Adsorption of Cobalt-60(II) on silica xerogel from rice husk

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Abstract. The primary cooling water system of a nuclear reactor contains Co-60 which requires treatments to avoid adverse effects on society and the environment. Experiment of Co-60 adsorption by using silica xerogel has been done. This experiment was intended to study the isothermal adsorption equilibrium and to determine thermodynamic parameters. Silica xerogel was made from rice husk ash using sol-gel method. The prepared of silica xerogel has a specific surface area of 142.034 m²/g. The adsorption experiments were carried out in a batch wise until it reaches an equilibrium state with variation of the initial concentration and temperature. The results show that Co (II) adsorption by silica xerogel following the Langmuir isotherm than Fruendlich model. Based on the experiment at three different temperatures, the maximum adsorption capacities depend on the temperature there are 25.71; 26.25; and 26.81 mg/g successively at a temperature of 30; 35; and 40 °C. The thermodynamic parameters showed that the cobalt-60 adsorption process by silica xerogel is spontaneous and endothermic with values of ΔH 117.084 kJ / mol and ΔS 35.582 kJ /K mol. The use of the silica xerogel on the adsorption of reactor cooling water system containing Co-60 showed a decreasing of activity of the waste until 85% from the initial activity. These results indicate that the silica xerogel can be utilized as material to treat radioactive liquid waste containing Co-60.

Keywords: silica xerogel, adsorption, cobalt-60

1. Introduction

Radioactive waste from nuclear reactors requires good management to avoid adverse impacts on the community and the environment. One of the radioactive wastes generated from nuclear reactors is liquid waste containing Co-60 from the cooling system. The half live of Co-60 is 5.271 year. One simple and economical method of processing the liquid radioactive waste is adsorption [1]. Several studies of cobalt (II) adsorption have been done. Thus the utilization of modified peat moss [2],
activated carbon [3], oxalate-treated activated carbon in sulfate medium, [4] and oxygenated apatite surface. [5].

The adsorption of cobalt in a solution using Fe₃O₄/bentonite nanocomposite has capacity of 18.76 mg/g [6] and adsorption of solutions containing Co and Cs by bentonite adsorbent has the adsorption capacity of cobalt 8.15 mg/g. [7].

To diversify the types of adsorbents and to overcome high of adsorbent prices, an alternative adsorbent is needed. In this research, silica xerogel adsorbent was made from natural materials such as rice husk ash so that it could be an alternative as an inexpensive adsorbent. Researches on making silica xerogel have been done, which utilized bagasse ash [8], by the sol-gel method [9], and using the sol gel method using silicate sources from sodium silicate [10].

There was a research of the adsorption using silica xerogel with TEOS as a precursor was reported to adsorb Pb(II) and Cd (II). The adsorption capacity of the silica xerogel for Pb²⁺ is 58.82 mg/g and for Cd²⁺ is 35.71 mg/g [11].

This paper uses rice husk waste as a source of silicate. Silica can be extracted from rice husk ash by using NaOH solution to produce sodium silicate solution or directly from rice husk by sulfuric acid [12-13]. This study utilizes silicates extracted from rice husk ash by using NaOH solution.

The adsorption process can be classified into two, physical adsorption that caused by van der Waals forces and chemical adsorption caused by chemical reactions between the adsorbate molecules and the atoms making up the surface of the adsorbent. Enthalpy change of the chemical adsorption is above 40 kJ/mol, while the physical adsorption is 5-40 kJ/mol. The adsorption process is affected by several factors, including (1) contact time, (2) adsorbate concentration, (3) adsorbent surface area, (4) acidity (pH), (5) temperature, and (6) adsorbate molecule size [14-15].

