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Models, kinetics, and thermodynamics for the adsorption of Pb^{2+} and Cd^{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 Pb^{2+} and Cd^{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 Pb^{2+} and Cd^{2+} metal ions in a batch system with pH = 5.3 and pH = 6 respectively. The initial concentration of the metal ions were 5, 10, 20, 30, 40, and 50 ppm respectively in a volume of 50 mL containing 0.5g of adsorbent mass. The optimum contact time for adsorption was 120 minutes. Absorption model of both ions followed BiLangmuir Model. The real adsorption capacity was between 0.337 mg/L to 3.474 mg/L for Pb^{2+} ions and 0.437 mg/L to 3.687 mg/L for Cd^{2+} ions. The Gibbs free energy for Pb^{2+} ions adsorption was 3015.45 J/mol within the initial concentration range of 5, 10 and 20 ppm and 3995.62 J/mol in the initial concentration range of 30,40, and 50 ppm, while for Cd^{2+} ion adsorption was 578.17 J/mol I the initial concentration range of 5 and 10 ppm and 2376.86 J/mol within the initial concentration range of 20, 30, 40, and 50 ppm. The results of the adsorption kinetics study showed that the average rate of initial adsorption of Cd^{2+} ions was greater than that of Pb^{2+} ions. The order of the adsorption kinetics for Pb^{2+} ions varied between: pseudo first order and pseudo second order. While the adsorption kinetics for Cd^{2+} ions were second order for a concentration range of 5-50 ppm while 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 Pb^{2+} ions (95.553 kJ/mol) and Cd^{2+} ions (122.249 kJ/mol). While the pH of zero charge potential (pH_{PCZ} of adsorbent was 8.40) and the optimum pH for the adsorption of Pb^{2+} ion and Cd^{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 their 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) and cadmium (Cd) [2]. There are several sources of Cadmium, these include natural sources, mining and industrial sources. Volcanoes are a major source of cadmium. Cadmium is a follow-up material from the extraction of black lead (Pb), zinc (Zn), copper (Cu), coal and oil production [3,4]. The release of cadmium into the food chain has resulted in the pollution of the aquatic environment. It is a toxic substance that causes chronic poisoning in humans. The maximum concentration of Cd that is allowed in drinking water is 0.003 mg/L [5]. Lead (Pb) is one of the four heavy metals with a high toxicity level. Some of its carcinogenic properties include the following; it causes mutation, it cannot be decomposed in a short period of time, and its toxicity value does not change easily [6]. Lead may pollute air, water, soil, plants, animals and humans. The entry of lead into the human body may be through food and beverage sources. This metal occurs naturally in waters or accumulates as a result of human activities. Lead enters the aquatic system through the crystallization of lead-free aerosols in the air, which are subsequently washed away by rainwater. In addition, the corrosion of minerals in rocks results in the release of lead into the aquatic ecosystem [2]. Other sources of lead include painting activities, piping materials, and the use of additives in gasoline, batteries, and coloring agents [6]. 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 [7]. A simple, effective, and relatively cheaper alternative is the adsorption method. 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, the models, kinetics, and thermodynamics of adsorption were studied for the adsorption of Pb^{2+} and Cd^{2+} metal ions in synthetic waste [8].

2. Experimental

2.1. Material

Solid tofu waste immobilized on silica, $Pb(NO_3)_2$, 3 $CdSO_4$.8 H_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 ions Pb(II) and Cd(II) by solid tofu waste immobilized on silica surface was carried out separately at room temperature (27^{o}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 Pb2 + and Cd2+ metal ions

Sample preparation involved the production of KBr pellets. Adsorbent samples with Pb^{2+} ions, Cd^{2+} ions 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 recorded ranged from 300 - 4000 cm^{-1}.

2.5. Determination of parameters thermodynamics of adsorption

A 50 mL volume of metal ions with varying concentrations (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 [9].

