Nitrate Removal Using Mg Modified Zeolite in Fluidized-Bed System

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Abstract: This study aimed to investigate the hydrodynamic of fluidized-bed column, the adsorption capacity for nitrate removal using zeolite modified with magnesium, the effect of flow rate and bed-height on nitrate removal efficiency, and the breakthrough point. In this study observed the effect of different flow rate 30 l/h, 60 l/h and 90 l/h and the effect of different bed-height 5 cm, 10 cm, 15 cm. In a hydrodynamic study showed that the superficial velocity conditions in fluidized-bed operation were between the minimum velocity 0,019 m/s and the terminal velocity 0,121 m/s and the increase of the flow rate showed an increase on bed expansion ratio in fluidized-bed operation In hydrodynamic.

1. Introduction
Nitrogen is an essential element for all living things and it compounds such as ammonia, nitrite and nitrate are present in water. Excess high nitrate contaminants present in ponds, lakes and rivers lead to eutrophication. Eutrophication is a phenomena where due to availability of nutrients like nitrate and phosphate are stimulating the growth of algae which renders it unsuitable as a source of drinking water [1]. Excessive levels of nitrate in drinking water may cause health problems, such as chronic inflammatory, baby-blue syndrome, enema of eyelids, tumour, muscle cramps, reproductive, neurological and genetic malfunctions [2].

The increasing use of nitrogen fertilizers in agriculture sector is the reason for the contamination caused by nitrate. Other factors such as sewage, untreated wastewater disposal and septic system leachate [3]. Because of the health problems and excessive concentration of nitrate in drinking water, the World Health Organisation and European Union have stipulated the nitrate concentration limit is 50 mg NO₃⁻/L [4].

There are some treatments process for nitrate removal from drinking water including physical methods such as; reverse osmosis, ion-exchange, catalytic reduction, electrodialysis and adsorption using activated carbon. The chemical methods such as; wetland remediation, ion-exchange membrane bioreactor, and microbial denitrification [5].

Adsorption is one of the most water treatment techniques owing to its simplicity design, low cost, and economical operations [6]. The potential method for nitrate removal is adsorption method using natural zeolite which it can be obtained easily with a large number and relative cheap. Zeolites are hydrated aluminosilicate with cage-like framework structure, consists of AlO₄⁻ and SiO₄⁻ tetrahedra units, which are linked to each other by the sharing oxygen atoms. Substitution of each Al³⁺ to Si⁴⁺ in tetrahedra framework introduces a net negative charge, which is balanced by the existence of alkali
metal or alkali earth metal cations such as Na\(^+\), K\(^+\), dan Ca\(^{2+}\) [7]. This negative charge reduces zeolite surface ability to anions adsorption [8]. The ability of zeolite adsorption can be increased by changing the zeolite surface using surfactant or cation metal [9].

Adsorption process mostly studied in fixed-bed and batch system [10,11,12,13,14]. However, water treatment using fluidized-bed system rarely reported in literature. Some advantages of fluidized-bed system compare to other system such as uniform particle distribution, vigorous mixing of fluid, and better control of temperature [15,16].

In this study, removal of nitrate was performed using zeolite clinoptilolite that were activated with NaOH solution, before modified with MgCl\(_2\).6H\(_2\)O. Then, adsorption in fluidized-bed system was investigated with different flow rate and bed-height. Modification of zeolite surface was expected to increase the anion exchange capacity of zeolite.

2. Materials and Methods

2.1 Zeolite Preparation
Natural zeolite used in this study was obtained from Banten. The zeolite was sieved between 0.5 mm – 1 mm. The zeolite was fully washed several times to remove impurities on zeolite surface. Then, the zeolite was dried in the oven at 110ºC for 4 hours.

2.1 Zeolite Activation
100 gr of zeolite was activated by adding to 300 ml NaOH solution (Merck) 1.25 M (M/V = 1:3), stirred for 2 hours using water bath shaker at a stirring rate of 200 rpm [17], stored for 24 hours. It was then washed with distilled water and dried in the oven at 160ºC for 5 hours and then stored in the desiccator for 2 hours.