The adsorption isotherm is a relationship in the equilibrium state of the concentration of solute that is adsorbed in the solid with the concentration of the solution at a certain temperature. In this study, it was associated with two models of adsorption isotherms, namely Freundlich and Langmuir isotherms. Langmuir’s theory explains that on the surface of the adsorbent there are a number of certain active sites that are proportional to the surface area with the assumption that: a) adsorbents and adsorbates form a single layer (monolayer); b) localized adsorption; c) adsorption heat does not depend on surface closure; d) all sites are the same and the surface of the adsorbent is homogeneous; and e) the ability of molecular adsorption on a site does not depend on other sites.

The isotherm of Langmuir adsorption for a single component system can be written as follow [16]:

\[ q_e = \frac{q_o K_L C_e}{1 + K_L C_e} \]  

(1)

Equation (1) can be converted into a linear equation as follows.

\[ \frac{C_e}{q_e} = \frac{1}{K_L q_o} + \frac{C_e}{q_o} \]  

(2)

Where the \( q_e \) is the amount of adsorbate adsorbed per weight of the adsorbent at equilibrium (g adsorbate/g adsorbent); \( q_o \) is the maximum adsorption capacity on the surface/weight of the solid (g adsorbate/g adsorbent); \( K_L \) is the Langmuir’s equilibrium constant (L/g adsorbate), and \( C_e \) is the concentration of adsorbate at equilibrium (g adsorbate/L) [16].
Freundlich's isotherm model explains that the adsorption process on the surface is heterogeneous and not all adsorbent surfaces have adsorption power. The Freundlich isotherm model shows that the adsorbate layer formed on the surface of the adsorbent is multilayer. This is related to the characteristics of physical adsorption by adsorption can occur in many layers (multilayer) (Dada, 2012). The Freundlich isotherm model can be expressed in Equation (3), and it can be applied to be Equation (4) [17].

\[ q_e = K_F C_e^n \]  

(3)

Equation (3) can be converted into a linear equation as follows.

\[ \log q_e = \log K_F + \frac{1}{n} \log C_e \]  

(4)

Where \( q_e \) is the amount of adsorbate adsorbed per gram xerogel solution at equilibrium (mg/g); \( C_e \) is the concentration of the adsorbate remaining in the solution at equilibrium (mg/L); \( K_F \) is the Freundlich isotherm constant (mg/g), and \( n \) is called adsorption intensity [17].

In the adsorption study, it is expected to determine the physical or chemical adsorption that can be known based on thermodynamic parameters of enthalpy change (\( \Delta H \)), entropy change (\( \Delta S \)), and change in Gibbs free energy (\( \Delta G \)).

If the increase in temperature causes a decrease in adsorption capacity, this indicates that the adsorption process is exothermic (\( \Delta H < 0 \)). Entropy shows the irregularity of the adsorbate during the adsorption process to be less random (\( \Delta S < 0 \)) or random (\( \Delta S > 0 \)). The value of \( \Delta G \) is a thermodynamic parameter that can be used to determine whether the adsorption process is running spontaneously or not. This thermodynamic parameter can be calculated using the following equation:

\[ \Delta G = \Delta H - T \Delta S \]  

(5)

\[ \Delta G = -RT \ln K_a \]  

(6)

Where \( K_a \) is the adsorption equilibrium constant, \( T \) is the absolute temperature (Kelvin), and \( R \) (gas constant). Equation (6) states that the magnitude of \( \Delta G \) is directly proportional to the temperature. Equation (5) and Equation (6) can be combined and simplified into linear equations as follows:

\[ \ln K_a = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \]  

(7)

By assumption that \( \Delta H \) and \( \Delta S \) are constant, equation (7) which states the relationship between \( \ln K_a \) and \( 1/T \) is linear, with \( \Delta H/R \) as the slope and \( \Delta S/R \) as the intercept. Based on experiments with temperature variations, the values of \( \Delta H, \Delta G, \) and \( \Delta S \) can be determined. The \( K_a \) value is the van Hoff equilibrium constant which can be calculated by the equation:

\[ K_a = \frac{q_e}{C_e} \]  

(8)

Equation (8) applies at low concentrations so that it is selected in the linear part of the isothermal graph. Based on the values of \( K_a \), equilibrium constant at several temperatures, the thermodynamic parameters can be determined by Equation (9).

\[ \ln K_a = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \]  

(9)
2. Experimental

2.1. Materials
Rice husk was taken from rice mills, made ash in a furnace at a temperature of 600°C. The ash obtained was extracted with 1M NaOH solution. Silica xerogel is made from the extract of rice husk ash by adapting the research conducted by Affandi, et. al (2009) and US Patent 20150360961A1 "Xerogel Production Method".

