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Models, Kinetics, and Thermodynamics for The Adsorption of Ni^{2+} Metal Ions by Solid Tofu Waste Immobilized on Silica's Surface

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Abstract

This research aimed to study the models, kinetics, and thermodynamics for the adsorption of Ni^{2+} metal ions by solid tofu waste immobilized on silica surface. The isothermal adsorption model developed in this study revealed that a temperature of 27°C was required for the adsorption of Ni^{2+} metal ions in a batch system with pH = 6. Absorption model of Ni^{2+} ion followed BiLangmuir Model. The real adsorption capacity was between 0.478 mg/L to 4.750 mg/L. The Gibbs free energy for Ni^{2+} ions adsorption was 2159.57 J/mol within the initial concentration range of about 5,10,20 and 30 ppm and -7769.27 J/mol in the initial concentration range about 40 and 50 ppm. The order of the adsorption kinetics for Ni^{2+} ions were second order for a concentration range of about 5-50 ppm. The thermodynamic study of adsorption carried out at temperature variations (from 30 to 60°C) was used to determine the average enthalpy adsorption values for Ni^{2+} ions (111.092 KJ/mol). While the pH of zero charge potential (pH_{PCZ} of adsorbent was 8.40) and the optimum pH for the adsorption of Ni^{2+} ion is 6.

Keywords: *adsorption; model; kinetics; thermodynamics*

1. Introduction

Over the years, there has been a continuous development in the industrial sector in different parts of the world. Many countries compete to advance their industrial sectors. In Indonesia, it focuses also on the development of the industrial especially metallurgical industry. The increase in the development of industries results in positive impacts on the community (through the production of goods and services) and negative impacts on the environment. The waste products from some industries results in the accumulation of heavy metals in the environment, especially the aquatic environment. These include industries that specialize in electro plating, metallurgy, melting, batik, and others [1]. Heavy metal waste impacts a high level of danger to the environment. Although these elements are commonly used in the industry, they are toxic to living organisms. Some examples of heavy metal ions that pollute the environment include lead (Pb), cadmium (Cd), and also nickel (Ni) [2]. Nickel is one of the metals used in industrial activities. Nickel (Ni) is generated from gilding industry activities, electronics, electroplating industry and metal cleaning. Excessive nickel ions can cause various health problems both chronic and acute [3,4]. The presence of heavy metals in aquatic ecosystems must be monitored continuously because they are difficult to degrade. The presence of these metals in the food chain may result in biomagnification in the human body. The concentration of heavy metals in wastes discharged into the aquatic ecosystem can be reduced through the process of *reverse* osmosis, membrane-based filtration and ion exchange. However, the reduced efficacy and expensive operation costs for this process affects the efficiency of these processes [5]. A simple, effective, and relatively cheaper alternative is the adsorption method [6]. This involves the use of different types of adsorbents, particularly those derived from biopolymer-based biomass waste such as tofu solids, soybeans, alginates, and others. This study used the adsorbents derived from solid tofu waste immobilized on the surface of silica to strengthen the mechanical properties, and resistance of solid tofu waste to bacterial and fungal attack and also resistance in acid medium. This increases the adsorption capacity of heavy metal ions. In addition, in this research the models, kinetics, and thermodynamics of adsorption were studied for the adsorption of Ni^{2+} in synthetic waste.

2. Materials and Method

2.1 Material and chemicals

Solid tofu waste immobilized on silica, $Ni(NO_3)_2.6H_2O$, NaOH and HCl.

2.2 Determination of the average optimum contact time of adsorption

The removal of heavy metal ions was carried out by using the batch method. The adsorption of heavy metal ion Ni(II) by solid tofu waste immobilized on silica surface was carried out separately at room temperature (27°C) and at the original pH of the solution containing the metal ion. The various metal ion concentrations include the following: 5, 10, 20, 30.40 and 50 ppm, in a volume of 50 mL. The contact time for adsorption include the following: 10, 20, 40, 60, 80, 100, 120, 140, 160 and 180 minutes. The adsorbent mass of solid tofu waste immobilized on silica was kept at a weight of 0.5 g that was continuously stirred at 120 rpm. The average contact time was calculated from the results obtained while the determination of the levels of metal ions that were not adsorbed was measured using AAS (Atomic Adsorption Spectroscopy, AA-7000 SHIMADZU).