2.7. Effect of pH on the adsorption of heavy metal Pb2+ and Cd2+ ions by adsorbent of solid tofu waste immobilized on silica

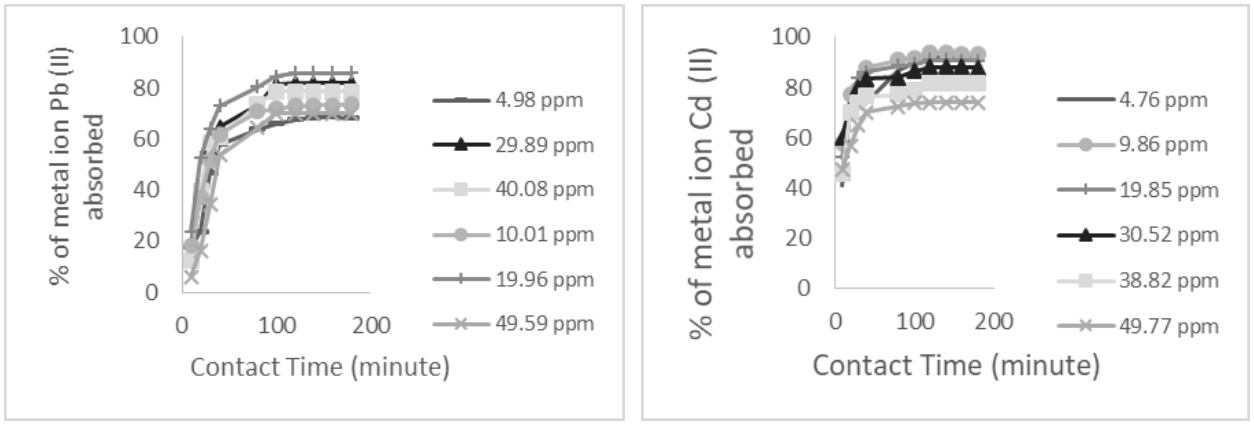
In 8 different Erlenmeyer flasks, 0.5 g of adsorbed solid tofu waste immobilized on silica was added to 50 mL of a solution containing Pb^{2+} and Cd^{2+} metal ions at a concentration of 50 ppm. The pH of the solutions were adjusted from

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 27°C an continuously stirred at 120 rpm.

3. Results and discussion

3.1. Determination of the optimum adsorption contact time

The graph showing the relationship between the percentage of Pb^{2+} and Cd^{2+} metal ions adsorbed within the adsorption contact time is shown in Figure 1. Figure 1 shows that the optimum contact time for the adsorption of Pb^{2+} and Cd^{2+} metal ions was 120 minutes. At The percentage of Pb^{2+} ions adsorbed at the initial concentrations of 4.98 ppm, 10.01 ppm, 19.96 ppm, 29.89 ppm, 40.08 ppm, and 49.59 ppm include 67.67%, 73.03%, 85.83%, 81.90%, 78.69%, and 70.05% while the percentage of Cd2+ ion adsorbed at the initial concentrations of 4.76 ppm, 9.86 ppm, 19.85 ppm, 30.52 ppm, 38.82 ppm, and 49.77 ppm, was 91.81%, 93.61%, 90.83%, 88.07%, 81.94%, and 74.08% in the same average contact time. At a contact time above 120 minutes, the adsorption process approached saturation or steady state.



(a) (b)

Figure 1. The percentage of metal ions absorbed within the contact time of batch system for: (a) Pb^{2+} ion (pH = 5.3) and (b) Cd^{2+} ions (pH = 6.0) (contact time of 180 min)

Figure 1 also showed that the percentage of Cd^{2+} heavy metal ions that was absorbed were greater than the percentage of Pb^{2+} metal ions between the time intervals of 10 minutes to 180 minutes. The radius of Cd^{2+} ion was smaller than the radius of Pb^{2+} ion (radius of Pb^{2+} ion = 1.19Å and Cd^{2+} = 0.97 Å) [3], and the Cd^{2+} ion mobility was greater than Pb^{2+} ion mobility. And also diffusion of coefficient of, the Cd^{2+} ions was greater than Pb^{2+} ion, therefore the Cd^{2+} ions were easily adsorbed by the solid tofu waste immobilized on silica compared to the Pb^{2+} ions. Theoretically, the bond strength between Pb^{2+} ions with donor groups of free electron in most cases were nitrogen atoms of the amide group in the crude protein component of solid tofu waste and O atoms (from the siloxane group on silica) is stronger than the bond between these donor groups with the metal ion Cd^{2+}. This is because the character of the covalent bond between Pb^{2+} metal ion and the donor groups of free electrons from the adsorbent is greater than the character of the covalent bond with Cd^{2+} ion. Thus, the bond between Pb^{2+} ion and donor groups are more stable in polar solvents (such as water) [4,10]. Based on these findings, it can be inferred that the size factor of heavy metal ions are more dominant compared to the strength of covalent bonds. Hence, Cd^{2+} ion are easily adsorbed compared to Pb^{2+} ion.

