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Equilibrium and Adsorption Kinetic Study of Metal Ni(II) using Persimmon Tannin Gel

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Abstract

Heavy metal concentration exceeding the threshold amount is hazardous to the environment, so it needs some treatment. The study aimed to know the capacity and kinetics of adsorption. This study used the adsorption method to remove the heavy metal Ni(II) ion using persimmon tannin gel. Influences of time contact, pH, and ion concentration in the adsorption process were also investigated. The results showed that the optimum adsorption contact time was 60 minutes at pH 5. The concentration variation decreased the adsorption as Ni(II) ion concentration increased. The maximum adsorption capacity was 23.14 mg/g by using pseudo-second-order adsorption kinetic model.

Keywords: Heavy metal, adsorption of Ni(II), persimmon tannin gel

Introduction

The increasing variety of industrial activities has produced liquid waste containing toxic materials that can harm humans and the environment. Heavy metals are dangerous because they can affect human health if the concentration exceeds the threshold. Due to heavy metals' nature, they are difficult to degrade and are cumulative (Keochaiyom et al., 2017). The heavy metals are cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), and nickel (Ni) (Ekpenyong et al., 2021).

Nickel metal produces nickel waste from the mining industry, the stainless steel industry, the electroplating industry, the ceramic industry, and the battery industry (Dim et al., 2021). Nickel (Ni) and its compounds are dangerous carcinogenic pollutants that can cause death to humans. According to the acceptable quality standard, nickel in the water's wastewater is 1.0 mg/L. Heavy metals have been removed from liquid waste in various techniques, including chemical precipitation, solvent extraction, ion exchange, reverse osmosis, and adsorption. The presence of these metals needs to be minimized or even removed, one of which is the adsorption method. The adsorption process using the suitable adsorbent is simple, effective in removing heavy metals from liquid waste (Yuan et al., 2020), and does not provide side effects of toxic gases (Azis et al., 2019).

Persimmon fruit that is still young contains many tannins, which are chemically classified as condensed tannins (proanthocyanidins) which are natural ingredients that have the potential to be developed as adsorbents because they are cheap and environmentally friendly (Ahmad et al., 2013). Tannins can form complexes with macromolecules like proteins, lipids, polysaccharides, and heavy metals and settle with them (Li et al., 2018; Saad et al., 2021; Zhang et al., 2021). Tannins are water-soluble compounds that function as absorbents (Zhou et al., 2019) and can be made into gels. Tannin gels can be made in various ways, according to research. Ahmad et al., (2013) and Flores et al., 2015) have made persimmon tannin gel using a formaldehyde crosslinker. Persimmon tannin gel will adsorb lead metal ions in aqueous systems. According to Widihati et al. (2012), adsorption kinetics is one of the essential factors in the adsorption process because it shows the absorption rate of the adsorbent against the adsorbate (Tanasale et al., 2020). This study will use persimmon tannin gel to adsorb nickel metal ions in water systems. The equilibrium and kinetics adsorption of nickel metal ions were studied. The effect of several parameters that affected the adsorption is further analyzed.

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Methods

The tools in this research are Spektrofotometer *Ultra Violet-Visible* (UV-Vis), analytical balance (Explorer Ohaus), Jartest, micropipette(*Biorad*), volume pipette (*Pyrex*), beaker (*Pyrex*), Erlenmeyer (*Pyrex*), magnet stirrer, funnel (*Pyrex*), 500 mL volumetric flask, 100 mL volumetric flask, and dropper. The materials used in this study were persimmon tannin gel, $NiSO_4.6H_2O$, Whatman filter paper, 0.1 M HCl, 0.1 M NaOH, and aquadest.

Preparation of Ni(II) solution1000 mg

A 1000 mg/L Ni(II) ion solution was prepared by dissolving 22,23 g $NiSO_4.6H_2O$ in 500 mL of distilled water.

Making a standard curve

A series of standard solutions of Ni(II) metal ions with a concentration of 2; 4; 6; 8; and 10 mg/L are required to make a standard curve for Ni(II) metal ions. The standard solution's absorption capacity is measured using atomic absorption spectrophotometers; then, a standard curve can be obtained by channeling absorbance to the concentration of standard solutions. From the standard curve above, we get the linear regression equation: y = a + bx

where a represents the intercept, b represents the slope, x represents the concentration, and y represents the absorbance.

