Removal of nitrate from groundwater by column using pumice as adsorbent as an effort for water resources conservation

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Abstract. As an effort for water resources conservation, a fixed-bed column was applied to remove nitrate from groundwater using pumice as adsorbent. The column performances were evaluated by varying the influent concentration (50 mg/L dan 80 mg/L) and influent flow rate (2 - 3 gpm/ft$^2$ equal to 43–65 mL/min) with 85 cm of adsorbent bed depth. The results indicated that the increase in influent concentration increased the amount of nitrate and cause the earlier breakthrough time. Furthermore, the increase in influent flow rate caused the column exhaustion time to occur earlier resulted in the shortened lifespan of the column. The column system with a bed depth of 85 cm and flow rate of 2 gpm/ft$^2$ (43 mL/min) for 80 mg/L of influent concentration showed the best nitrate uptake performance in this study with a total removal of 31.42% and adsorption capacity of 1.394 mg/g. The results revealed that the pumice in column has potential for nitrate removal from groundwater.

1. Introduction

In soil, fertilizers containing inorganic nitrogen is first decomposed to give ammonia, which is then oxidized to nitrite and nitrate. The nitrate is taken up by plants during their growth and used in the synthesis of organic nitrogenous compounds. Excessive application of nitrogenous fertilizer not only pollutes surface water, it also pollutes groundwater [1]–[3]. Beside as a consequence of agricultural activity, nitrate also can reach groundwater from wastewater treatment and oxidation of nitrogenous waste products in human and animal excreta, including septic tanks. The natural nitrate concentration in groundwater under aerobic conditions is a few milligrams per liter, however, as a result of agricultural activities, the nitrate concentration can easily reach several hundred milligrams per liter [4]. For example, in an agricultural area of India, concentrations of up to 1500 mg/L were found in groundwater [5].

The maximum permissible level 50 mg/L of nitrate concentration in drinking water was recommended by WHO [4]. When drinking water loaded with higher level of nitrogen in the form of nitrate, it causes potential health problems among people including blue-baby syndrome or methemoglobinemia in infants, cyanosis, shortening of breath, enlargement of the thyroid gland, hyper tension, very fast heartbeat, frequent urination etc [6].

For removal of nitrate from water, various purification technology were applied [7] such as denitrification, electro-dialysis, reverse osmosis, ion exchange, adsorption etc. [8], [9]. Among them, adsorption technology is the most effective and easy to perform and regenerate the exhausted adsorbent...
In the previous literature, many adsorbents are reported for removal of nitrate from groundwater such as clay [12], wheat straw [13], amino clay [14] and chitosan modified zeolite [15]. Many studies also have been conducted to minimize the operational costs of adsorption process by using natural materials which are abundantly available for alternative adsorbents. Pumice is one of the natural materials which has a low weight, porous structure (up to 85%) and a high specific surface area. Recently, pumice also has been utilized as adsorbent for pollutant removal from water and wastewater [11].

In the present study, the performance of pumice through a fixed-bed column for nitrate removal from aqueous solution as simulated groundwater was evaluated. The natural pumice was collected from Sungai Pasak, West Sumatera, Indonesia as byproduct of sand mining process in that location and has potential for removal of iron and manganese from water, as previous investigations [11], [16]. The application of column adsorption is practical and economic as the operation is performed continuously and the process is controllable [17], [18]. The effect of parameters including influent concentration and flow rate on the shape of the breakthrough curve was studied. The total removal percentage of nitrate ions and the adsorption capacity of adsorbent was calculated to examine the column performance.

2. Methodology

Preparation of adsorbent and aqueous solution

Pumice were washed with distilled water several times, dried out at room temperature, crushed and sieved to obtain the desired particle size fractions. To observe the surface morphology and the oxide content of pumice, a scanning electron microscopy (SEM, model S-3400N, Hitachi, Japan) and eEnergy dispersive x-ray (EDX) spectroscopy were employed. Nitrate aqueous solutions were prepared by dissolving potassium nitrate (KNO₃) in tap water.