3.2. Determination of models and adsorption kinetics of Pb^{2+} and Cd^{2+} ions

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

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

Initial concentration of Pb^{2+} ions (ppm)	**Ce (mg/l)**	**qe (mg/g)**	**$\frac{C_e}{q_e}$(g/l)**
A= 4.98	1.61	0.34	4.78
B= 10.01	2.70	0.73	3.69
C= 19.96	2.83	1.71	1.65
D=29.89	5.41	2.45	2.21
E=40.08	8.54	3.15	2.71
F=49.59	14.85	3.47	4.27

Table 2. Analysis of Langmuir, BiLangmuir and Freundlich adsorption models for Cd^{2+} ion adsorption batch system

Initial concentration of Cd^{2+} ions (ppm)	**Ce (mg/l)**	**qe (mg/g)**	**$\frac{C_e}{q_e}$(g/l)**
A= 4.76	0.39	0.44	0.89
B=9.86	0.63	0.92	0.68
C=19.85	1.82	1.80	1.01
D=30.52	3.64	2.69	1.35
E=38.82	7.01	3.18	2.20
F=49.77	12.90	3.69	3.50

The equation for Langmuir isotherm adsorption method is shown in equation 1 [11–13]:

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

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

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

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

$$R_L = \frac{1}{1+K_L C_0} \text{……. (3)}$$

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:

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

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 (g): mass of adsorbent

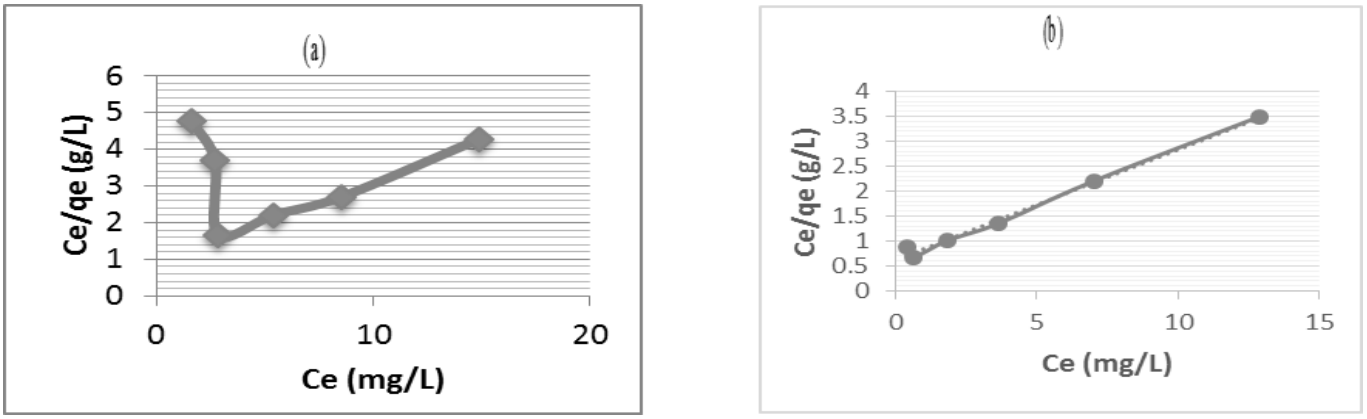
q_m (mg/g): the maximum adsorption capacity of the adsorbent