2.3 Zeolite Modification
100 gr of activated zeolite was modified by adding to 300 ml MgCl\(_2\) solution (Merck) 2.5 M (M/V = 1:3). Stirred using water bath shaker for 2 hours at a stirring rate of 200 rpm. It was then washed with distilled water, dried in the oven at 160ºC for 5 hours and stored in the desiccators for 2 hours.

2.4 Influent Solution
Synthetic waste was prepared by dissolving the crystalline powder of NaNO\(_3\) (EMSURE) into distilled water at concentration of 30 mg/l.

2.5 Nitrate Analysis
The final concentration (C\(_t\)) of nitrate was analyzed Pastel UV Analyzer Secomam RS232.

2.6 Fluidized-bed Study
Adsorption study was performed by pumping the nitrate solution through the fluidized-bed column. Fluidized-bed experiments were conducted using an acrylic glass tube of 1.5 cm internal diameter and length of 100 cm. The efficiency determination of nitrate removal can be obtained uses the following equation.

\[
\text{Removal efficiency (\%) } = \frac{C_0 - C_t}{C_0} \times 100
\]

Which:
\(C_0\) = Pre-treatment concentration of nitrate
\(C_t\) = After treatment concentration of nitrate
3. Results and Discussion

3.1 SEM and EDS Analysis

SEM-EDS analysis were performed to identify the morphology or the framework of zeolite and oxide contents. Scanning Electron Microscopy (SEM) is a type of microscope which describes the surface of the sample through scanning process by using high energy of electron jet. SEM-EDS results are shown in Figure 1 which describes homogenous formation of the small spherical crystals and several large crystals on the zeolite surface. This different shape is indicated that zeolite surface consists of several different minerals. On the crystals formation describes the black gaps like small holes which showed pores distribution on the zeolite surface.

Figure 1 SEM Analysis of Mg-Zeolite Surface: (a.) Magnification 100x; (b.) Magnification 1000x; (c.) Magnification 3000x; (d.) Magnification 5000x

EDS analysis result shown in Figure 2 which describes composition of minerals on zeolite surface such as C, O, Na, Mg, Al, Si, Ca, K, and Fe. Chemical composition contained on zeolite surface close to chemical composition contained in clinoptilolite zeolite [18, 19]. Based on EDS analysis the sample was obtained Si/Al ratios of 4.88. Si/Al ratio was calculated from the appeared weight percent values of elements in the EDS-spectra [20].
### 3.2 Physical characteristics of Particle and Fluid

Particles in fluidized-bed column is the green clinoptilolite zeolite sized 1 mm with a density of 2.00 g/cm³. There are physical characteristics of particle and fluid shown in **Table 1**.

**Figure 2** Chemical Composition of Mg-Zeolite

| Element        | (keV) | Mass% | Sigma | Mol% | Compound Mass% | Cation Mass% | K     |
|----------------|-------|-------|-------|------|---------------|--------------|-------|
| C K            | 0.277 | 15.12 | 0.36  | 48.35 | C             | 15.12        | 0.00  | 4.8276 |
| O              | 41.84 |       |       |      |               |              |       |        |
| Na K           | 1.041 | 1.82  | 0.09  | 1.52 | Na2O          | 2.45         | 0.72  | 3.7482 |
| Mg K           | 1.253 | 2.49  | 0.09  | 3.22 | MgO           | 3.38         | 0.77  | 3.6115 |
| Al K           | 1.486 | 6.02  | 0.17  | 4.28 | Al2O3         | 11.37        | 2.05  | 12.3497 |
| Si K           | 1.739 | 29.41 | 0.42  | 40.22 | SiO2       | 62.91        | 9.61  | 65.9230 |
| K K            | 3.312 | 1.57  | 0.07  | 0.99 | K2O           | 2.43         | 0.47  | 5.0568 |
| Ca K           | 3.690 | 0.83  | 0.06  | 0.80 | CaO           | 1.17         | 0.19  | 2.1867 |
| Fe K           | 6.398 | 0.91  | 0.08  | 0.62 | FeO           | 1.17         | 0.15  | 2.2966 |
| Total          | 100.00| 100.00| 100.00| 13.97|               |              |       |        |

