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# Removal of Nitrate from Water using a Fluidized Bed Ion Exchange Column

Ammar Arab Beddai, V.V.Basava Rao+ and S. Ram Mohan Rao

University College of Technology (A), Osmania University, Hyderabad-07, India

**Abstract.** Experimental and theoretical studies were carried out to investigate the performance of a fluidized bed ion exchange system to remove nitrate. The exchange of nitrate on strong anion exchange resin (TULSION A-27) was studied in the flow rate range of 2 to 7 L/h. Nitrate removal was done at five conditions of the expanded bed height (Z). The results showed that the experimental data can be fitted to Richardson and Zaki equation, and the comparison between the experimental and calculated terminal velocities showed low relative error.

**Keywords:** Nitrate Removal, Fluidized Bed, Ion Exchange Column, TulsionA-27, Adsorption

## 1. Introduction

Increased levels of nitrate in ground water have made many wells unsuitable as sources for drinking water. Nitrate is so toxic, especially to pregnant women and infants, that the USEPA (United States Environmental Protection Agency) standard of 10 mg $NO_3^{-}$N/L or less in drinking water was established for human health [Taekyung *et al* [1]; Kavita *et al* [2]; Lucija *et al* [3]]. Ion exchange is a chemical treatment process used to remove unwanted ionic species from wastewater [M. Matosic *et al* [4]; Robert Kunin [5]; Ammar Arab [6]].

Solid-liquid fluidized beds (SLFB) are used in industry for hydrometallurgical operations, catalytic cracking, chromatographic separation, ion exchange, adsorption, crystallization and sedimentation, etc [Prakash and Jyeshtharaj [7]; Srikuma *et al* [8]]. However, the packed bed ion exchange process has some disadvantages such as high pressure drop and bed clogging. These disadvantages can be eliminated if the packed bed is replaced by a fluidized bed [Shyh-Jye and Wen-Jang [9]; Hideaki *et al [10]*; Seung-Jai *et al* [11]]. The purpose of this study was to investigate nitrate removal in a liquid-solid fluidized bed ion-exchange system. The effects of operating parameters including liquid flow rate and height of the bed on the removal rate of nitrate were studied. The experimental data of voidage versus superficial velocity were successfully correlated using the Richardson-Zaki Equation.

## 2. Fludidized Bed Theory

### 2.1 Minimum fluidization velocity

The minimum fluidization velocity can be obtained using the Ergun Equation by sitting the pressure drop equal to the pressure required to suspend the bed or the weight of the bed divided by the cross sectional area [McCabe *et al* [12]; Vassilis *et al[13]*]:

$$\frac{150\mu u_{fm}}{\Phi_s^2 d_p^2}\frac{1-\varepsilon_{fm}}{\varepsilon_{fm}^3}+\frac{1.75\rho u_{fm}^2}{\Phi_s d_p}\frac{1}{\varepsilon_{fm}^3}=g(\rho_p-\rho) \tag{1}$$

and

+ Corresponding author. Tel.: + (91-40-27098901); fax: +(91-40-27098472).
*E-mail address*: profbasavarao_1964@yahoo.com

$$\mathrm{Re}_{fm} = \frac{u_{fm}\rho d_p}{\mu} \tag{2}$$

## 2.2 Estimation of bed voidage (ε)

Bed voidage was obtained by substitution of data into the following equation [Mohsen *et al* [14]]:

$$\varepsilon = \left[1 - \frac{V_p}{V_L}\right] = \left[1 - \frac{V_p}{A_T.H}\right] = \left[1 - \frac{m_p}{\rho_p.A_T.H}\right] \tag{3}$$

## 2.3 Bed expansion characteristics

Before processing with feedstock, determination of the bed expansion characteristics was necessary. It was decided to use the well-known Richardson–Zaki Equation [Mohsen *et al* [14]]:

$$\frac{U}{U_t} = \varepsilon^n \tag{4}$$

The expanded bed height is [Inglezakis and Poulopoulos [15]: $Z_f = Z\frac{1-\varepsilon}{1-\varepsilon_f}$ (5)