2.3 Determination of model and adsorption kinetics

The adsorption isotherm model was determined by using the Langmuir, biLanguir and Freundlich models. The parameters for adsorption kinetics were determined based on determination of the pseudo first and second order as well as initial adsorption rate.

2.4 FTIR Analysis of solid tofu waste immobilized on silica with Ni^{2+} metal ion

Sample preparation involved the production of KBr pellets. Adsorbent samples with Ni^{2+} ion, and KBr powders were homogenized with a sample mass ratio of about 1 mg of sample: 100 mg of KBr powder mass. The mixing process involved the use of mortar to smoothen the KBr powder and sample mixture. The pellets were placed in a sample holder and analyzed using Fourier Trasform Infra-Red Spectroscopy (FTIR, Shimadzu Prestige 21 brand). The wave number of the spectrum ranged from 300 - 4000 cm^{-1}.

2.5 Determination of parameters thermodynamics of adsorption

A 50 mL volume of Ni metal ion with varying concentrations about 5, 10, 20, 30, 40 and 50 ppm was used to determine the parameters for the adsorption of lead and cadmium. The average optimum contact time and mass of adsorbent obtained in previous procedure was used for this analysis. The adsorption process was carried out at the following temperatures: 30ºC, 35ºC, 45ºC, 55ºC and 60ºC. Adsorption was carried out in a batch system that was stirred continuously at 120 rpm. The data obtained were then processed and used to plot a graph that showed the relationship between ln (qe/Ce) versus q_e for each temperature, where qe is the adsorption capacity (mg/g or mass of solute adsorbed equilibrium) and Ce is the concentration of metal ions in a bulk solution at the state of equilibrium (mg/L and intercept of the graph plot). The graph plot was used to determine the thermodynamic equilibrium constant value of adsorption (K_{ads}) for each temperature. The ΔG_{ads} value for each temperature was calculated using different K_{ads} values. Finally a graph was used to show the relationship between ln K_{ads} and 1/T and the average adsorption enthalpy value (ΔH_{ads} average) and can be determined from slope value of this graph plot and adsorption entropy values (ΔS_{ads}) were also determined at each temperature variation.

2.6 Determination of zero charge potential (pH_{pcz}) from solid tofu waste immobilized on silica

A gram of adsorbent of solid tofu waste was immobilized on silica and 50 mL of 0.01M NaCl solution were added into 12 different Erlenmeyer flasks. The pH of the mixture was adjusted from 2 to 12 using HCl (0.1M) and NaOH (0.1 M). The mixture was agitated for 24 hours at 27ºC using a shaker at a speed of 200 rpm. The initial and final pH of the 12 solutions in the Erlenmeyer flask was recorded [7].

2.7 Effect of pH on the adsorption of heavy metal Ni^{2+} ion by adsorbent of solid tofu waste immobilized on silica

In 8 different Erlenmeyer flasks, 0.5 g of adsorbed solid tofu waste immobilized on silica was added to 50 mL of a solution containing Ni^{2+} metal ion at a concentration of 50 ppm. The pH of the solutions were adjusted from 2 to 9 through the addition of HCl (0.1M) and NaOH (0.1 M) solutions. The calculated average adsorption contact time obtained in previous procedure was used in this investigation. The adsorption temperature was maintained at 27ºC an continuously stirred at 120 rpm [8].

3. Result and Discussion

3.1 Determination of the optimum adsorption contact time

The relationship between the percentage of Ni^{2+} metal ion adsorbed within the adsorption contact time is shown in Figure 1. Figure 1 shows that the optimum contact time for the adsorption of Ni^{2+} metal ion was 120 minutes. At The percentage of Ni^{2+} ions adsorbed at the initial concentrations of 4.94 ppm, 9.57 ppm, 19.68 ppm, 30.15 ppm, 38.98 ppm and 49.98 ppm include 96.76%, 95.61%, 95.27%, 94.73%, 94.92%, and 95.04%. At a contact time above 120 minutes, the adsorption process approached saturation or steady state.

