentration of the adsorbate was fixed while the amount of the adsorbent was varied. For the experiments under equipotent conditions, an adequate amount of adsorbent (1.0, 2.5, and 5.0 g/L) was added to a 100 mL solution containing 10–200 mg/L of NO3-N. A constant temperature shaker was used to shake the solution for 2 h at a temperature of 20 °C and a speed of 150 rpm. For experiments under equimolal conditions, 0.1–2.0 g of the adsorbent was added to a 100 mL solution containing 30, 60, and 100 mg/L of NO3-N. The other conditions were established to match those of the experiment with the different concentrations. The adsorbate that remained in the solution after the completion of the experiments was measured, and Equation (1) was used to calculate the adsorbed quantity.

\[
q_e = \frac{(C_0 - C_e)V}{W}
\]  
(1)
In the above equation, \( q_e \) is the amount of adsorbate (in mg/g), adsorbed per unit mass of adsorbent at equilibrium, \( C_0 \) is the initial concentration of the adsorbate (in mg/L), \( C_e \) is the equilibrium concentration of the adsorbate (in mg/L) in the solution, \( V \) is the volume of the solution (in L), and \( W \) is the adsorbent dosage (in g). The solution was preprocessed according to the pollution processing test method to reach the prescribed NO\(_3\)-N concentration, and subsequently analyzed using a UV spectrometer (Shimadzu UV-2410PC, Japan) for confirmation. For the adsorption rate experiments, in order to determine the amount of the NO\(_3\)-N adsorbed at various times during the reactions, 1.0 g of the adsorbent was added to 400 mL of the solution containing 15, 31, 62, and 124 mg/L of NO\(_3\)-N. The resulting solution was shaken at a temperature of 20 \( ^\circ \mathrm{C} \) and a speed of 150 rpm, and 2 mL of the supernatant was collected at a range of 1–90 min. The concentration of NO\(_3\)-N in the supernatant collected at each reaction time was analyzed and compared with the initial concentration of the solution, in order to determine the adsorption amount.

**Fixed bed column tests**

The fixed bed column studies were conducted using columns with varying lengths in the range of 10–20 cm. The columns were made of cylindrical acryl and the inflow and outflow of the columns were blocked using absorbent cotton. The columns were packed with the adsorbent, which had been ground down to a size of 1–2 mm. The columns were charged with varying initial NO\(_3\) concentrations from 15–57 mg/L in the up-flow mode, with varying volumetric flow rates in the range of 0.5–2 cm/s. The effluent was collected every 5 L and its concentration was analyzed using a UV spectrometer as well as by the standard method for water analysis.

**RESULTS AND DISCUSSION**

**Batch adsorption experiments**

**Isothermal adsorption using different adsorption experimental methods**

The isothermal adsorption experiments were conducted under equipotent and equimolal conditions. For the experiments under equipotent conditions, the amount of adsorbent was fixed and the adsorbate concentration (NO\(_3\)-N) was varied within the wide range of 10–200 mg/L. For the experiments under equimolal conditions, the adsorbate (NO\(_3\)-N) concentration was fixed at 30, 60, and 100 mg/L and the adsorbent dosage was varied in the range of 1.0–20 g/L.

Figure 1(a) shows the change in the equilibrium adsorption capacity \( (q_e) \) of the anion exchange resin as a function of the initial concentration of NO\(_3\)-N \( (C_i) \). While a linear relationship between the initial and adsorbed amounts of NO\(_3\)-N was observed for an anion exchange resin dosage of 5.0 g/L, when the anion exchange resin dosage was reduced to 2.5 and 1.0 g/L, the relationship became logarithmic in nature. Figure 1(b) shows the equilibrium adsorption capacity and adsorption removal rate of NO\(_3\)-N as a function of the anion exchange resin dosage. As the dosage increased, the equilibrium adsorption capacity decreased exponentially and the adsorption removal rate increased algebraically, as a result of the decrease in the remaining adsorbate concentration in the solution. Furthermore, the

![Graphs showing adsorption capacity and removal rate](https://iwaponline.com/wst/article-pdf/72/8/1364/466380/wst072081364.pdf)
competition between the deionized shift components and the adsorbate as well as the solvent and adsorbate, for adsorption sites on the adsorbent, increased exponentially. The isothermal adsorption according to the adsorption experiment method exhibited a logarithmic curve. According to the adsorption equilibrium isotherm categorization suggested by Giles et al. (1960), this form of isotherm belongs to the L-type (Langmuir-type) (Langmuir 1918).