Effect of contact time

A 250 mL Ni(II) ion solution with a 200 mg/L concentration was combined with 0.1-gram persimmon tannin gel. After that, the mixture was agitated at 150 rpm in a test jar. The duration of contact varies at intervals of 10, 20, 30, 40, 50, 60, 70, and 80 minutes. The filtrate was separated using Whatman filter paper, and the concentration of the unadsorbed Ni(II) metal ion was determined using an Atomic Absorption Spectrophotometer (AAS).

Effect of pH solution

40 mL of Ni(II) solution at a concentration of 200 ppm was put into six varied (variation of pH 500 mL beakers with the pH 2, 3, 5, 6, 7, 9, 11, and 13) with the addition of 0.1 M HCl and 0.1 M NaOH and added drop by drop. The pH value was measured using a pH meter. Furthermore, the Ni(II) solution with a different pH was contacted with 0.1 gram of persimmon tannin gel. Then, the mixture was filtered using Whatman filter paper. The resulting filtrate was analyzed using an atomic absorption spectrophotometer to determine the metal ions adsorbed by the adsorbent (Zekavat et al., 2020).

Effect of Ni(II) metal ion concentration

40 mL of a solution of Ni(II) ions with 100, 200, 300, and 400 mg/L were mixed with 0.1 gram of persimmon tannin gel. Then it was stirred using the test jar at a speed of 150 rpm at the optimum contact time and pH. The filtrate was separated using Whatman filter paper, and the concentration of Ni(II) metal ions that had not been adsorbed was determined by SSA. The results were plotted against the Freundlich Equation and Langmuir Equation to assess the adsorption capacity and energy of the persimmon tannin gel.

Determination of Ni(II) ion adsorption capacity

The concentration of Ni(II) metal ions adsorbed by persimmon tannin gel can be calculated using the following equations:

$$[Ni(II)] \text{ adsorbed} = [Ni(II)] \text{ initial} - [Ni(II)]_{end} \quad (1)$$

$$\% [Ni(II)] \text{ adsorbed} = \frac{[Ni(II)] \text{ teradsorpsi}}{[Ni(II)] \text{ awal}}$$

Weight of adsorbed [Ni(II)]= [Ni(II) adsorbed x solution volume [Ni(II)]

$$\text{Adsorption Power} = \frac{Weight\ of\ adsorbed\ [Ni(II)]}{Weight\ of\ Absorbent(mg)} \quad (2)$$

Isothermal analysis

The adsorption equation in this study was determined using the Freundlich or Langmuir isotherm equation. In a graph that shows the progression of events for the Freundlich isotherm, we used Ce against log qe (equation 4). The slope value is log KF, and the intercept is 1/n. A graph of Ce versus Ce /qe (equation 3) for the Langmuir isothermal. The slope value (b) is 1/qm, while the intercept (a) is 1/Ka.qm. Langmuir equation.

$$\frac{Ce}{Qe} = \frac{1}{qmK} + \frac{Ce}{qm} \quad (3)$$

With qe indicating the amount of substance absorbed per unit weight of the adsorbent (mg/g), Ce representing the concentration of adsorbate at equilibrium (mg/L), q_m representing the maximal adsorption capacity (mg/g), and KL representing the Langmuir constant (Langmuir) (constant) (L/mg). Freundlich equation,

$$Log\ q_e = log(K_F) + {}^{1}/_{n}\ \text{logCe} \quad (4)$$

where qe represent the amount of material absorbed per unit weight of adsorbent (mg/g), Ce represents the adsorbate concentration at equilibrium (mg/L), n represents the maximal adsorption capacity (mg/g), and KF representing the Freundlich constant (L/mg).

Study of kinetics (reaction order and K value)

The data obtained were analyzed for the order of the reactions using the pseudo-first-order and pseudo-second-order formulas, and the value of k can be determined. By connecting log (qe-qt) to t (equation 3) and t/qt to t (equation 4), it will be obtained the equation of a straight line. Slope in equation 5 can be used to calculate the value of k1 and the intercept of equation 6) to get the value of k2, where k1 and k2 are constant values of the kinetic order.

$$log(q_e - q_t) = \log q_e + \frac{K_1}{2{,}303} t \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e} t \quad (6)$$

Thermodynamic studies (ΔG)

If adsorption is considered an equilibrium reaction, then in the equilibrium state $\Delta G = 0$, The adsorption energy can be calculated using equation 9 (Kooh et al., 2016).

$$E=\Delta G=- RT \ln K \quad (7)$$

Results and Discussion

Effect of contact time

Contact time aims to determine how long it takes for the adsorbent to absorb Ni(II) ions in reaching adsorption equilibrium. The optimum time for the adsorption of Ni(II) metal ions by persimmon tannin gel was determined by the amount of adsorbate absorbed in each gram of adsorbent. **Figure 1** shows that as time increases, more Ni(II) metal ions are adsorbed by persimmon tannin gel.