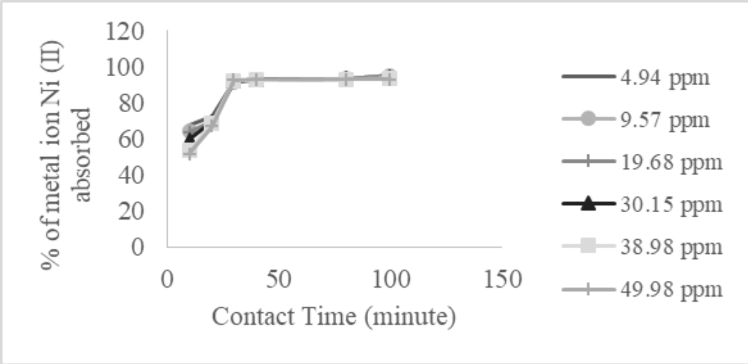

Figure 1: The percentage of Ni(II) metal ion absorbed within the contact time of batch system (at pH of 6.0)

Figure 1 showed that at the contact time of 120 minutes in the range of six types of initial concentrations the average percentage of adsorption of Ni(II) ions has almost the same percent adsorbed, this is because the size of Ni(II) ions is very small around 0.69 Å - 0.72 Å**.** So its mobility is very height as well as with its diffusion coefficient. Therefore, the variation factor of the initial concentration does not significantly affect on the adsorption percentage of Ni(II) ions.

3.2 Determination of models and adsorption kinetics of Ni^{2+} ion

The adsorption data of Ni^{2+} ion isotherms with the adsorbent from solid tofu waste immobilized on silica are shown in Table 1.

Table 1: Analysis of Langmuir, BiLangmuir, and Freundlich adsorption models for Ni^{2+} ion adsorption with batch system

Initial solution concentration (ppm)	Ce (mg/l)	qe (mg/g)	$\frac{C_e}{q_e}$(g/l)
A= 4.94	0.16	0.478	0.335
B= 9.57	0.42	0.915	0.459
C= 19.68	0.93	1.875	0.496
D=30.15	1.59	2.856	0.557
E=38.98	1.98	3.700	0.535
F=49.98	2.48	4.750	0.522

The equation for Langmuir isotherm adsorption method is shown in equation 1[9,10]:

$$\frac{C_e}{q_e} = \frac{1}{q_m . K_L} + \frac{1}{q_m} C_e \quad (1)$$

The Scatchard Plots for the BiLangmuir method is shown in equation 2:

$$\frac{q_e}{C_e} = q_m . K_L \pm K_L . q_e \quad (2)$$

In order to predict the suitability of the Langmuir and BiLangmuir method of adsorption system, the separation factor (R_L) was formulated as follows:

$$R_L = \frac{1}{1+K_L C_0} \quad (3)$$

If R_L: 0 <R_L<1, the BiLangmuir adsorption model is appropriate. The equation for the Freundlich's isotherm adsorption method is shown in equation 4:

$\text{Log } q_e = n \log C_e + \log K_F$ (4)

Where: C_e (mg/L): solute equilibrium concentration in bulk solution

q_e (mg/g): mass of solute adsorbed at equilibrium = $\frac{V\,(C_0 - C_e)}{m}$

V (mL): volume of solution of heavy metal ions

C_0 (mg/L): initial concentration of heavy metal ions,

m: mass of adsorbent

q_m (mg/g): the maximum adsorption capacity of the adsorbent

K_L (L/mg): Langmuir adsorption constants related to adsorption free energy (ΔG_{ads}).

n: adsorption intensity or index of surface heterogeneity..

K_F ($mg^{1-n}g^{-1}L^{n}$): Adsorption capacity of adsorbents or parameters related to bond affinity.