Langmuir adsorption isotherm versus the adsorbate concentration under equipotent conditions

The Langmuir adsorption isotherm describes monolayer adsorption and was constructed by observing the effect of the adsorbent’s binding power as a function of the thickness of the monolayer, and using a model that takes into account the fact that adsorption does not occur in other separated layers. The Langmuir adsorption isotherm is expressed as linear equations in various forms. Of these, the linear equation proposed by Stum & Morgan (1981) and that proposed by Weber (1972), shown in Equations (2) and (3), respectively, are the most widely used.

\[
\frac{1}{q_e} = \frac{1}{bq_m} \frac{1}{C_e} + \frac{1}{q_m} \tag{2}
\]

\[
\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m b} \tag{3}
\]

When we tried to apply the experimental results to the Langmuir adsorption isotherm, we found it difficult to fully express all the concentrations in the form of any one linear equation. Nevertheless, the experimental data best fit to the linear representations of the Langmuir isotherm proposed by Weber, with relatively high \(R^2\) values in the range of 0.9538–0.9756 (Figure 2(a)).

Table 1 presents the \(q_m\) and \(b\) values obtained from the slope and intercept for each linear curve. When 1.0 g/L of the anion exchange resin was saturated with the maximum adsorption amount, the \(q_m\) value was 33.33 mg/g. Similar \(q_m\) values corresponding to the adsorbent dosages of 2.5 g/L and 5.0 g/L were 29.85 mg/g and 27.78 mg/g, respectively, indicating that the \(q_m\) value increases with a decrease in the adsorbent dosage.

The Freundlich adsorption isotherm versus adsorbate concentration under equipotent conditions

The Freundlich adsorption isotherm is based on the Langmuir adsorption isotherm and accounts for the exponential decrease in the heat of adsorption with surface coverage amount, the \(q_m\) value was 33.33 mg/g. Similar \(q_m\) values corresponding to the adsorbent dosages of 2.5 g/L and 5.0 g/L were 29.85 mg/g and 27.78 mg/g, respectively, indicating that the \(q_m\) value increases with a decrease in the adsorbent dosage.

<table>
<thead>
<tr>
<th>Adsorbent (g/L)</th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(q_m) (mg/g)</td>
<td>(b)</td>
</tr>
<tr>
<td>1.0</td>
<td>33.33</td>
<td>0.1648</td>
</tr>
<tr>
<td>2.5</td>
<td>29.85</td>
<td>0.1321</td>
</tr>
<tr>
<td>5.0</td>
<td>27.78</td>
<td>0.1330</td>
</tr>
</tbody>
</table>
When the adsorbent dosage was 1.0 g/L, the highest adsorption was observed, indicating facile adsorption. The values of $b$ of the adsorbent dosage, which were greater than 2, indicated that adsorption occurs easily and when it is below 1, no adsorption occurs (Treybal 1960). The relationship between the amount of adsorbate adsorbed on the adsorbent, and the concentration of the adsorbate in the solution is defined by Equation (4) and the linearized form of Equation (4) is shown in Equation (5) (Halsey 1952).

$$q_e = K_F C_e^{1/n}$$

(4)

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

(5)

where $q_e$ is the amount of adsorbate (mg/g) adsorbed per unit mass of the adsorbent, $K_F$ and $n$ are Freundlich constants, and $C_e$ is the equilibrium concentration of the adsorbate in the solution (mg/L). The Freundlich constant $K_F$ is a measure of the adsorbent’s adsorptivity (with units of mg$^{-1/(1/n)}$L$^{1/n}$g$^{-1}$) and typically, the larger the value of $K_F$, the better the adsorbent performance; $n$ is the adsorption power of the adsorbate. Typically, when $n$ is greater than 2, adsorption occurs easily and when it is below 1, no adsorption occurs (Treybal 1989).

Figure 2(b) shows the fit of the experimental data to the Freundlich adsorption isotherm; $K_F$ values of 9.0666 mg$^{-1/(1/n)}$L$^{1/n}$g$^{-1}$, 5.6712 mg$^{-1/(1/n)}$L$^{1/n}$g$^{-1}$, and 3.9848 mg$^{-1/(1/n)}$L$^{1/n}$g$^{-1}$ were obtained for anion exchange resin dosages of 1.0 g/L, 2.5 g/L, and 5.0 g/L, respectively. These results indicate that adsorption is favorable at low anion exchange resin dosages. The $n$ values obtained from the experimental results were greater than 2, regardless of the adsorbent dosage, indicating facile adsorption. When the adsorbent dosage was 1.0 g/L, the highest $n$ value of 5.2 was obtained, implying easier adsorption at this dosage compared to the other dosage levels.