**Table 1** Physical characteristics of Particle and Fluid

| Parameter                             | Value       |
|---------------------------------------|-------------|
| Zeolite density ($\rho_s$)            | 2.00 g/cm³  |
| Zeolite diameter ($D_p$)              | 0.5-1 mm    |
| Viscosity of nitrate solution ($\mu$) | 1x10⁻³ Pa. s |
| Density of nitrate solution ($\rho_f$)| 1.065 g/cm³ |
| pH of nitrate solution                | 7.0         |

### 3.3 Minimum-Fluidization Velocity and Terminal Velocity

Minimum-fluidization velocity is an important parameter in the design of fluidized-bed reactor. Minimum fluidization velocity is a liquid superficial velocity at which bed of solid particles becomes incipiently fluidized and at this velocity the upward force (drag force) becomes equal to the downward force (weight of solids) [21]. Terminal velocity is a fall velocity of particles. Minimum-fluidization
velocity and terminal velocity can be calculated theoretically uses the equation 1 and 2. Fluidization occurs when \( U_{mf} < U_0 < U_t \). [16]

\[
U_{mf}^2 = \frac{D_p (\rho_p - \rho_f) g}{1.75 \rho_f} \varepsilon_{mf}^3 \phi
\]  

(1)

\[
U_t = \left( \frac{1.78 \times 10^{-2} (g (\rho_p - \rho_f))^2}{\rho_f \mu} \right)^{1/3} \left( \frac{D_p}{\mu} \right), \quad 0.4 \leq \text{Re} \leq 500
\]  

(2)

| Bed-Height (cm) | \( U_{mf} \) (m/s) | \( U_0 \) (m/s) | Re | \( U_t \) (m/s) |
|----------------|-----------------|----------------|-----|---------------|
| 5              | 0.019           | 0.045          | 95.4| 0.121         |
| 10             | 0.019           | 0.056          | 120.84| 0.121       |
| 15             | 0.019           | 0.071          | 154.76| 0.121       |

3.4 Bed Expansion

Bed expansion in fluidized-bed column can be observed visually. Figure 3 shows the increasing of flow rate linearly with the bed expansion and allows a vigorous mixing between particles and fluid. Nevertheless, high bed expansion ratio showed the faster saturation time when compared to small bed expansion [22].

![Figure 3 Flow rate Vs Bed Expansion Ratio](image)

3.5 Nitrate Removal Efficiency

As shown in Figure 4, the highest nitrate removal efficiency of 36.66 % is obtained at a flow rate of 30 l/h and the lowest nitrate removal of 21.33 % is obtained at a flow rate of 90 l/h. It is because the fluid residence time in fluidized-bed column decreases with the increasing of flow rate so that nitrate does not have enough time to diffuse in to the pores of adsorbents [23]. In addition, zeolites have a relatively slow loading kinetic hence the need for long residence times [24]. While on the bed-height effect, the highest nitrate removal efficiency of 34 % is obtained at a bed-height of 15 cm and the lowest nitrate removal of 16.66 % is obtained at a bed-height of 5 cm. This showed that difference in
bed height affects the efficiency of nitrate removal because as the bed-height increases, the greater mass of adsorbents in the column so that the active site available for adsorption process is increasing. In addition, the nitrate residence time will also increase in the column to allow the nitrate solution to diffuse deeper into the adsorbent [25, 26].