The Co(II) simulation solution is made from Merck's Co(NO₃)₂.6H₂O crystal, liquid radioactive waste from reactor coolant containing Cobalt-60, available at the Center for Radioactive Waste Technology, National Nuclear Energy Agency.

Other materials are NaOH, HCl, Acetone, Potassium Thiocyanate (KSCN), and AgNO₃ p.a made by BDH, aquadest, and technical alcohol.

2.2. Tools
The tools used are Teflon beaker, hot plate, oven, magnetic stirrer, furnace, analytical balance, thermometer, stirring rod, whatman filter paper no. 41, UV-Vis spectrophotometer, XRD (X-Ray Diffraction), Fourier Transform Infra-Red Spectrophotometer (FTIR), BET Surface Area Analyzer, gamma spectroscopy, and a set of laboratory glassware.

2.3. Procedure
Determination of the equilibrium time was carried out by weighing 0.1 grams of silica xerogel, mixed with the Co(II) solution with a concentration of 200 ppm. The mixtures were stirred at 200 rpm with stirring time varying from 5, 10, 20, 30, 40, 50, and 60 minutes, then were filtered, and the filtrate obtained were analyzed using a UV-VIS spectrometer to determine the Co(II) content.

The determination of isothermic adsorption was carried out by weighing 0.1 grams of silica xerogel, mixed with Co(II) solution with initial concentrations varying from 100, 150, 200, 250, 300, 350, and 400 ppm then stirred at 200 rpm during equilibrium time. After that, the mixture were filtered, the filtrates were analyzed by UV-VIS spectrophotometer. Based on the measurement it can be known the concentration of adsorbate in the solution in the equilibrium state, so that it can be used to determine adsorbate that is adsorbed in silica xerogel material. The thermodynamics parameters of the adsorption were determined based on experiments such as isothermal adsorption with temperature variations of 30, 35, and 40 °C.

The adsorption test of liquid radioactive waste containing Co-60 was carried out by weighing 0.1 gram of silica xerogel, mixed with 100 mL of radioactive liquid waste from the reactor coolant containing Cobalt-60. The adsorption process was carried out at 200 rpm constant stirring and stirring time for 180 minutes. The mixture was filtered and the filtrate is analyzed by gamma spectroscopy (HPGE) for 10 minutes.

3. Results and Discussion

3.1. Silica xerogel product
The silica xerogel products were characterized to determine the physical properties of silica xerogel silica and proved that the material in accordance with what was expected to be used as adsorbent material for radioactive liquid waste containing Co-60. The first characterization process was performed using FTIR (Fourier Transform Infra-Red) to determine the presence of silica xerogel
groups consisting of silanol groups and siloxane groups and the second was performed using XRD. Figure 1 shows the FTIR spectra results of silica xerogel and Figure 2 is the result of the XRD.

The FTIR spectra showed that the wide band absorption in the region of wave number 3481.18 cm\(^{-1}\) is the absorption band of the vibration of the hydroxyl group (-OH) in the silanol group (Si-OH).

The strong and sharp absorption bands at the wave number 1092.24 cm\(^{-1}\) are absorption bands of asymmetric stretch vibrations of Si-O groups in siloxane groups (Si-O-Si). The bending vibration of the siloxane group is shown in the absorption band 795.88 cm\(^{-1}\). The absorption band at a wave number of 1645.51 cm\(^{-1}\) shows that the bending vibration of the hydroxyl group of the silanol group [9]. In general, the absorption band on the silica xerogel shows that the functional groups found in silica xerogels are silanol (Si-OH) and siloxane (Si-O-Si) groups.