### Sips adsorption isotherm versus adsorbate concentration under equipotent conditions

The Sips adsorption isotherm is an empirical equation that combines the Langmuir and Freundlich adsorption isotherms and can competently predict the adsorption equilibria across a relatively large concentration range (Sips 1948). When the Sips adsorption isotherm is modified to the Weber linear equation, the following formula is obtained.

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e^{\beta} + \frac{1}{q_m b}$$

(6)

where $b$ and $\beta$ are the Sips (Langmuir-Freundlich) constant and index, respectively. The constant $\beta$ is in the range $0 < \beta < 1$. Various $\beta$ values are typically used to calculate $C_e^{\beta}$ values. When a plot of $1/q_e$ versus $1/C_e^{\beta}$ and $C_e^{\beta}/q_e$ versus $C_e^{\beta}$ for a given $\beta$ value yields a linear relation, we say that the experimental results follow the Sips adsorption isotherm for that $\beta$ value. Using the intercept or the slope of the linear relationships, the value of $q_m$ corresponding to the maximum adsorption amount and the Sips index value $b$ can be obtained.

For the adsorbent dosages of 1.0, 2.5, and 5.0 g/L, the $\beta$ value was set within the range of 0.5–6.0. Each resulting $C_e^{\beta}$ value was applied to Equation (6) and the results are displayed in Figure 3 and Table 2. As shown in Figure 3, depending on the adsorbent dosage, while the $\beta$ value and the maximum adsorption amount $q_m$ exhibited some differences, the $R^2$ value exhibited a range of 0.9996–0.9999, which indicated an excellent fit between the experimental results and the Sips adsorption isotherm. Therefore, compared to the Langmuir and Freundlich adsorption isotherms, which are based on the adsorption mechanism, the Sips adsorption isotherm explains the experimental results of this study better. The same trend was also observed in previous studies (Shahryari et al. 2010; Varank et al. 2012; Brdar et al. 2012). In addition, these results show that the adsorption mechanism of NO$_3$ can change depending on the adsorbate and the adsorbent. In other

<table>
<thead>
<tr>
<th>Adsorbent (g/L)</th>
<th>$\beta$</th>
<th>$q_m$ (mg/g)</th>
<th>$b$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.50</td>
<td>49.50</td>
<td>0.2036</td>
<td>0.9997</td>
</tr>
<tr>
<td>2.5</td>
<td>0.53</td>
<td>46.30</td>
<td>0.1391</td>
<td>0.9999</td>
</tr>
<tr>
<td>5.0</td>
<td>0.60</td>
<td>44.64</td>
<td>0.0999</td>
<td>0.9996</td>
</tr>
</tbody>
</table>

**Table 2** | Parameters calculated from Sips isotherm models

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Figure 3 | Sips isotherm plots of NO$_3$-N adsorption on the anion exchange resin under equipotent conditions.
words, the adsorption characteristics of NO₃⁻, according to the adsorbent, is dominated by the dualistic adsorption mechanism, in which changes to Langmuir’s uniform surface-monolayer adsorption and Freundlich’s uniform surface-monolayer take place depending on the adsorbate NO₃⁻-N.

**Langmuir adsorption isotherm versus the adsorbent concentration under equimolal conditions**

The result of applying the Langmuir adsorption isotherm to the experimental results obtained under equimolal conditions is displayed in Figure 4(a). Unlike the adsorption isotherm obtained under the equipotent conditions, Figure 4(a) exhibited a favorable linear relationship for the entire linear formula.

The values of $q_m$ and $b$ obtained from the slope and the intercept of the Langmuir adsorption isotherm are displayed in Table 3. The $q_m$ value corresponding to the maximum single-layer adsorption was calculated as 49.75–57.80 mg/g. In addition, all the $q_m$ values calculated were similar, regardless of the linear representation methods of the Langmuir adsorption isotherm. However, these values were different from the $q_m$ values of 27.78–33.33 mg/g obtained when the adsorption isotherm obtained under equipotent conditions was applied to the Langmuir adsorption isotherm, or from the $q_m$ value 44.64–49.50 mg/g obtained from the Sips adsorption isotherm. Therefore, the results may vary depending on the adsorption experiment conditions.