The average bed voidage can be estimated from Eq. (3) or the following equation:

$$\varepsilon_f = 1 - (1-\varepsilon)\frac{Z}{Z_f} \tag{6}$$

Where $\varepsilon_0$=0.41 is the packed-bed voidage. Values of the Richardson–Zaki coefficients n, and the apparent terminal velocities of the particles $U_t$ were calculated from linear regression of plots of ln(U) versus ln(ε). For the particles which had a mean diameter of 750 μm, the apparent terminal velocities of the particles $U_t$ were calculated from Allen's equation, Eq. (7). For adsorbents with an approximate mean particle size of 200 μm one can calculate $U_t$ using Stokes' law. $U_t$ Stokes is given by Eq. (8) [Mohsen *et al* [14]].

$$U_t = 0.27\sqrt{\frac{d_p(\rho_p-\rho)g}{\rho}}\,\mathrm{Re}_t^{0.4} \tag{7}$$

And

$$U_{t-stokes} = \frac{g(\rho_p-\rho)d_p^2}{18\mu} \tag{8}$$

Where (n) is the index which depends on the particle size and sedimentation velocity. The expansion index (n) was calculated by following equations [Yong-Hong *et al* [16]]:

$$\begin{aligned} &n = 4.65 && \mathrm{Re}_t < 0.2 \\ &n = 4.4\,\mathrm{Re}_t^{-0.03} && 0.2 < \mathrm{Re}_t < 1 \\ &n = 4.4\,\mathrm{Re}_t^{-0.1} && 1 < \mathrm{Re}_t < 500 \\ &n = 2.4 && 500 < \mathrm{Re}_t \end{aligned} \tag{9}$$

The expansion behavior can also be estimated from empirical considerations. Hartmann obtained a good fit of their experimental data for n using Eq. (10) [Mohsen *et al[14]*].

$$n = \frac{5.09 + 0.2309\,\mathrm{Re}_t^{0.877}}{1 + 0.104\,\mathrm{Re}_t^{0.877}} \tag{10}$$

The model of Shiller and Naumann is commonly used for the prediction of terminal velocity of a spherical particle [M.H.Shahavi *et al* [17]]:

$$G_a = 18\,\mathrm{Re}_t + 2.7\,\mathrm{Re}_t^{1.687} \qquad 3.6 < G_a < 10^5 \tag{11}$$

Where the Grashof number is given by the following equation:

$$G_a = \frac{\rho(\rho_p-\rho)gd_p^3}{\mu^2} \tag{12}$$

The fluidization behavior of particles is based on the Gallileo number [Vassilis *et al* [13]]:

$$\mathrm{Ga} = \frac{\rho_{\mathrm{p}} \mathrm{g} \left(\rho_{\mathrm{p}} - \rho\right) \mathrm{d}_{\mathrm{p}}^{3}}{\mu^{2}} \tag{13}$$

From Ga the terminal velocity Reynolds number can be calculated for different column and particle diameters:

$$\mathrm{Re}_t = \left[\frac{23}{Ga} + \frac{0.6}{Ga^{0.5}}\right]^{-1} \left[1 + 2.35\frac{d_p}{d_c}\right]^{-1} \tag{14}$$

The expansion index was estimated from Ga:

$$\frac{5.1 - n}{n - 2.4} = 0.016 Ga^{0.67} \tag{15}$$

For the relatively large particles (of several millimeters) in water, the equation proposed by Lewis, Gilliland, and Bauer can be used to calculate bed voidage [Inglezakis and Poulopoulos [15]]:

$$\varepsilon_f = \left[\frac{u_s}{u_{fm}}\right]^{1/m} \varepsilon \tag{16}$$

The exponent m is a function of the particle Reynolds number based on the minimum fluidization velocity. It can be estimated by the following correlation:

$$m = 4.21 \mathrm{Re}_{fm}^{-0.0804} \tag{17}$$

The value of m is between 4.2 and 4.5 for $0.1<\mathrm{Re}_{fm}<1$ and between 2.5 and 4.2 for $1<\mathrm{Re}_{fm}<1000$.

