Effect of pH and complementary ion concentration on nitrate removal using puroliteA400 Resin impregnated Cu in batch system

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Abstract: The total nitrogen content in water bodies should be below 50 mg NO3-/L (11.3 mgN/l) World Health Organization (WHO) 2006. The content of nitrogen exceeding the quality standard threshold will cause damage to the aquatic ecosystem and be carcinogenic to humans. The Purolite A-400 resin will be modified with Cu metal by batch method to see the adsorption allowance of nitrate in synthetic liquid waste with nitrate concentration of 50 mg/l. This study will evaluate the effect of pH and complementary ions on the adsorption process. From the result of the research, the second order pseudo model is the most suitable adsorption kinetics model. For the adsorption isotherms the most suitable model is the Freundlich adsorption isotherm model. The optimum pH conditions were at the range of 8.5. The addition of complementary ions sulfate and phosphate did not show any significant change, but sulfate is the most effective complementary ion with a content of 20 mg/l.

1. Introduction
Nitrate is an essential nutrient for plant growth and microorganisms, but the excess content in water bodies causes disruption of ecosystems in water (eutrophication) and is harmful to humans [1]. The excessive use of chemical fertilizers in the agricultural sector and poor waste water treatment systems are sources of nitrate pollutants [2]. Under World Health Organization (WHO) regulations 2006, the permitted nitrate content in water bodies is 50 mg NO3-/L (11.3 mg N/l). Reclamation and reuse of wastewater is one of the solutions in water supply. In recent decades, the wastewater treatment industry has identified that there are inorganic anionic materials such as nitrate, phosphate, and fluoride in water bodies [3].

There are many technologies available for nitrate removal such as Reverse Osmosis, Electrodialysis, Biological Denitrification, and Ion Exchange [2]. The previous case study states that ion exchange resins can adsorb nitrate optimally [2]. Ion exchange resins are a method capable of removing various types of pollutants in wastewater, with operational, easy, economical and capable of handling large waste loads [3],[4],[5]. There are several types of anion exchange resins used in the previous study: Purolite A520E [1]; [6], IONAC SR-7 [7], Amberlite IRN-78 [8], IND NSSR [9], Indion NSSR [10], Amberlite IRA 400 [11]. The results of the study showed that ion exchange...
technology using resin as a cation or anion exchanger from the solution phase proved very effective in removing the nitrate content. The resin adsorption capacity by anion exchange can be increased by metal impregnation method. Metal impregnation can increase the positive charge on the resin surface. The ion exchange resin method by impregnation of metals using various types of resins can eliminate the content of Cd, Hg, and Pb [12].

Resin impregnated with metal causes the surface of the resin to be positive which can increase the ability to adsorb nitrate [8]. The ion exchange resin method with metal impregnation has several advantages such as soluble selectivity selectivity characteristics at simple operation (fixed bed column method and fluidized bed) [12]. In this study, a Purolite A-400 resin was impregnated with Cu metal to remove nitrate ions.

2. Research Method

2.1. Resin Purolite A400 Impregnation

The Purolite A400 resin is obtained from Purolite Pte Ltd, Singapore which is a strong base anion exchange resin, faded yellow spherical beads with a particle size of 300-1200 μm. The Purolite A400 resin is impregnated with copper (Cu) metal. 10 g of Purolite resin is introduced into 1 L CuCl₂·2H₂O concentration, stirred for 1 hour at a stirring rate of 120 rpm. The pH was increased to 8.0 by adding a 1 M NaOH solution and stirred for 1 hour at a stirring rate of 30 rpm. The resin is filtered and washed with distilled water and dried in the oven for 24 hours at ± 45 °C [1].

2.2. Influent Solution

Synthetic waste is prepared by dissolving the crystalline powder of NaNO₃ into distilled water at concentrations of 50 mg/l.

2.3. Nitrate Analysis

The final concentration (Ct) of nitrate was analyzed by Pastel UV Analyzer Secomam RS232 and nitrite content analyzed by Cary 50 Conc UV-Visible Spectrophotometry-Variant.

2.4. Batch Study

The Batch test was performed using Water Bath where the results of the research will be incorporated into kinetics model and adsorption isotherm on pure resin and Cu impregnation resin. The efficiency determination of the nitrate removal uses the following equation.

\[ E = \frac{C_1 - C_2}{C_1} \times 100\% \]  

which:

- \( E \) = Efficiency
- \( C_1 \) = Pre-treatment Concentration of Nitrate or Nitrite
- \( C_2 \) = After treatment Concentration of Nitrate or Nitrite

2.5. Effect of pH on adsorption test

1g of adsorbent is placed on an erlenmeyer containing 50 mg/l of nitric synthetic waste. pH was varied (7, 7.5 and 8.5) by adding a NaOH 1 M or HCL 1 M solution then stirred at a rate of 120 RPM.