The result of the analysis showed that the adsorption of Ni^{2+} metal ion by adsorbents of solid tofu waste immobilized on silica were more likely to follow the BiLangmuir model. The graph plotted between $\frac{C_e}{q_e}$ to Ce can is shown in Fig 2.

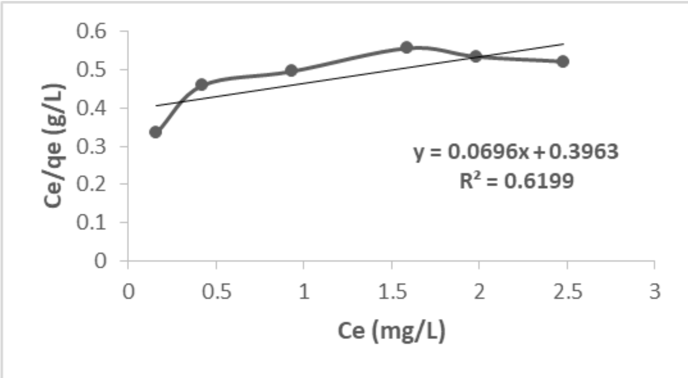

Figure 2: Langmuir isotherm adsorption graph for the adsorption of Ni^{2+} metal ion

The shape of the curve of a graph in Figure 2 provides evidence of the surface heterogeneity of the bonding site on the solid tofu waste adsorbent immobilized on silica. The heterogeneity can be analyzed by using the Scatchard Plot. This involves modeling the curvature of the isothermal adsorption graph as two separate straight lines (BiLangmuir model). The limiting slope method produced two linear lines with different slopes; a high slope indicates a high adsorption affinity site while a low slope indicates a lower adsorption affinity site. The graph is shown in Figure 3:

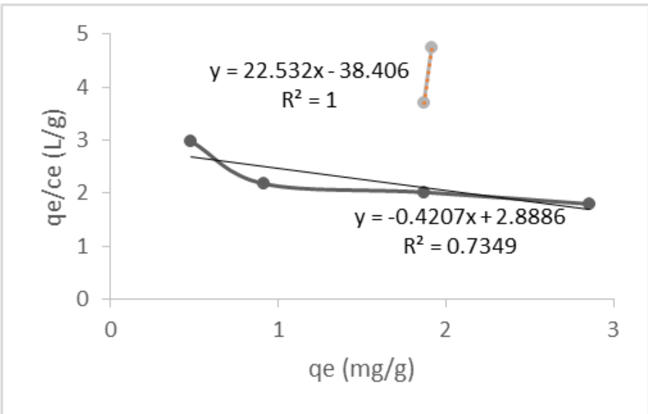

Figure 3: Scatchard graph plot Ni^{2+} ion at a temperature of 27°C

The Bilangmuir adsorption model analysis for Ni^{2+} ion received a $K_L$value of 0.4207 L/mg, the Gibbs free energy adsorption value ((ΔG_{ads}) = -RT lnK_L) was +2159.57 J/mol, and the value of q_m was 6.866 mg/g. For areas within the initial concentration range (4.94 ppm, 9.57 ppm, and 19.68 ppm and 30.15 ppm), while the K_L was 22.532 L/mg, the value of ΔG_{ads} was -7769.27 J/mol, and the value of q_m was 1.7045 mg/g. For areas within the initial concentration range (38.98 ppm and 49.98 ppm). To predict the value of adsorption energy accurately can be used equation of Dubinin-Raduskevirch, as follow [11]:

$$\ln q_e = \ln q_m - K_{DR}\varepsilon^2 \quad (5)$$

Where: K_{DR}: Dubinin-Raduskevirch constants related to adsorption free energy ($mol^2 J^{-2}$).

ε: Polanyi potential (RT ln $(1 + \frac{1}{C_e})$) ($J.mol^{-1}$)

E: adsorption energy ($((2\ K_{DR})^{-1/2})$) ($J.mol^{-1}$)

If value of $K_{DR} << 1$, indicate that surface of adsorbent has rough and lot of holes.