Fixed-bed column

A glass column with a length of 130 cm and an inner diameter of 2.6 cm was used for the column experiments. A glass wool were placed at the bottom of the column to avoid loss of adsorbent during the adsorption process. A known weight of adsorbent was packed into the column to obtain 85 cm of the bed depth. The particle size of pumice was 0.5 – 1 mm. To withdraw the trapped air between the particles, before the experiment started, the adsorbent packed in the column was wetted with deionised water in downward flow direction. The solution sample were continuously fed downward into the column by a peristaltic pump (Kamoer, China). The experiment was conducted at room temperature 27
The effects of influent concentration (50 mg/L and 80 mg/L) and flow rates (2 gpm/ft\(^2\) and 3 gpm/ft\(^2\) equal to 43 and 65 mL/min) were examined. Every 60 minutes samples were collected from the bottom of the column and were measured for the remaining nitrate by Spectrometer UV-Vis (Shimadzu UV-2600). The column performance was investigated by calculating the breakthrough time and adsorption capacity. The schematic of fixed-bed column system is shown in Figure 1.

**Mathematical description of fixed bed column studies**

The performances of column were evaluated through the breakthrough curve of the continuous fixed bed system. The breakthrough curve was expressed by \( C_t/C_0 \), in which \( C_t \) and \( C_0 \) represent the effluent and influent concentrations, respectively. The curve was described as \( C_t/C_0 \) against the contact time. The adsorbed ion concentrations in the column were confirmed by a plot of the adsorbed concentration \( (C_{ad} = \text{inlet concentration } (C_0) - \text{outlet concentration } (C_t)) \) or normalized concentration assigned as the ratio of effluent concentration to influent concentration \( (C_t/C_0) \) as a function of time or volume of effluent \( (V_{eff}) \), as presented in equation (1) [19].

\[
V_{eff}(mL) = Q \times t_{total} \quad (1)
\]

The \( Q \) and \( t_{total} \) describe the volumetric flowrate (mL/min) and total flow time (min), respectively. The total adsorbed ion \( (q_{total}) \) by the column can be calculated by integrating the plot of adsorbed concentration \( (C_{ad}) \) versus the flow time \( (t) \). The area \( (A) \) under this integrated plot is substituted in equation (2) to determine \( q_{total} \).

\[
q_{total}(mg) = \frac{QA}{1000} = \frac{Q}{1000} \int_{t=0}^{t_{total}} C_{ad} \, dt \quad (2)
\]

The total amount of ions delivered to the column system \( (m_{total}) \) is gained from equation (3).

\[
m_{total}(mg) = \frac{C_0 Q t_{total}}{1000} \quad (3)
\]

The column performance can be examined by the total removal percentage of ions from the ratio of total adsorbed ions in the column to the total amount of ions delivered to the column, as shown in equation (4).

\[
\text{Total removal of metal ions } (\%) = \frac{q_{total}}{m_{total}} \times 100 \quad (4)
\]

The equilibrium adsorption was also calculated from the column data to obtain the capacity of adsorbent required for ions removal. Equation (5) declares the equilibrium ion uptake \( (q_{eq}) \), also known as the column maximum capacity.

\[
q_{eq}(mg/g) = \frac{q_{total}}{X} \quad (5)
\]

where, \( X \) is the unit mass of adsorbent packed in the column.

**3. Result and Discussion**

3.1 **Physical characteristics of natural pumice**

As determined by EDX, Si, Al and Fe are the major elements in natural pumice from Sungai Pasak, as shown in Table 1. Other elements, except K, Ca, Na and Mg were present in relatively smaller amounts (less than 3%). The elemental compositions of the pumice also indicate the absence of hazardous or carcinogenic substances; thus the pumice is considered appropriate as adsorbent to treat polluted water.
The SEM image showed the surface morphology of natural pumice from Sungai Pasak, West Sumatra was displayed in Figure 2. The image indicated that the pumice had a smooth surface, cellular, irregular texture and highly porous with larger cavities, which serves suitable sites for adsorption.