2.6. Kinetics Adsorption

The adsorption kinetics test is carried out by inserting 1g of Purolite A-400 pure adsorbent resin and Purolite A-400 resin Cu impregnation at optimum pH (procedure 2.5) into 50 mg/l of nitrate synthetic waste. Erlenmeyer stirred at Water Bath with a speed of 120 rpm of effluent from nitrate will be taken and tested at 40, 80, 120, 160, and 200 minutes.

The amount of nitrate (qt, mg N/g) adsorbed over time is calculated using the following equation.
\[ q_t = \frac{(C_0 - C_t)V}{M} \]  
\[ C_0 \text{ is the initial concentration of nitrate (mg N / l),} \]
\[ C_t \text{ is the concentration of nitrate at time } t \text{ (mg N / l),} \]
\[ V \text{ is the volume of the solution, and} \]
\[ M \text{ is the adsorbent mass (g).} \]

The adsorption kinetics model used is the first order Pseudo kinetics model and the second order Pseudo with the following equation.

First order pseudo model:
\[ \frac{dq_t}{dt} = K_1(q_1 - q_t) \to \log q_1 = \frac{k_1t}{2.303} \]  
(3)

Second order pseudo model:
\[ \frac{dq_t}{dt} = K_2(q_2 - q_t)^2 \to \frac{t}{qt} = \frac{1}{k_2q_2^2} + \frac{t}{q_2} \]  
(4)

Which:
- \( q_t \) = Absorption of nitrate at time \( t \) (mg/g)
- \( q_1 \& q_2 \) = Maximum adsorption capacity for first and second order pseudo (mg/g)
- \( k_2 \& k_4 \) = Constants for nitrate and nitrite in the sorption process for pseudo first order \((minute^{-1})\) and second order.

### 2.7. Isotherm Adsorption

To determine the adsorption equilibrium of Purolite A-400 pure resin and Purolite A-400 Cu impregnation, this research used Langmuir and Freundlich model equations. Langmuir models that apply to surface adsorption monolayers are:

\[ \frac{1}{q} = \frac{1}{q_{max}K_L} \times \frac{1}{C_e} + \frac{1}{q_{max}} \]  
(5)

- \( q_{max} \) = Maximum capacity of adsorbed nitrate per unit of sorbent weight for monolayer formation in the surface area of the adsorbent (mg/g)
- \( K_L \) = Constants associated with the affinity of the region bound by the sorbent (Langmuir isotherm constants) \((mg^{-1})\)

Langmuir \( Q_{max} \) dan \( K_L \) parameter values are calculated by slash and intercept of linear plot \( 1/q \) vs \( 1/C_e \), to predict the efficiency of the adsorption process, calculated using the equation:

\[ r = \frac{1}{1+K_LC_o} \]  
(6)

- \( r \) = Dimension of adsorption quantity

The Freundlich isotherm model corresponds to the adsorption capacity and intensity of each adsorption, applied to non-ideal adsorption with surface monolayer in repeated experiments with the following equation.

\[ q_e = KfC_e^{1/n} \]  
(7)

- \( Ce \) = nitrate concentration at the time of equilibrium (m N/L)
- \( Qe \) = amount of nitrate absorbed per unit of adsorbent mass at the time of equilibrium (mgN/g)
- \( Kf \) = Freundlich adsorption isotherm constant corresponding to the adsorption capacity
level
\[ \frac{1}{n} \] = the intensity of adsorption, which varies according to the heterogeneity of the material (the range of values \( n = 1-10 \))

2.8. Influence of complementary ions on adsorption test
Effect of sulfate and phosphate complementary ions on nitrate removal with concentrations (10, 20, and 30 mg / l). The test was performed at a concentration of 50 mg / l nitrate synthetic waste and 1 g of adsorbent. Sulfate and phosphate ions are chosen because they are often found at high concentrations in surface water and groundwater just like nitrates.

3. Result and Discussion

3.1. Effect of pH on Nitrate Adsorption
pH is a factor that greatly affect the adsorption rate. The pH may affect the charge on the surface of the adsorbent during the ion exchange process [3]. The effect of pH on nitrate removal can be seen in Figure 1. The maximum adsorption capacity on Purolite A-400 resin without modification is at pH condition 7.5. When the pH>7.5 adsorption capacity continues to decline, this may be due to competition between Cl⁻ and NO₃⁻ on the resin surface due to the addition of HCL and NaOH to the pH setting [13].

In the Purolite A-400 modified Cu resin obtained the optimum pH range at pH 8.5, it can be seen in Figure that the pH base also increases the adsorption rate [12, 13, 14].