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

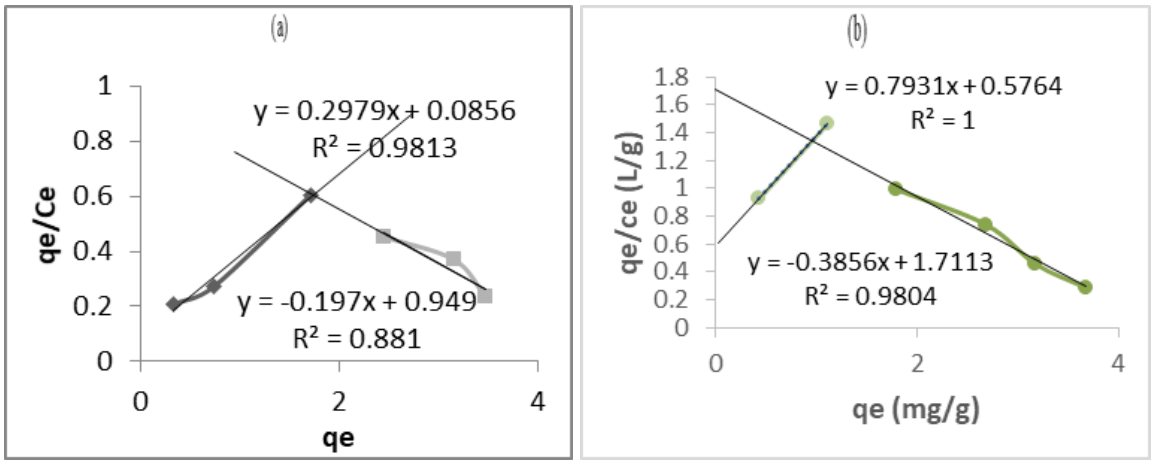
The result of the analysis showed that the adsorption of Pb^{2+} and Cd^{2+} metal ions by adsorbents of solid tofu waste immobilized on silica were more likely to follow the BiLangmuir model. The graph plotted between $\frac{C_e}{q_e}$ to Ce can is shown in Figure 2.



(a) (b)

Figure 2. Langmuir isotherm adsorption graph for the adsorption of: (a) Pb^{2+} metal ions and (b) Cd^{2+} metal ions

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 (Figure 3).



(a) (b)

Figure 3. Scatchard graph plot of: (a) Pb^{2+} and (b) Cd^{2+} ions at a temperature of 27°C

The Bilangmuir adsorption model analysis for Pb^{2+} ion received a $K_L$value of 0.2985 L/mg, the Gibbs free energy adsorption value ((ΔG_{ads}) = -RT lnK_L)was +3015.45 J/mol, and the value of $q_m$was 0.2854 mg/g. For areas within the initial concentration range (4.98 ppm, 10.01 ppm, and 19.96 ppm) and (29.89 ppm, 40.08 ppm, and 49.59 ppm), the KL was 0. 2015 L/mg, the value of ΔG_{ads} was +3995.62 J/mol, and the value of $q_m$was 4.7820 mg/g. While for the Cd^{2+} ion yielded a $K_L$value of 0.7931 L/mg for the area in the initial concentration range (4.76 ppm and 9.86 ppm) at a value of ΔG_{ads} = + 578.17 J/mol, and qm of 0.7268 mg/g. The initial concentration range (19.85 ppm, 30.52 ppm, 38.82 ppm, and 49.77 ppm) had a $K_L$value of 0.3856 L/mg, ΔG_{ads} of + 2376.86 J/mol, and q_m price of 4.438 mg/g. To predict the value of adsorption energy accurately can be used equation of Dubinin-Raduskevirch, as follow [14]:

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

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 Pb^{2+} ion was 561.96 J/mol, and Cd^{2+} ion was 1589.07 J/mol. The greater positive value of ΔG_{ads} means the adsorption process undergoes unspontaneously or the bonding between heavy metal ions with donor groups of free electron become unstable. From statement above, therefore Pb^{2+} ions have weaker bond strength with donor groups of free electron (N and O atoms of active groups of solid tofu waste and silica) than Cd^{2+} ions. However, the smaller radius of Cd^{2+}contributed to its greater adsorption compared to Pb^{2+} ions. The analysis of adsorption kinetics parameters is shown in Table 3:

Table 3. Parameters of adsorption kinetics for: (a) Pb^{2+} metal ions and (b) Cd^{2+} metal ions in the adsorbent of solid tofu waste immobilized on silica

a)