The result of adsorption energy for Ni^{2+} ion was 2380.95 J/mol. Adsorption of energy value of 2380.95 J/mol is classified as a type of physical adsorption that reflects the type of interaction between metal ions and donor atomic dipoles (in this case N atoms in crude protein within amide groups from solid tofu wastes and O atoms from siloxane groups of silica), it also includes the interaction of Van Der Walls. While the analysis of adsorption kinetics parameters is shown in Table 2.

Table 2: Parameters of adsorption kinetics for Ni^{2+} metal ions in the adsorbent of solid tofu waste immobilized on silica

Initial concentration of Pb^{2+} ions (ppm)	**Reaction Order**	**Value of adsorption rate constant**	**Initial absorption rate**
4.94	Pseudo second order	0.34555	0.08620
9.57	Pseudo second order	0.14974	0.14302
19.68	Pseudo second order	0.07600	0.30400
30.15	Pseudo second order	0.04745	0.44512
38.98	Pseudo second order	0.03151	0.50456
49.98	Pseudo second order	0.02304	0.60966

The pseudo first order adsorption kinetics equation is is shown below [5,12]:

$$\text{Log}\,(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (6)$$

$$h_1 = k_1 q_e \quad (7)$$

The pseudo second order adsorption kinetics equation is shown below [5,12]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

$$h_2 = k_2 q_e^2 \quad (9)$$

Where :

q_t ($mg.g^{-1}$) is the adsorbate mass that adsorbed at any time t (minute)

k_1 ($minute^{-1}$) is an adsorption rate constant of pseudo first order

h_1 ($mg.g^{-1}minute^{-1}$) is an initial adsorption rate of pseudo first order

k_2 ($g.mg^{-1}.minute^{-1}$) is an adsorption rate constant of pseudo second order

h_2 ($mg.g^{-1}minute^{-1}$) is an initial adsorption rate of pseudo second order

3.3 *FTIR analysis results*

The FTIR spectrum shows stretching vibration of the OH group from free silanol at wave number 3749.62 cm^{-1}, stretching vibration of the OH group of hydrogen-bonded silanol at wave number 3425.58 cm^{-1}, and the stretching vibration of the CH_2 group of hydrocarbon chains in the crude protein polypeptideat wave numbers 2924.09cm^{-1} and 2854.65 cm^{-1} [13]. Moreover, the spectrum showed stretching vibration from C≡C bonds of the hydrocarbon chain components of fatty acids in crude fat at wave numbers 2368.59 cm^{-1} and 2337.73 cm^{-1}, the stretching vibration of the amide region I and the amide region II of the poplipeptide chain in the crude protein component at wave numbers 1651.07cm^{-1}, 1543.05 cm^{-1}, and 1527.62 cm^{-1} [14], and the expression of asymmetric stretching vibrations of the hydrogen-bound Si-O-Si group of silica at wave number 1089.82 cm^{-1}. The band of absorption at wave number 956.72 cm^{-1}shows the presence of Si-O-Ni^{2+}, and the band absorption at wave number 790.84 cm^{-1}indicates the presence of Si-O-Si symmetrical stretching vibration of silica [15]. Furthermore, the spectrum shows symmetrical stretching vibration of Ni^{2+} -N bond (N atom in amide in peptide bond) at wave number 410.85 cm^{-1} [16]. The result of the FTIR analysis predicted the the bond structure between the active groups and free electron donor in solid tofu waste immobilized on silica with Ni^{2+}. The hypothetical structureis shown in Figure 4.