3.2. Effect of Complement Ion on Nitrate Adsorption
The effect of sulfate and phosphate complementary ions on nitrate adsorption capacity on Purolite A-400 pure resin and Purolite A-400 resin Cu impregnation at optimum pH is shown in Figure 2. From the figure shows that the efficiency of nitrate removal increases with the increase of complementary ion concentration. Optimum occurs at a complementary ion concentration of 20 mg/l. After that, the nitrate removal efficiency tends to decrease with the increase in the complementary ion concentration, this is due to the competition between complementary ions [13]. From the figure also shows, the removal efficiency is higher with the presence of sulfate ions than the phosphate ions. The results of this test are consistent with previous research which states that the removal capacity with the addition of sulfate complementary ions is greater than phosphate [3].

![Figure 1. Effect of pH on Adsorption Efficiency](image-url)
3.3. Contact Time Against Nitrate Adsorption Rate

The contact time test is conducted to determine the time required by the adsorbent to achieve the adsorption equilibrium and to know the maximum adsorbent ability in absorbing nitrate. Figure 3 shows the relationship between contact time and the absorbed nitrate concentration. The picture shows the increasing of contact time so that the adsorption efficiency will increase until equilibrium is reached. The optimum nitrate ion absorption process at Purolite A-400 pure resin at 160 min contact time and Purolite A-400 impregnation Cu resin at 120 min. Modified Cu resin Purolite higher efficiency of removal than unmodified resin this proves that the surface of the modified resin has greater adsorption efficiency [1], [3], [13].

![Figure 2. Effect of Complementory Ion on Adsorption Efficiency](image1)

![Figure 3. Effect of Time on Adsorption Efficiency](image2)

3.4 Kinetics Adsorption

The determination of the adsorption kinetics serves as a determinant of the rate of adsorption adsorption rate. The adsorption rate greatly affects the residence time of a treatment [15]. To review the adsorption kinetics in this study, we use first order and second order pseudo pseudo model. From equation 3 in the plot of the vs. t log curve (qe-qt) for the first-order equation presented in Figure 4 and 5, and equation 4 is plotted curve t vs with slope \( \frac{1}{4t} \) and intercept \( \frac{1}{k_2q_e^2} \) for the second order Pseudo model presented in Figures 6 and 7.

Based on the analysis in Figures 4, 5, 6, and 7 it can be concluded that the most suitable kinetic model is a first-order model. This is indicated by the value of the correlation coefficient closest to the number one. The selection of a second-order model indicates that the adsorption process occurs chemically [6]. In a previous study using an Amberlite IRA 400 kinetics model after the nitrate removal was a second order pseudo model [11].
3.5. Isotherm Adsorption

The adsorption isotherm model aims to find out the characterization of adsorption of nitrate on the adsorbent so that the adsorption process is carried out chemically or physically [12]. In this study, adsorption isotherm data was fitted on Langmuir and Freundlich models. The Langmuir model (equation 5) is shown in Fig. 8, while the Freundlich model (equation 7) is shown in Fig. 9. Based on Figures 8 and 9 it can be seen that the value of the correlation coefficient $R^2$ is greatest following the Freundlich model than the Langmuir model. Freundlich isotherm model signifies that the adsorption process takes place physically [11].
Table 1 shows the value of the adsorption intensity and Freundlich constant value obtained from the equation in the figure above, can be seen in the table of adsorption intensity value at nitrate removal more effectively by using Purolite A-400 impregnation Cu resin because the value of adsorption intensity is greater than resin without Modification with value 2,325 (mg N/g). The greater the value of $K_f$, the greater the intensity of the adsorption, it can be concluded that the Purolite A-400 resin impregnation of Cu is greater in the adsorption capacity compared with the purolite A-400 pure resin.

Table 1. Isotherm Parameters for the Adsorption Nitrate by Resin

| Freundlich Model | Nitrate              |
|------------------|----------------------|
|                  | Unmodified Resin Purolite A-400 | Modified Resin Purolite A-400 Cu |
| Intensity of Adsorption (mgN/g) | 2,518 | 2,325 |
| $K_f$ (l/mg) | $4.321 \times 10^{-3}$ | $0.011$ |
| $R^2$ | 0.999 | 0.956 |

4. Conclusion
Purolite A-400 impregnation Cu resin has a higher efficiency of nitrate adsorption, the optimum pH found in this study for Purolite A-400 pure resin under pH 7.5 conditions and for Purolite A-400 impregnation Cu resin at pH 8.5. The most suitable adsorption isotherm model for nitrate discharge is Freundlich isotherm model. This is indicated by $R^2$ value of 0.999 in unmodified resin and 0.956 in Cu impregnation resin. The most appropriate kinetic model equation in nitrate removal is a second order model for purolite A-400 pure resin and Purolite A-400 impregnation Cu resin. The addition of sulfate complementary ions at a dose of 20 mg/l can improve the efficiency of the nitrate removal.
5. References

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