**Freundlich adsorption isotherm versus the adsorbent dosage under equimolal conditions**

The adsorption data obtained under equimolal conditions were applied to the Freundlich adsorption isotherm, and the results are displayed in Figure 4(b). As shown in the figure, a good linear regression constant ($R^2$) of 0.9922 was obtained, considering the fit for the entire adsorbent dosage range. Therefore, it may be concluded that the experimental data obtained under equimolal conditions could be fit to some extent to the Freundlich adsorption isotherm.

As stated previously, the Freundlich constant ($K_F$) is a measure of the adsorptivity of the adsorbent, and the adsorptivity is typically better when the value is large. The $K_F$ values generated from the Freundlich adsorption isotherm in this case were in the range of 1.7679–3.1340 mg$^{1-(1/n)}$L$^{1/n}$g$^{-1}$, which is starkly different from the $K_F$ values of 3.9848–9.0666 mg$^{1-(1/n)}$L$^{1/n}$g$^{-1}$ generated with experimental data obtained under equipotent conditions. Similarly, the $n$ values of 1.3310–1.4397 obtained under equimolal conditions were lower than the $n$ values
of 1.9936–3.2394 obtained under equipotent conditions. In other words, the adsorption reaction under equimolal conditions occurs more easily compared to that under equipotent conditions.

**Fixed bed column experiments**

**Breakthrough curves for NO\textsubscript{3}-N removal**

The breakthrough curves (Figure 5) are obtained by plotting the NO\textsubscript{3}-N concentration in the solution as a function of time for various initial concentrations of NO\textsubscript{3}-N in the solution (15–37 mg/L), at different flow rates (0.5–2.0 cm/s) and a 200 mm ion exchange bed height. The results show that NO\textsubscript{3}-N in the influent was completely adsorbed during the initial time period. After breakthrough occurred, the effluent concentration increased with time, until it reached a saturation point where the NO\textsubscript{3}-N concentration in the effluent equalled that in the influent.

When the initial concentration and the flow rate were increased, the breakthrough and saturation times were found to decrease. This behavior can be explained in terms of the residence time of NO\textsubscript{3}-N in the column. At low initial concentrations, the mass transfer of NO\textsubscript{3}-N decreased. As a result, the amount of the ion exchange per unit flow rate decreased, with decreasing initial concentration delaying the occurrence of both the breakthrough and the saturation points. At a low flow rate, NO\textsubscript{3}-N had more time to contact with the adsorbent, which resulted in the removal of NO\textsubscript{3}-N in the column with a higher efficiency. At the highest flow rate, the lowest NO\textsubscript{3}-N removal efficiency was observed, due to insufficient contact time between the NO\textsubscript{3}-N ions and the adsorbent.

**Modeling of the breakthrough curves**

To predict the breakthrough curves of the effluent, many mathematical models such as Bed Depth Service Time (BDST), the Bohart–Adams, Clark, and Wolborska models have been used to describe the ion exchange in fixed bed columns. The average percentage errors (APE), calculated using Equation (7), indicate the quality of fit between the experimental and predicted values used for plotting breakthrough curves.

\[
\text{APE}(\%) = \frac{\sum_{i=1}^{N} |C_{\text{experimental}} - C_{\text{predicted}}|/C_{\text{experimental}}| \times 100}{N}
\]

where \(N\) is the number of experimental data points and the other variables are self-explanatory.
Application of the BDST model

The experimental data obtained were fit to the linear form of the BDST model developed by Hutchins (1973), which is shown in Equation (8).

\[ t_b = \frac{N_0}{C_0 U_0} (Z - Z_0) \]  

(8)

where \( t_b \) is the breakthrough time (h), \( N_0 \) is the exchange capacity (mg/L), \( C_0 \) is the initial concentration (mg/L), \( U_0 \) is the superficial fluid velocity (mm/h), \( Z \) is the height of the fixed bed (mm), and \( Z_0 \) is the length of the dynamic bed mass-transfer zone (mm), which is equivalent to the adsorption front where the adsorbent material is partly saturated.