Pavlov (1979) gave a simpler equation for $\varepsilon_f$ based on the Archimedes number:

$$\varepsilon_f = \left(\frac{18\mathrm{Re}_p + 0.3\mathrm{Re}_p^2}{Ar}\right)^{0.21} \tag{18}$$

Where

$$Ar = \frac{d_p^3 \rho (\rho_p - \rho) g}{\mu^2} \tag{19}$$

# 3. Materials and Methods

## 3.1 Resin Material

The ion-exchange resin employed was the $OH^{-1}$ type TULSION A-27 which was a strong base anion exchange resin. TULSION A-27 ($OH^{-1}$) was obtained from the Thermax Company. The particles are in the shape of almost perfect spheres with an average diameter 0.7 mm (700 µm) and a wet density of 1.08 g/mL. The capacity of the resin was measured from the breakthrough curve of the $OH^{-}/NO^{-3}$ exchange experiments. The total exchange capacity was about 1.2 meq/ml of resin.

## 3.2 Fluidized Bed System

The overall experimental apparatus is depicted in Figure 1. The column was filled with resin and washed with distilled water. Experiments were carried out in a glass column having 1 cm diameter and 100 cm high. To obtain the hydroxide, the resins were regenerated in downflow with four bed volumes of 4% NaOH solution and washed with distilled water. The temperature was maintained at 31 ± 1 $^{o}$C. As the fluidized bed showed a quiescent behavior, the height of the bed could be determined visually.

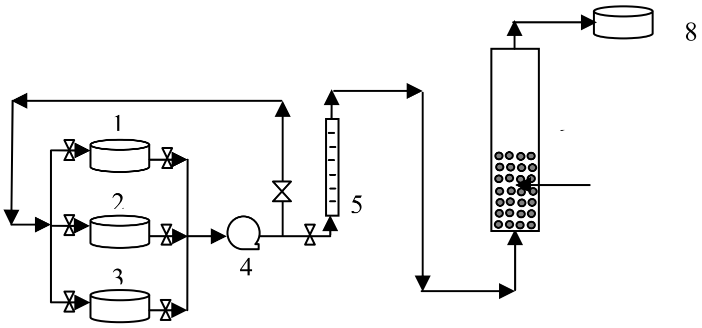


Fig. 1: Experimental system: (1) $NaNO_3$,(2) $H_2O$, (3)NaOH ,(4) Pump, (5) Rotameter, (6)Column, (7)Resin, and (8)effluent.

## 4. Chemical Analysis

Nitrates were measured by a UV-Vis spectrophotometer. The absorbance was measured at 220 nm and a second reading was taken at 275 nm. This allowed correction for the interference due to dissolved organic matter. The difference between the two absorbance measurements was then calculated by the formula given below;

$$Abs220 - 2*(Abs275) \tag{20}$$

## 5. Results and Discussion

The effect of Reynolds number on fluidization voidage is presented in Figure 2. Values of the Richardson-Zaki coefficients n, and the apparent terminal velocity of the particle were calculated from linear regression of the plots of log (U) versus log (ε), and the results are shown in Figure 3. The parameters correlated are listed in Table 1. An experimental value of n=3.0007 was obtained. The theoretical values of n were calculated by Equations 9, 10, and 15. A comparison of results showed a good agreement between the experimental and theoretical values of n and $U_t$. This comparison showed the operation of bed agreed with theory. The diffusion of nitrate ion with a resin particle at height 2 cm was slower than that at 3, 6, and 10 cm in the bed.

Table 1: Experimental and theoretical values of $U_t$ and n.

| $U_t$ (cm/s) | | n | | | |
|---|---|---|---|---|---|
| Experimental | Eq. (7) | Experimental | Eq. (9) | Eq. (10) | Eq. (15) |
| 2.162 | 2.16 | 3.0007 | 3.261 | 3.4 | 2.68 |

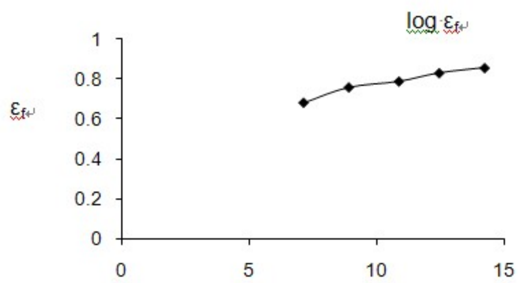


Fig. 2: Effect of $Re_p$ on fluidized bed voidage ($\varepsilon_f$)