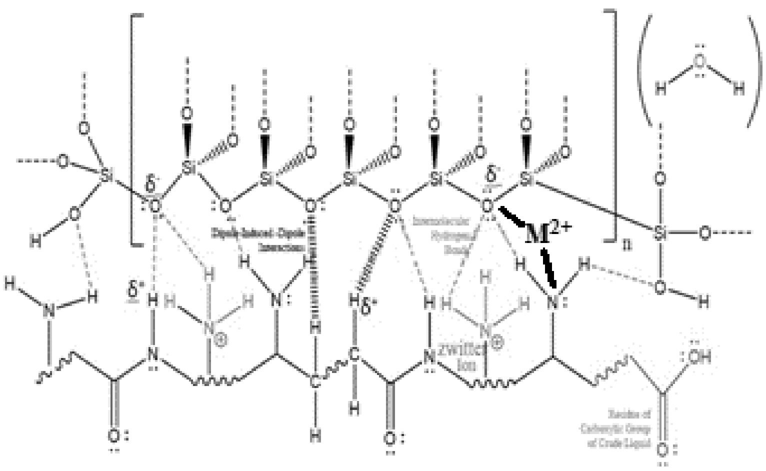

Figure 4: Hypothetical structure of the interaction between metal ions M^{2+} (Ni^{2+}) and free electron donor (O and N atoms) from the active groups of solid tofu waste immobilized on silica

3.4 *Parameter determination thermodynamics of adsorption*

The thermodynamic study of the adsorption of Ni^{2+} metal ions by adsorbents of solid tofu waste immobilized on silica had aim to determined the average adsorption value of enthalpy (noncalorimetric method) at various temperatures (30ºC, 35ºC, 45ºC, 55ºC, and 60ºC). The graph showing the relationship between lads of K_{ads} (adsorption equilibrium constant) and $\frac{1}{T}$ (K^{-1}) for the adsorption of Ni^{2+} metal ions are shown in Figure 5. Using formula for the Vant Hoff equation is [17]:

$$\frac{d \ln K_{ads}}{d(\frac{1}{T})} = - \frac{\Delta H_{ads}}{R} \qquad (10)$$

At an R value of 8.314 J/mol. K, the average enthalpy value for the adsorption of Ni^{2+} ion was 111.092 KJ/mol (endothermic process). The average enthalpy value for the adsorption for Ni^{2+} ion was positive. This means to obtain the percentage adsorption of large metal ions requires greater heat (heat). Thus, the percentage adsorption of Ni^{2+} metal ion becomes greater with an increase in adsorption temperature.

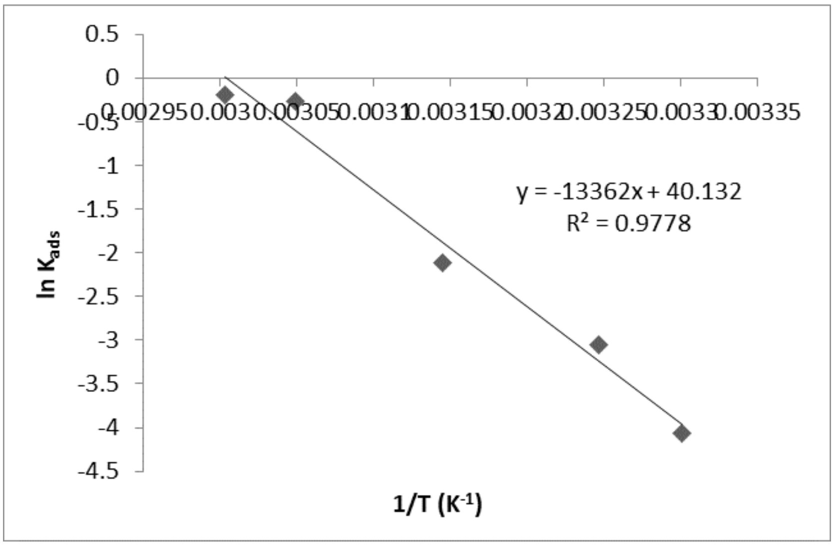

Figure 5: The relationship between ln K_{ads} with $\frac{1}{T}$ for Ni^{2+} ion.