Initial concentration of Pb2+ ions (ppm)	**Reaction Order**	**Value of adsorption rate constant**	**Initial absorption rate**
4.98	Pseudo first order	0.03823	0.0166
10.01	Pseudo second order	0.0271	0.0265
19.96	Pseudo first order	0.03455	0.0566
29.89	Pseudo second order	0.00436	0.0634
40.08	Pseudo second order	0.00328	0.0822
49.59	Pseudo first order	0.06241	0.2168

b)

Initial concentration of Cd^{2+} ions (ppm)	Reaction Order	Value of adsorption rate constant	Initial absorption rate
4.76	Pseudo second order	0.1587	0.0357
9.86	Pseudo second order	0.1480	0.1384
19.85	Pseudo second order	0.0749	0.2728
30.52	Pseudo second order	0.0714	0.5426
38.82	Pseudo first order	0.0506	0.5351
49.77	Pseudo first order	0.0334	0.5187

The pseudo first order adsorption kinetics equation is is shown below [7,15]:

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

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

The pseudo second order adsorption kinetics equation is shown below[7,15]:

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

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

Where:

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

k1 ($minute^{-1}$) is an adsorption rate constant of pseudo first order

h1 ($mg.g^{-1}.minute^{-1}$) is an initial adsorption rate of pseudo first order

k2 ($g.mg^{-1}.minute^{-1}$) is an adsorption rate constant of pseudo second order

h2 ($mg.g^{-1}.minute^{-1}$) 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} [10]. 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} [16], 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 956.84 cm^{-1}shows the presence of Si-O-Pb^{2+}, and the band absorption at wave number 790.84 cm^{-1}indicates the presence of Si-O-Si symmetrical stretching vibration of silica [17]. Furthermore, the spectrum shows symmetrical stretching

vibration of Pb^{2+} -N bond (N atom in amide in peptide bond) at wave number 459.07 cm^{-1}, the stretching vibration of the Si-O-Cd^{2+}at wave number 956.72 cm^{-1}, and the expression of symmetrical stretching vibrations of Cd^{2+} -N bonds (N atoms in amide in peptide bonds) at wave number 412.78 cm^{-1} [10]. 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 Pb^{2+} and Cd^{2+}. The hypothetical structure shown in Figure 4.

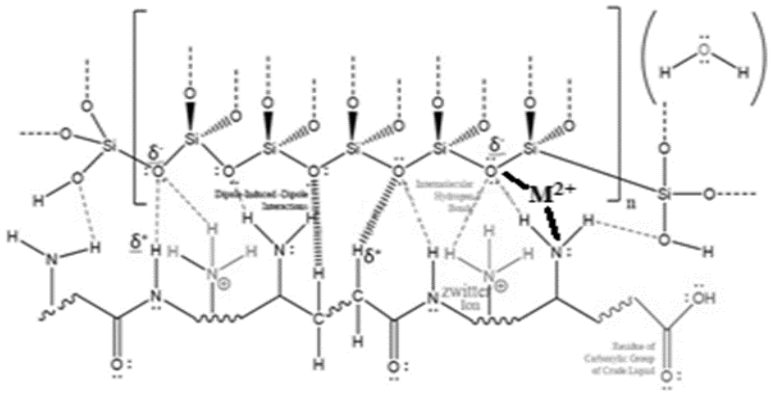


Figure 4: Hypothetical structure of the interaction between metal ions M^{2+} ($Pb^{2+}$and Cd^{2+}) and free electron donor (O and N atoms) from the active groups of solid tofu waste waste immobilized on silica

3.4. Parameter determination thermodynamics of adsorption

The thermodynamic study of the adsorption of Pb^{2+} and Cd^{2+} metal ions by adsorbents of solid tofu waste immobilized on silica had aim to determine 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 Pb^{2+} and Cd^{2+} metal ions are shown in Figure 5.