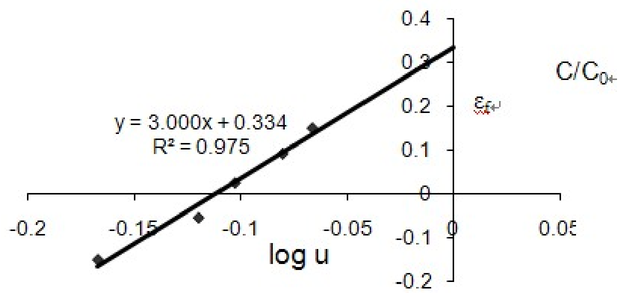


Fig. 3: Richardson-zaki correlation between flow velocity and bed voidage for determination of n and $U_t$

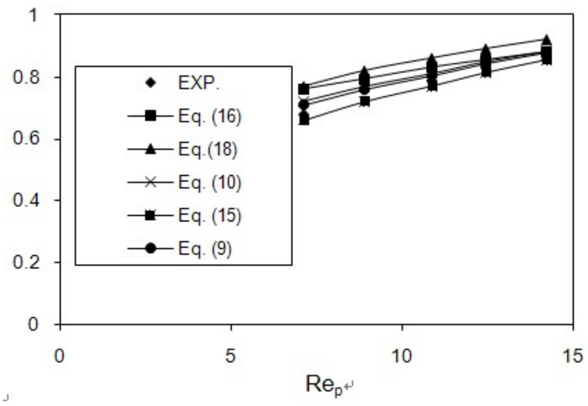


Fig. 4: Comparison of overall voidage estimation models with experimental data

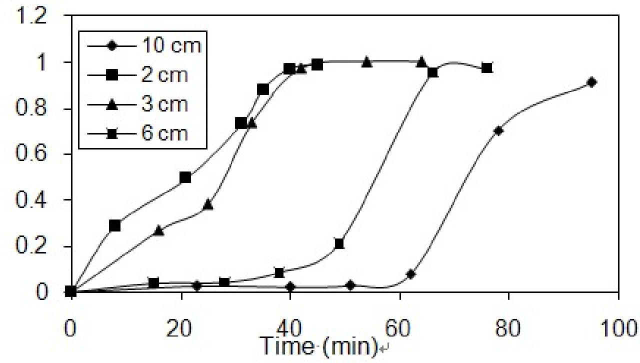


Fig. 5: Breakthrough curves of $NO_3$ ions in the fluidized bed at different bed heights Z and a constant flow rate of 2 L/h

Figure (4) shows a comparison of the voidage estimated by various models at different particle Reynolds numbers. Figure (5) shows the experimental breakthrough curves at various bed heights.

## 6. Conclusions

An experimental study of $NO_3$ removal from water by using a fluidized bed was carried out, and the following conclusion were made:

- The Richardson and Zaki model showed a good fit with the experimental data, and can be use for voidage estimation.
- Results of a fluidized bed operation using an ion exchange resin indicate that nitrate removal was improved significantly by increasing the bed height.

## 7. Acknowledgement

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## 8. Notation

| | |
|---|---|
| Abs | absorbance measurements |
| Ar | Archimedes number |
| $A_T$ | area of the cross-section of the column ($m^2$) |
| C | concentration ($mol/m^3$) |
| $C_o$ | initial concentration ($mol/m^3$) |
| $d_p$ | particle diameter (m) |
| g | gravity ($m^2/s$) |
| Ga | Gallileo number |
| $G_a$ | Grashof number |
| H | bed height (m) |
| $m_p$ | mass of particles (kg) |
| $Re_{fm}$ | minimum fluidization Reynolds number |
| $Re_p$ | particle Reynolds number |
| $Re_t$ | terminal velocity Reynolds number |
| $u_{fm}$ | minimum fluidization velocity (m/s) |
| $u_s$ | superficial fluid velocity (m/s) |
| U | fluid velocity (m/s) |
| $U_t$ | terminal fluid velocity (m/s) |
| $V_L$ | liquid volume ($m^3$) |
| $V_p$ | particle volume ($m^3$) |
| Z | bed height (m) |
| $Z_f$ | bed height at fluidization (m) |
| $\varepsilon$ | bed voidage |
| $\varepsilon_f$ | voidage at fluidization. |

$\varepsilon_{fm}$ voidage at minimum fluidization
$\mu$ dynamic viscosity of the fluid (Kg/m.s)
$\rho$ density of the fluid (kg/m$^3$)
$\rho_p$ density of the particles (Kg/m$^3$)
$\Phi_s$ the spherity of the particle

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