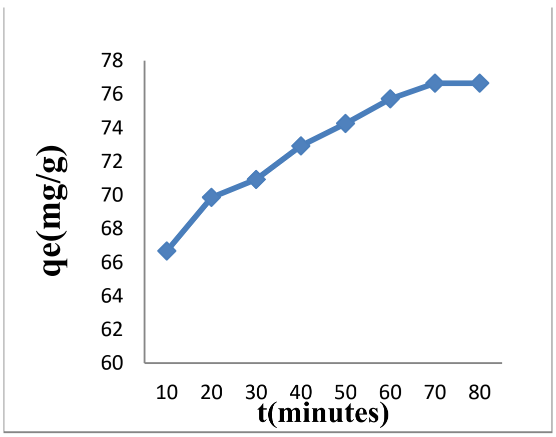

Figure 1. Effect of Ni(II) ions contact time on Ni(II) metal adsorption capacity (weight of adsorbent adsorbate concentration of 200 mg/L)

The adsorption of Ni(II) metal ions occurs very quickly at 60 minutes because many active sites are still available, so the interaction occurs quickly. After 60 minutes, the amount of adsorbed Ni(II) metal ions gradually decreased because the surface of the adsorbent was saturated, and some Ni(II) ions were desorbed. (Elass et al., 2011).

The effect of pH

The pH conditions of the solution strongly influence the adsorption process of metal ions. Changes in pH can change the charge on the surface of the solution's adsorbent or metal ion species, which is essential in the adsorption process. Calculating the quantity of adsorbed Ni(II) ions as a function of pH can be used to estimate the optimum pH value for Ni(II) ion adsorption by persimmon tannin gel. Calculating the quantity of adsorbed Ni(II) ions as a function of pH can be used to estimate the optimum pH value for Ni(II) ion adsorption by persimmon tannin gel. The condition of the hydroxyl group on the persimmon tannin gel and the speciation of the metallic Ni(II) ion are both affected by the pH value, which determines the adsorption efficiency. **Figure 2** depicts the correlation between pH and the amount of Ni(II) ions adsorbed by tannin gel.

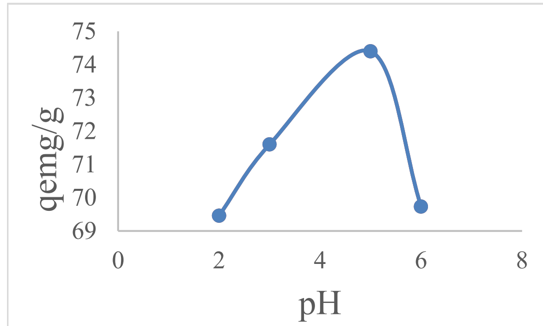

Figure 2. The relationship between pH and the number of metal ions NI(II) adsorbed (qe) by persimmon tannin gel (adsorbent weight 0.1 gram, adsorbate concentration 40 mg/L with a time of 60 minutes)

Figure 2 shows a change in the amount of Ni(II) ion adsorbed from pH 2 to pH 8. The number of Ni(II) ions absorbed at pH 8 is minimal at only 69,3 mg/g. The more positive charges (H+ ions) minimize the chance of Ni metal ions being bound to the adsorbent, reducing Ni(II) ion removal efficiency. At pH 5, the number of Ni(II) ions adsorbed was 74,4 mg/g, with a 93 percent effectiveness (percent) adsorption. There is competition between H^+ ions and Ni(II) ions at acidic pH interacting with the tannin gel's active site, which has a negative charge (Gupta et al., 2006).