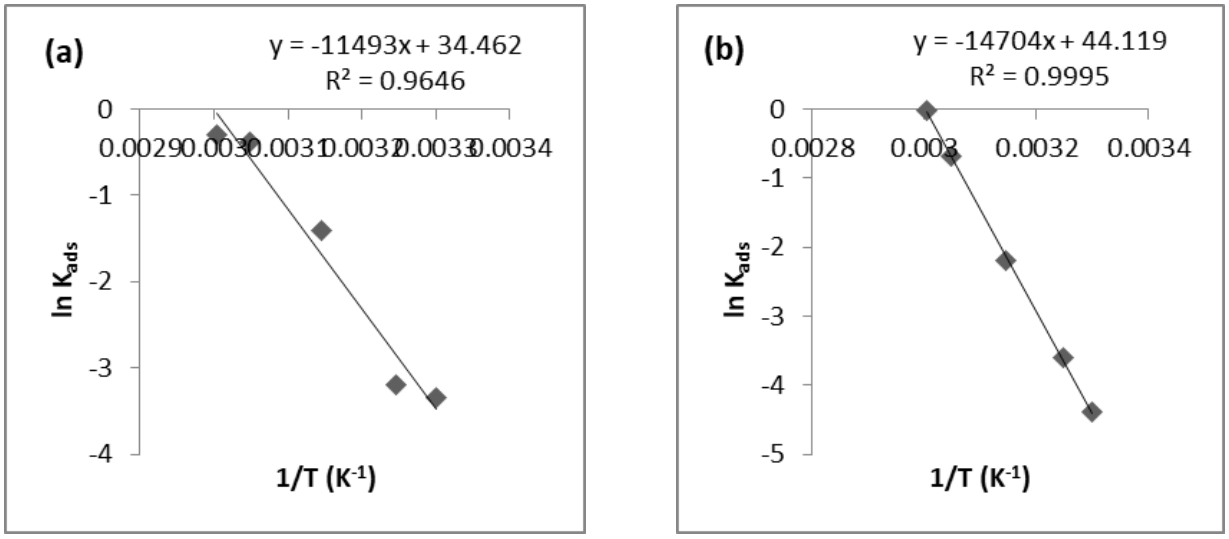


Figure 5. The relationship between ln K_{ads} with $\frac{1}{T}$ for (a) Pb^{2+} and (b) Cd^{2+} ions

Formula for Vant Hoff equation is [18]:

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

At an R value of 8.314 J/mol.K, the average enthalpy value for the adsorption of $Pb^{2+}$and Cd^{2+} ions was 95.553 kJ/mol and 122.249 kJ/mol (endothermic process). The average enthalpy value for the adsorption for Pb^{2+} and Cd^{2+} ions was positive. This means to obtain the percentage adsorption of large metal ions requires greater heat (heat). Thus, the percentage adsorption of $Pb^{2+}$and Cd^{2+} metal ions becomes greater with an increase in adsorption temperature. The average adsorption enthalpy value shows that, the adsorption of Cd^{2+} metal ions requires greater heat energy compared to Pb^{2+} ions. This is because the character of the covalent bond between Pb^{2+} ion and donor groups of free electron (N and O atoms) from solid tofu waste immobilized is greater than the character of covalent bond between Cd^{2+} ion and these donor. Thus the bonding Pb^{2+} ions with donor groups of free electrons is stronger than Cd^{2+} ions.

Table 4. Thermodynamic parameters of adsorption for: (a) Pb^{2+} metal ions and (b) Cd^{2+} metal ions by the adsorbent of solid tofu waste immobilized on silica

(a)

T (K)	ln Kads	ΔGads (kJ/mol)	ΔS (kJ/mol.K)
303	-3.341	8.416	0.288
308	-3.202	8.199	0.284
318	-1.416	3.744	0.289
328	-0.370	1.025	0.288
333	0.299	-0.828	0.289

(b)

T (K)	Ln Kads	ΔGads (kJ/mol)	ΔS (kJ/mol.K)
303	-4.393	11.067	0.367
308	-3.608	9.239	0.367
318	-2.188	5.785	0.366
328	-0.676	1.844	0.367
333	-0.033	0.091	0.367

Where:

ΔGads = - RT ln Kads,[19]

$$\Delta Sads = \frac{\Delta H_{ads\ average} - \Delta G_{ads}}{T}$$

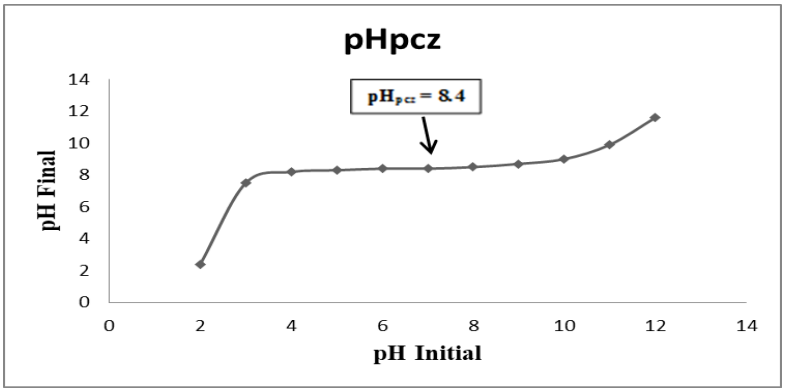


Figure 6. Relationship between initial and final pH for determination of pH_{PCZ} of adsorbent