The BDST model plots obtained for the removal of NO\(_3\)-N by the PP-g-AA-Am non-woven fabric at different flow rates are shown in Figure 6 and the parameters of the BDST equation are listed in Table 4. The high values of correlation coefficient (>0.9) confirm the good fit of the experimental data to this model and indicate that the BDST model could be used to describe the successful breakthrough for the removal of NO\(_3\)-N by the adsorbent. The exchange capacities of NO\(_3\)-N and the reaction zone values are strongly dependent on the flow rate. Furthermore, a higher amount of NO\(_3\)-N was exchanged as the bed height was increased, indicating that high bed depths may be required for NO\(_3\)-N removal. The thickness of the mass-transfer zone increased with an increase in the flow rate, showing the widening reaction zone and the appearance of a faster breakthrough.

Application of Bohart-Adams model

The model developed by Bohart & Adams (1920) was applied to investigate the breakthrough behavior of NO\(_3\)-N by ion exchange. The equation of the Bohart-Adams model is given by Equation (9):

\[ \ln \left( \frac{C_0}{C} - 1 \right) = K_{BA} N_0 Z - K_{BA} C_0 t \]  

(9)

where \( C \) is the effluent concentration (mg/L), \( K_{BA} \) is the rate coefficient (L/mg h), and \( t \) is the time (h).

The values of the parameters were determined from the experimental data by plotting \( \ln(\frac{C}{C_0} - 1) \) versus \( t \) at different flow rates and initial concentrations. These values, shown in Table 3, were used to calculate the breakthrough curve. The breakthrough curves predicted by the Bohart-Adams model are shown in Figure 7. In this figure, the theoretical curves are compared with the corresponding experimental data, and the APE values obtained are shown in Table 5. The results indicate that the experimental breakthrough curves fit those predicted by the Bohart-Adams model for various initial concentrations and flow rates, with a good correlation. The values of the kinetic constant were influenced by the flow rate and increased with increasing flow rate. In addition, the maximum exchange capacity increased with an increase in the initial concentration and a decrease in the flow rate.

Application of the Clark model

Clark has developed a model based on the use of the mass transfer concept in combination with the Freundlich isotherm (Clark 1987). The Clark model is given by Equation (10)

\[ \left( \frac{C_0}{C} \right)^{n-1} - 1 = Ae^{-rt} \]  

(10)

where \( n \) is the Freundlich parameter, which was found to be 3.57 from the equilibrium study in our previous paper (Na et al. 2011). \( A \) and \( r \) are the Clark constants, which can be given by Equations (11) and (12), respectively.

\[ A = \exp \left[ \frac{K_C N_0 Z}{U} \right] \]  

(11)

\[ r = K_C C_0 \]  

(12)
The values of the parameters of the Clark model can be determined from the plot of $\ln\left(\frac{C_0}{C_1}^{n-1} - 1\right)$ versus time, and these values are summarized in Table 6. The high correlation coefficients obtained indicate a good agreement of the Clark model with the experimental data. It may be noted that the Clark constant, $r$, increased with an increase in the initial concentration and flow rate.

The theoretical curves are compared with the corresponding experimental data in Figure 7 and the APE values obtained are shown in Table 6. The results show that the model is very close to the experimental results and predicts the effects of initial concentration and the flow rate quite well.

Application of the Wolborska model

The model developed by Wolborska (1989) is based on the general equations of mass transfer describing diffusion mechanisms in the low concentration range breakthrough curves. The equation is given as follows:

$$\beta_a = \frac{U_0^2}{2D} \left( \sqrt{1 + \frac{4\beta_0 D}{U_0^2}} - 1 \right)$$

Table 5 | Bohart–Adams model parameters for the removal of NO$_3$ by the PP-g-AA-Am non-woven fabric at different initial concentrations and flow rates

<table>
<thead>
<tr>
<th>$C_0$ (mg/L)</th>
<th>$Q$ (cm/s)</th>
<th>$K_{BA}$ (L/mg.h)</th>
<th>$N_0$ (mg/L)</th>
<th>$R^2$</th>
<th>APE (%)</th>
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<td>0.0476</td>
<td>28,678</td>
<td>0.9850</td>
<td>77.8</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>0.0808</td>
<td>25,603</td>
<td>0.9944</td>
<td>11.7</td>
</tr>
</tbody>
</table>

Table 6 | Clark model parameters for the removal of NO$_3$ by PP-g-AA-Am non-woven fabric at different initial concentrations and flow rates