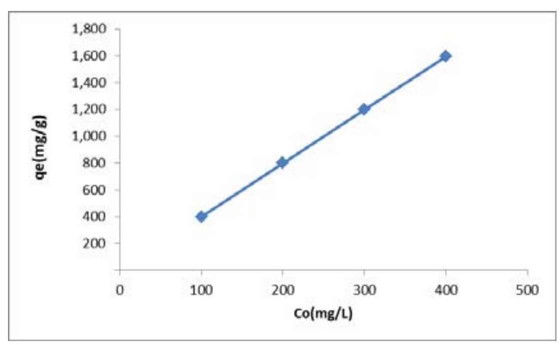

Figure 3. The relationship between concentration and the number of adsorbed Ni(II) ions (qe) by persimmon tannin gel (adsorbent weight 0.1 g, contact time 60 minutes, and pH 5)

Effect of concentration

Concentration optimization aims to determine the amount of the optimum adsorbate concentration that adsorbents can adsorb. The concentration of

Ni(II) ions in contact with the adsorbent will decrease Ni(II) ion adsorption. It happens because the active site of the adsorbent is saturated. The number of adsorbed Ni(II) ions decreased as the concentration increased. The effect of concentration on the number of adsorbed Ni(II) ions can be seen in **Figure 3**.

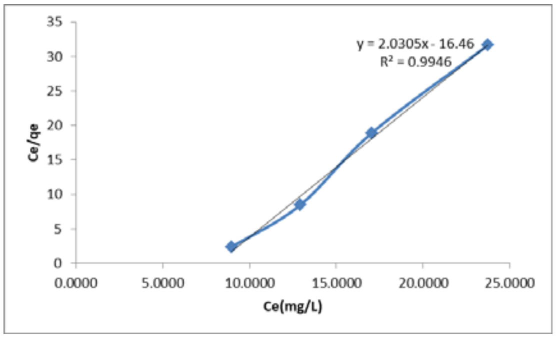

Figure 4. Adsorption of Langmuir metal ion Ni(II) by persimmon tannin gel.

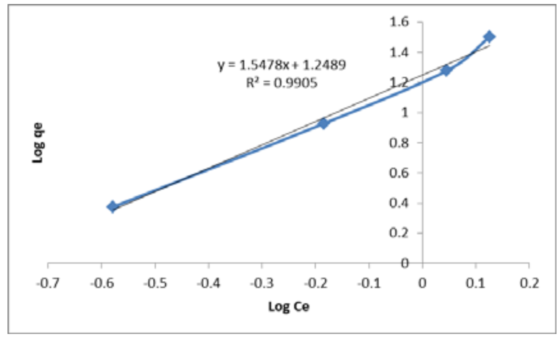

Figure 5. Adsorption of Freundlich Ni(II) metal ion by persimmon tannin gel

The results showed that the highest adsorbed Ni(II) ion was 17.62 mg/g at 100 ppm. It happens because of the large number of OH and phenolic groups in persimmon tannin gel, so the adsorption power of Ni(II) ions is also higher. The OH and phenolic groups can interact with Ni(II) ions (Aksu et al., 2010).

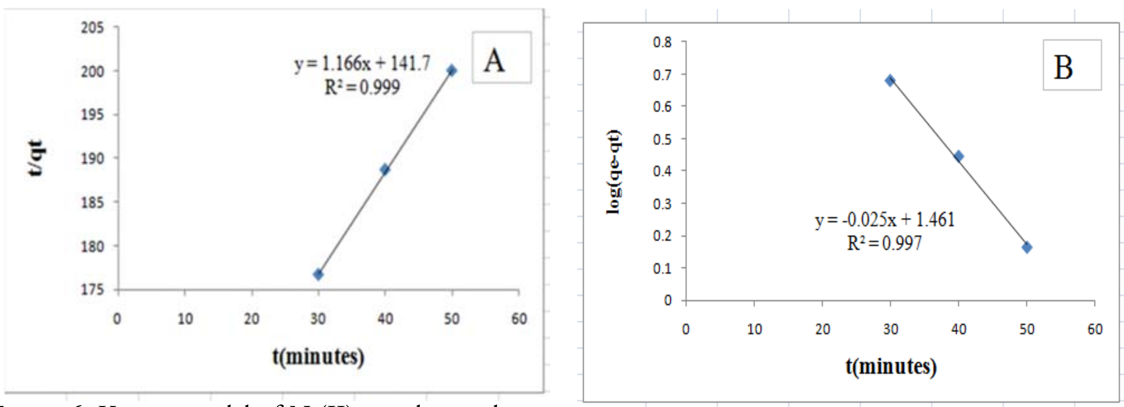

Figure 6. Kinetic model of Ni(II) metal ion adsorption by persimmon tannin gel. (A). pseudo-first-order and (B). pseudo-second-order

Maximum adsorption capacity

The adsorption capacity of Ni(II) ions can be determined based on the Freundlich isothermal and Langmuir isothermal equations. The isotherm model appropriate for adsorption is determined by comparing the linearity values of the two equations. The data in **Figures** 4 and 5 are then processed to obtain the Langmuir and Freundlich equation graphs. Based on **Figure** 4, the equation of the line y = 2.0305 x+16.46, with a slope value of 2.0305 and an intercept of 16.46. In **Figure** 6, the equation of the line y = 1.5478x+1.2469 has a slope value of 1.5478 and an intercept of 1.2469. Slope and intercept values are substituted into equations 5 and 6.