Table 3: Thermodynamic parameters of adsorption for Ni^{2+} metal ions by the adsorbent of solid tofu waste immobilized on silica

T (K)	ln Kads	∆Gads (KJ/mol)	∆S (KJ/mol.K)
303	-4.702	11.845	0.328
308	-3.058	7.831	0.335
318	-2.116	5.594	0.332
328	-0.265	0.723	0.336
333	-0.200	0.555	0.332

Where $\Delta G_{ads} = - RT \ln K_{ads}$, [18] $\Delta S_{ads} = \frac{\Delta H_{ads\ average} - \Delta G_{ads}}{T}$

3.5 ***The result of determination of the zero charge potential (pH pcz) from the adsorbent of solid tofu waste immobilized on silica***

Determination of pH_{pcz} can be calculated based on the relationship between the initial pH and the final pH is shown in Figure 6. At a pH_{PCZ} value of 8.4, the surface of the adsorbent has a neutral charge below the pH of the PCZ, the surface of the adsorbent tends to be positively charged while above the pH of the PCZ, the surface of the adsorbent tends to be negatively charged [19]. The adsorption of metal ions is expected to be more advantageous when it is carried out above the pH of PCZ. However, the adsorption of heavy metal ions is constrained reaction of precipitation become their hydroxide form when carried out above the pH of the pcz. This is because the Ksp value of $Ni(OH)_2$ is $6x\ 10^{-18}$ at 25°C [20]. The effect of pH variations on the percentage adsorption of Ni^{2+} ion is shown in Figure 7. Figure 7 shows that the optimum pH for the adsorption of Ni^{2+} is 6. Above this pH, there is a decrease in the percentage of metal ions absorbed. This is due to the phenomenon of the Ni^{2+} metal ion precipated in the hydroxide form.

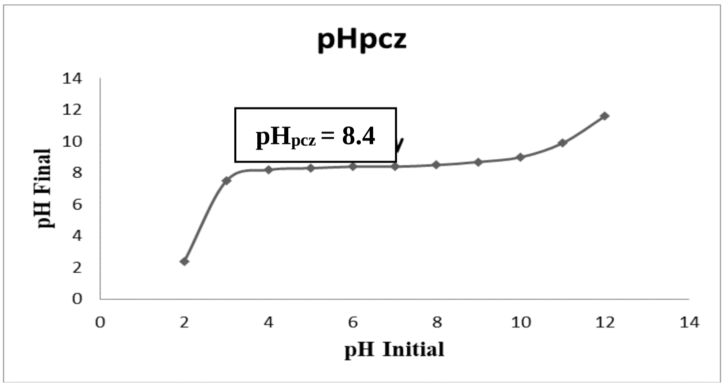

Figure 6: Relationship between initial and final pH for determination of pH_{PCZ} of adsorbent

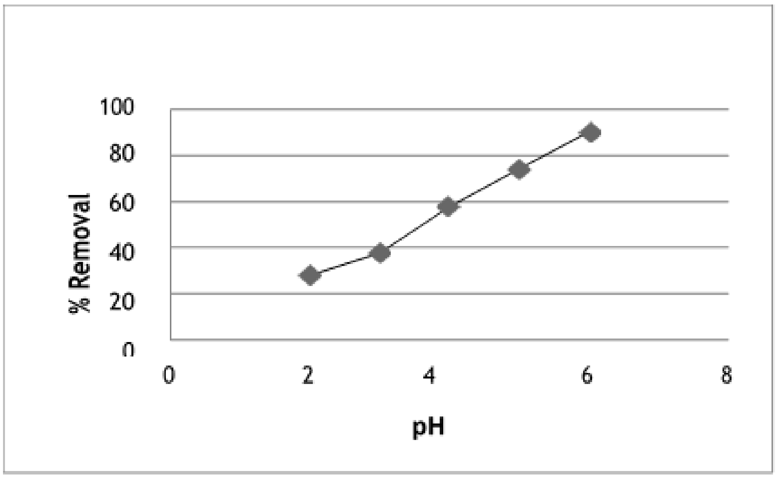

Figure 7: The effect of pH on the percentage of Ni^{2+} absorbed

4. Conclusion

The result of the analysis showed that the adsorption model for Ni^{2+} is the BiLangmuir model with a second order reaction (pseudo second order), for the average enthalpy of adsorption at a temperature range of 30°C - 60°C for Ni^{2+} was 111.092 KJ/mol (endothermic process). The higher the temperature, the greater the ability of adsorption of the adsorbent of solid tofu waste immobilized on silica's surface.

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