Based on the XRD results of Figure 2, it is known that silica xerogel has a wide peak at an angle of 2\(\Theta\) = 21.78\(^{\circ}\). This shows that the silica xerogel is amorphous. The results of this spectrum are similar to the studies conducted by Affandi et al (2009) [8] who made silica xerogel from bagasse ash. This widened peak is caused by x-rays which cannot be differentiated by the amorphous silica xerogel structure so that the x-ray diffraction angle read irregular due to scattering.

In addition, it is also necessary to determine the specific surface area of the silica xerogel. The specific surface area obtained using BET analysis is 142.034 m\(^2\)/g. These results are included in the range carried out by Affandi et al (2009) [8] who made xerogel silica from bagasse ash with a specific surface area of 69 - 160.2 m\(^2\) / g. In addition to the specific surface area, BET analysis will also determine the pore volume and pore diameter of xerogel silica. The pore volume and pore diameter of silica xerogel are 0.5632 cc/g and 15.84 nm respectively. According to the classification of the International Union of Pure and Applied Chemistry (IUPAC), the silica xerogel can be classified as mesoporous material, which the pore size ranges 2-50 nm.

3.2. Effect of time, initial concentration, and temperature

Contact time is one of the factors that influence the adsorption process, the longer the contact time, the higher the amount of adsorbed substance until it reaches equilibrium. The effect of contact time on the amount of cobalt adsorbed by weight of adsorbent (q) by silica xerogel is shown in Figure 3. Based on Figure 3 it is known that in the 10\(^{th}\) minute the amount of cobalt adsorbed reaches a maximum and relatively constant, so this time is used as equilibrium time.
Initial concentration is one factor that influences the amount of Co(II) that can be adsorbed at the equilibrium. The higher the initial concentration of Co(II) the higher the cobalt adsorbed and at equilibrium state result the relationship of $q_e$ and $C_e$ as shown in Figure 4.

Figure 4 shows an increase in the amount of cobalt adsorbed by silica xerogel at different cobalt concentrations at 3 different temperatures. This indicates that the initial concentration of cobalt affects the adsorption process. High concentration causes the number of Co(II) to be higher, resulting in higher driving force. This driving force makes it easier for the Co(II) diffuse to the active silica xerogel groups.

3.3. Isotherm adsorption

The isotherm adsorption model was evaluated based on variations of initial concentration at a certain temperatures experiments. The temperature variations can be used to determine the cobalt adsorption properties by silica xerogel. Adsorption isotherms have certain characteristics which are characterized by constant values that describe the surface properties and affinity of the adsorbent [19]. The adsorption isotherm model may follow the Langmuir and Freundlich isotherm models.

By using equations (2) and (4) the data are matched to determine the appropriate model. The parameter values obtained correspond to the intercept and slope of the graph plot between $C_e/Q_e$ to $C_e$ (Langmuir isotherm) and $\log Q_e$ to $\log C_e$ (Freundlich isotherm). Figure 5 and Figure 6 show a linear graph of the Langmuir and Freundlich isotherm models.
Figure 5. Graph of Langmuir isotherm model for Co(II) adsorption by silica xerogel at 3 temperatures

Figure 6. Graph of Freundlich isotherm model for Co(II) adsorption by silica xerogel at 3 temperatures

Parameters of the adsorption isotherm and determination coefficient ($R^2$) that obtained by linear regression method are presented in Table 1.