Figures 4 **and** 5 show that the adsorption of Ni(II) metal ions on persimmon tannin gel follow the Freundlich isothermal. The value of adsorption constant capacity (KF) and adsorption intensity (n) was 174,9041 (mg/g) (L/mg)1/n and n = 13,6612 L.mg^{-1}. The value of n above indicates that the adsorption process occurs physically.

Based on **Figures** 4 and 5, the adsorption of metal ions Ni(II) by persimmon tannin gel follows the Freundlich isothermal because the R2 value is 0.042, which is greater than the Langmuir isothermal coefficient, which is 0.003. The value of the adsorption constant capacity (KF) and adsorption intensity (n) was 174.9041 (mg/g)(L/mg)1/n and n = 13.6612 L.mg^{-1}. The value of n above one indicates that the adsorption process takes place physically (Zhou et al., 2019; Tanaydina et al., 2021),

The constants KL and qm can predict the attraction between the adsorbed material and the adsorbent using the separation factor or the dimensionless equilibrium parameter, R. The RL value for Ni(II) at one different concentration is 0.8780. The value of the RL separation factor is<1, indicating that the isotherm shape obtained is in an excellent category.

Persimmon tannin gel adsorption capacity to the Ni(II) ions was 23.14 mg/g. This value is much smaller than the activated carbon adsorption of 151.52 mg/g (Imawati & Adhitiyawarman, 2015; Setiawan et al., 2017). However, it is bigger than the adsorption of natural clay 4.0263 mg/g (Widihati et al., 2012) and smaller than the natural zeolite adsorbent of 23.21 mg/g.

Thermodynamic study(ΔG°)

Thermodynamic parameters in the adsorption system can be calculated using the Van't Hoff equation $\Delta G° = - RT \ln K$. The K value is obtained from the value of n in the Freundlich isothermal. AG is used to determine the nature of the adsorption process. The adsorption process is spontaneous if a constant temperature gives a negative ΔG value.

The value of ΔG obtained is -4.65909 kJ.mol. According to Ye et al. (2011), Gibb's free energy for chemical adsorption is -80 kJ/mol to -400 kJ/mol, and physical adsorption is -20 kJ/mol to 0 kJ/mol. The findings of this investigation suggest that adsorption occurs physically. It further strengthens the assumption of physical adsorption based on the value of n described previously.

Adsorption kinetics

The adsorption rate can be determined by the constant (K) adsorption rate and the reaction order generated from an adsorption kinetics model. The adsorbed metal concentration (qe) data can be processed to determine the kinetic equation for the reaction. The testing stage for the rate of Ni(II) metal ion adsorption can be done by estimating the reaction order, either pseudo-first-order or pseudo-second-order.

Figure 6 shows an adsorption kinetics model of Ni(II) metal ions by persimmon tannin gel based on pseudo-first-order and pseudo-second-order equations. **Figure 6A** is a pseudo-first-order with an R2 value and adsorption rate constant (k1), 0.9973 and 0.0575 g/mg. While **Figure 6B** is a pseudo-second-order kinetics model, the R2 value = 0.9997 and the k2 value = 0.0096 $g.mg^{-1}$. Based on the value of R2 of the two models, which is close to 1, it is a pseudo-second-order equation. Thus the adsorption of Ni(II) metal ions by persimmon tannin gel follows a pseudo-second-order kinetics model. That means adding the adsorbate concentration or the amount of adsorbent will double the adsorption rate.

Conclusions

The optimum time for the adsorption process is 60 minutes, and the pH value suitable for the adsorption of Ni(II) ions is pH 5. Variation in concentration causes a decrease in adsorption with the concentration of Ni(II) ions in the solution increase. The adsorption capacity of the persimmon tannin gel is 23.14 mg/g. The kinetics suitable for the adsorption process for Ni(II) metal are pseudo-second-order kinetics.

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