<table>
<thead>
<tr>
<th>$C_0$ (mg/L)</th>
<th>$Q$ (cm/s)</th>
<th>$r$ (min$^{-1}$)</th>
<th>$R^2$</th>
<th>APE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.5</td>
<td>16.0498</td>
<td>1.1246</td>
<td>0.9916</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>15.2606</td>
<td>2.3055</td>
<td>0.9929</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>10.8957</td>
<td>3.4358</td>
<td>0.9856</td>
</tr>
<tr>
<td>24</td>
<td>0.5</td>
<td>22.8936</td>
<td>1.7010</td>
<td>0.9895</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>14.5315</td>
<td>2.3936</td>
<td>0.9928</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>12.5182</td>
<td>4.2218</td>
<td>0.9892</td>
</tr>
<tr>
<td>37</td>
<td>0.5</td>
<td>38.0514</td>
<td>4.9289</td>
<td>0.9909</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>21.6079</td>
<td>5.2801</td>
<td>0.9780</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>13.5147</td>
<td>6.1989</td>
<td>0.9979</td>
</tr>
</tbody>
</table>
\[
\ln \left( \frac{C}{C_0} \right) = \frac{\beta_a C_0}{N_0} t - \frac{\beta_a Z}{U_0}
\]

where \(\beta_a\) is the kinetic coefficient corresponding to the external mass transfer (h\(^{-1}\)), \(D\) is the axial diffusion coefficient (mm\(^2\)/h), and \(\beta_0\) is the external mass-transfer coefficient with a negligible axial dispersion coefficient \(D\).

In short beds or at high solution flow rates through the bed, the axial diffusion was observed to be negligible and \(\beta_a\) equalled \(\beta_0\). The migration velocity (mm/h) of the steady-state front satisfies the relation, known as Wicke’s law:

\[
v = \frac{U_0 C_0}{N_0 + C_0}
\]

The values of the parameters of the Wolborska model can be determined from the plot of \(\ln(C_0/C)\) versus time. These values are given in Table 7 along with the correlation coefficient obtained, and the migration velocities \((v)\) were calculated by the Wolborska method. The values of migration velocity were found to increase with an increase in the flow rate. Furthermore, increasing the initial concentration and flow rate resulted in an increase in the mass transfer coefficient \(\beta_a\).

The theoretical curves are compared with the corresponding experimental data in Figure 7, and the obtained APE values are also shown in Table 7. The results show that the model is close to the experimental results with an acceptable correlation, and the model adequately describes the effects of initial concentration and flow rate.

**CONCLUSIONS**

In this study, we investigated the adsorption characteristics of the PP-g-AA-Am non-woven fabric for NO\(_3\)-N removal and suggested models that could be utilized for a successful design of the column exchange. The adsorption isotherm experiments were conducted by changing the adsorbate concentration with a fixed adsorbent dosage (equipotent conditions). When the dosage rate increased, the equilibrium adsorption capacity decreased exponentially and the adsorption removal rate increased algebraically. The competition between the deionized shift components and the adsorbate, as well as the solvent and the adsorbate, for sites on the adsorbent, increased exponentially. The Langmuir, Freundlich, and Sips adsorption isotherms were studied and it was found that the experimental data fit well to these isotherms, with relatively high \(R^2\) values. The \(n\) values obtained from the adsorption experiment results were shown to be greater than 2, regardless of the adsorbent dosage, showing that adsorption occurred easily. The adsorption reactions conducted with a constant adsorbate concentration and a changing adsorbent dosage was found to occur more easily compared to the previous case.

Furthermore, the breakthrough curves for NO\(_3\) adsorption were studied at various flow rates and initial concentrations. The breakthrough and saturation times showed an inverse relationship with both the superficial velocity and the initial concentration. To predict the breakthrough curves and determine the column kinetic parameters, models including the BDST, Bohart–Adams, Clark and Wolborska models were applied to the experimental data obtained from the ion exchange study in fixed bed columns. These models showed good approximations to the experimental behavior observed. The BDST model fit the breakthrough data well, indicating that the BDST model was successful in describing the breakthrough for the removal of NO\(_3\) by the adsorbent. While both the Bohart–Adams model and the Clark model were very close to the experimental data obtained, the fit of the experimental data to the Clark model was better. Furthermore, the curves predicted from the Wolborska model fit the experimentally obtained breakthrough curves well, allowing the kinetic coefficients of mass transfer in the fixed bed to be estimated.

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REFERENCES


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