Determination of pHpcz 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 [20]. 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 $Pb(OH)_2$ and $Cd(OH)_2$ are 1.4×10^{-20} and 1.1×10^{-14}, respectively, at 25°C [21]. The effect of pH variations on the percentage adsorption of Pb^{2+} and Cd^{2+} ions is shown in Figure 7.

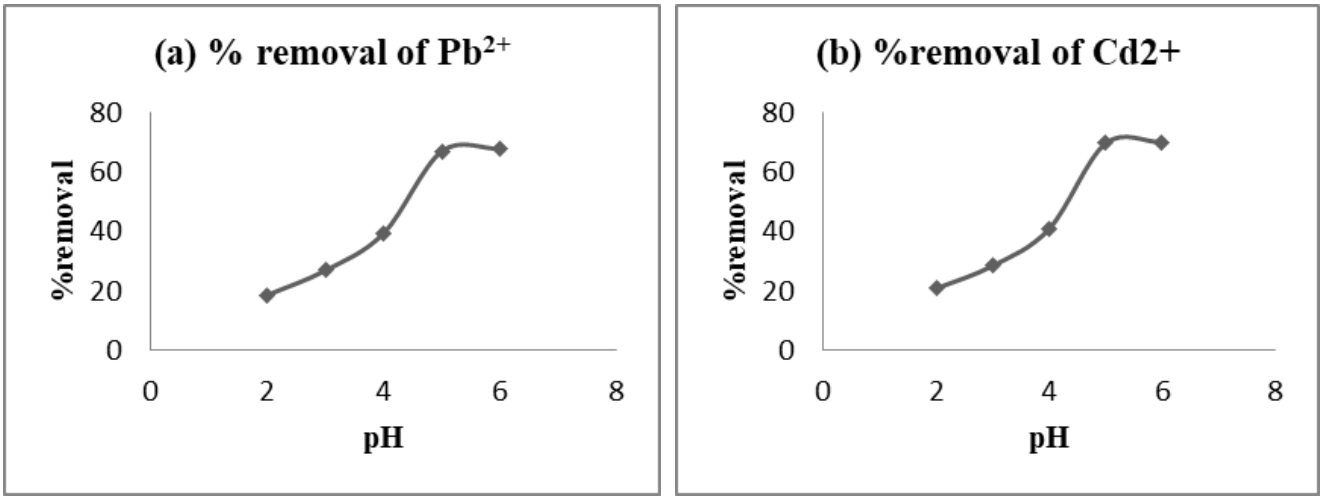


Figure 7. The effect of pH on the percentage of absorbed metal ions for: (a) Pb^{2+} and (b) Cd^{2+} ions

Figure 7 shows that the optimum pH for the adsorption of Pb^{2+} and Cd^{2+} metal ions is 6. Above this pH, there is a decrease in the percentage of metal ions absorbed. This is due to the phenomenon of the two metal ions deposited in the hydroxide form.

4. Conclusion

The initial adsorption rate of Cd^{2+} ion is greater than that of Pb^{2+} ion due to its smaller radius. Furthermore, the mobility and diffusion coefficient of Cd^{2+} ion is greater than that of Pb^{2+} ion. The result of the analysis showed that the adsorption model for Pb^{2+} and Cd^{2+} metal ions is the BiLangmuir model with a varying order reaction (pseudo first order and pseudo second order), for Pb^{2+} ions and the same reaction order for Cd^{2+} ion is the same (pseudo second order). The average enthalpy of adsorption was at a temperature range of 30°C - 60°C for both metal ions was indotermic. The higher the temperature, the greater the adsorption power of the adsorbent on both metal ions.

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