![Graph of bed height vs. nitrate removal efficiency](image)

**Figure 4** Nitrate Removal Efficiency: (a) Flow rate Effect; (b) Bed-Height Effect
(Initial Concentration 30 mg/l; $V_{\text{effluent}}$: 100 ml)

3.6 Flow rate Effect on Nitrate Removal

The flow rate has a great influence in breakthrough behavior because changes in the flow rate can affect the residence time in the column [27]. Nitrate solution was pumped upward through fluidized-bed column at different flow rate 30 l/h; 60 l/h; 90 l/h with bed-height of 10 cm. In Figure 5 is seen that the curve formed will be steeper as an increase of the flow rate. This indicates that as high the flow rate, the ratio of $C_t/C_0$ will increase so that adsorbents will reach early equilibrium. The early saturation is occurred due to minimization of contact time between fluid and adsorbents so that the fluid leaves the column before the equilibrium is reached [28]. Increased flow rate can also be attributed to the reduce of external mass transfer resistance [29].
Figure 5 Breakthrough Curve of Flow rate Effect on Nitrate Removal (Bed Height 10 cm; Effluent; 100 ml; Initial Concentration 30 mg/L)

3.7 Bed Height Effect on Nitrate Removal

The effect of bed height on nitrate removal was carried out at a flow rate of 60 l/h with the different bed height of 5 cm; 10 cm; 15 cm. As shown in Figure 6, the curve becomes steeper as the bed height increased. This indicates that the time to get saturated will be longer with an increase of the bed height. This phenomena occurs because additional space will be available for the nitrate molecules to be adsorbed on these unoccupied areas of adsorbents, furthermore, increasing the bed height will give a sufficient contact time for these nitrate molecules to be adsorbed [30]. This is evidenced in the previous study, as the bed height in the fluidized-bed column increased, the longer the time to reach equilibrium, then the bed height can also increase the residence time in the column [31].

Figure 6 Breakthrough Curve of Bed Height Effect on Nitrate Removal (Flow rate 60 l/h; Effluent 100 ml; Initial Concentration 30 mg/l)
3.8 Adsorption Capacity

Nitrate adsorption in fluidized-bed column can be calculated uses the equation 3 and 4 [32].

\[ q_{\text{total}} = \frac{Q}{1000} \int_{t=0}^{t_{\text{total}}} (C_0 - C_t) \, dt \]  
\[ q_{\text{eq}} = \frac{q_{\text{total}}}{w} \]  

Which:

- \( Q \) = Influent flow rate (ml/minute)
- \( C_0 \) = Concentration of nitrate influent
- \( C_t \) = Nitrate concentration at time, \( t \)
- \( q_{\text{total}} \) = adsorption maximum capacity (mg)
- \( q_{\text{eq}} \) = Equilibrium adsorption (mg/g)
- \( w \) = mass of adsorbents (g)

The results are shown in Table 3, the adsorption capacity increased as the flow rate increased. While based on the effect of bed height from 5 cm to 15 cm the adsorption capacity increased. This indicates that the adsorption capacity increased as the amount of adsorbent in the column increased so that the removal efficiency will becomes greater [33].

| Flow rate (l/h) | Bed Height (cm) | Zeolite Mass (gr) | \( q_t \) (mg) | \( q_{\text{eq}} \) (mg/g) |
|----------------|-----------------|------------------|---------------|-----------------|
| 60             | 5               | 10,40            | 109.33        | 10.51           |
| 60             | 10              | 19,22            | 176           | 9.19            |
| 60             | 15              | 25,20            | 254.67        | 10.11           |
| 30             | 10              | 19,17            | 142.33        | 7.42            |
| 90             | 10              | 19,14            | 148           | 11.60           |

4. Conclusions

The superficial velocity conditions in fluidized-bed operation were between the minimum fluidization velocity of 0.019 m/s and the terminal velocity of 0.121 m/s (Umf <U0 <Ut). Increased the flow rate of 30 L/h; 60 L/h; 90 l/h at a constant bed height of 10 cm increased the bed expansion ratio. Efficiency of nitrate removal decreased with an increase of the flow rate while the nitrate efficiency increased with an increase of the bed height. The higher the flow rate the adsorbent will get saturated rapidly, the higher the bed then the time of adsorbents to get saturated will be longer.
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