### Table 1 Chemical components of pumice from Sungai Pasak, West Sumatra, Indonesia

| Oxide | % weight |
|-------|----------|
| MgO   | 0.876    |
| Al₂O₃ | 13.913   |
| SiO₂  | 76.586   |
| P₂O₅  | 0.822    |
| K₂O   | 3.604    |
| CaO   | 2.11     |
| TiO₂  | 0.197    |
| MnO   | 0.044    |
| Fe₂O₃ | 1.485    |
| ZnO   | 0.006    |

**Figure 2.** SEM image of pumice from Sungai Pasak, West Sumatra, Indonesia

### 3.2 Column studies

#### 3.2.1 Effect of influent concentration

In order to determine the effect of the influent concentration on the breakthrough curves, samples of nitrate solution with initial concentrations of 50 mg/L and 80 mg/L were passed through the column of pumice at a bed depth of 85 cm and flow rates of 2 gpm/ft² and 3 gpm/ft². The effect of influent concentration on the breakthrough curve was evaluated plotting the effluent/influent concentration ratio versus elution time (Figure 3). From the Figure 3, at all of various flow rates, it was observed that the higher nitrate concentration provided the earlier breakthrough time. This earlier breakthrough time at higher concentration could be explained based on the improved diffusion of nitrate compounds into the pores of pumice. Abdolali et al. [20] found that at higher influent concentration due to existence of greater concentration gradient lesser resistance is encountered during mass transfer of solute particles. **Figure 1** shows that steepness of the breakthrough curve is dependent upon influent concentration i.e. greater the concentration steeper is the curve.
3.2.2 Effect of flow rate
The effect of flow rate in the fixed bed of pumice was investigated from 2 gpm/ft$^2$ and 3 gpm/ft$^2$ with 85 cm of bed depth. The breakthrough curve, $C_t/C_0$ versus time with various flow rates at various influent concentration is shown in Figure 4. The results indicate that a decrease in flow rate at all various influent concentration increased the breakthrough time ($t_b$). From Figure 4, it was shown that the shape of the breakthrough curve is saturated earlier at higher flow rates because the front of the adsorption zone quickly reached the top of column. In addition, the increased flow rate resulted the shorter contact time between the adsorbate and adsorbent. It may cause uncompleted adsorption and led to steep breakthrough results at the beginning of the operation [6], [16]. The results indicated that lower flow rate or longer contact time would be required for nitrate adsorption in the column of pumice.

3.3 Total removal and adsorption capacities
To obtain information on the influence parameters, the column data were calculated into the mathematical theories of the column system. The equilibrium uptake of nitrate ions were observed to increase with the increase in influent concentrations (Table 2). The unadsorbed nitrate concentrations at the equilibrium also showed increased along with the higher influent concentration. This also indicated that the bed saturates faster when higher amounts of nitrate ions were introduced to the adsorbent column. Table 2 shows that exhaustion time of 80 mg/L of influent concentration is faster than 50 mg/L. Direct proportionality of adsorption capacity with concentration gradient of sorbate is also confirmed by experimental results of Dong and Lin [21].
Table 2 Removal percentages and adsorption capacities of nitrate by column of pumice at various concentrations of influent and flow rates

| Bed Depth (cm) | Concentration of influent (mg/L) | Flow rate (gpm/ft²) | Removal percentages (%) | Adsorption capacities (mg/g) | Exhaustion time (t_e) (minutes) |
|---------------|---------------------------------|---------------------|-------------------------|-------------------------------|-------------------------------|
| 85            | 50                              | 2                   | 30.92                   | 1.073                         | 450                           |
|               | 80                              | 2                   | 31.42                   | 1.394                         | 360                           |

4. Conclusion
For the conservation of groundwater as one of water resources, a fixed-bed column using pumice as adsorbent was investigated for removal of nitrate from aqueous solution as simulated groundwater. The effect of influent concentrations and flow rates on the adsorption process were examined. The results indicate that the nitrate adsorption through fixed-bed columns is dependent on the influent concentration and flow rate. The higher nitrate concentration provided the earlier breakthrough time and the increase in flow rate led to accelerate the exhaustion of the column. The total removal percentages of nitrate were increased with the increase in the influent concentration and decrease of the flow rate. For the optimum performance of the column operation system, suitable parameters are necessary to be investigated. The obtained results suggested that pumice in the column system has potential for the removal of nitrate from groundwater or other polluted waters.

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