| Isotherm model | Parameter | 303 K | 308 K | 313 K |
|----------------|-----------|-------|-------|-------|
| Langmuir       | $q_o$ (mg Co/gSX) | 25.71 | 26.25 | 26.81 |
|                | $K_L$ (L/mg)      | 0.059 | 0.069 | 0.082 |
|                | $R^2$             | 0.9951| 0.9967| 0.9984|
| Freundlich     | $K_F$ (mgCo/gSX)  | 13.35 | 13.84 | 14.42 |
|                | $1/n$             | 0.1041| 0.1049| 0.1063|
|                | $R^2$             | 0.9503| 0.9759| 0.9777|

At the same temperature, the Langmuir isotherm determination coefficient value is greater than the Freundlich isotherm. This shows that the cobalt adsorption process by silica xerogel is more in line with the Langmuir isotherm model but not significantly different from the Freundlich model.

Based on the parameter values in Table 1, the constant values $K_L$, $q_o$, and $K_F$ all increase by increasing temperature. This result shows that silica xerogel can easily adsorb cobalt. Silica xerogel adsorption capacity increases with increasing temperature at the temperature range studied.

The maximum capacity ($q_o$), describes the monolayer saturation under equilibrium conditions. The Langmuir ($K_L$) mono-component constant shows the affinity for Co(II) adsorption. The high $K_L$ value shows that the level of affinity or ability of silica xerogel in Co(II) adsorption process. The $K_L$ value increases slightly with increasing temperature. Freundlich's isotherm model does not describe the condition of adsorbent saturation such as the Langmuir isotherm model. Based on the Table 2, the $K_F$ values indicate that cobalt can be adsorbed by silica xerogel with adsorption capacity increasing with increasing the temperature. The values obtained from $1/n$ (0.1 < $1/n$ <1) show that the adsorption ability of cobalt at all temperatures used is running well.
Based on Table 1, the maximum adsorption of silica xerogel will increase slightly with increasing the temperature. Values of the adsorption capacity, $q_0$, obtained were 25.71; 26.25; and 26.81 mg/g at the temperatures of 30; 35; and 40 °C respectively.

If the adsorption capacity for Co(II) is compared with other adsorbents in the same conditions for, the adsorption capacity (mg/g) of bentonite from Vietnam is 8.15 [7], bentonite nanocomposite Fe$_2$O$_4$ is 18.76 [6], while this study is 25.71. Thus the silica xerogel made from the rice husk ash has the ability to adsorb relatively well, so that it can be expected to be one of alternative of Co-60 adsorbent.

Thermodynamic parameters include changes in free energy ($\Delta G$), enthalpy change ($\Delta H$), and entropy change ($\Delta S$), determined by drawing a graph of the relationship between 1/T and $K_a$. The $K_a$ value is the equilibrium constant which is followed by equation (9) obtained to determine the thermodynamic parameters $\Delta H = 117.084$ kJ/mol and $\Delta S = 35.582$ kJ/ K mol, so that the $\Delta G$ value in the range of temperature studied is negative.

The thermodynamic parameters obtained, $K_a$, indicates that the capability of the silica xerogel to retain a solute and also the extent of its movement in a solution phase. Value of $\Delta G^0$ can be calculated based on equation (5). It is slightly increasing by the increasing of the temperature from 30°C to 40°C. The negative values of $\Delta G^0$ at different temperatures indicate the feasibility of the process and the spontaneous nature of the adsorption. Generally, the change in adsorption enthalpy for physical adsorption is in the range of -20 to 40 kJ mol$^{-1}$, but chemisorption is between -400 and -80 kJ mol$^{-1}$. The $\Delta H^0$ (117.084 kJ mol$^{-1}$) reveals the adsorption is endothermic and chemical in nature. Furthermore, slightly positive $\Delta S^0$ Co(II) adsorption process indicates an irregular increase of the randomness at silica xerogel interface during adsorption.

The application of silica xerogel to adsorb liquid radioactive waste containing Co-60 from the primary reactor water coolant which is carried out in batches wise within 180 minutes produces the data presented in Table 2.

| Initial activity (µCi) | Initial activity (µCi) | % adsorbed |
|-----------------------|------------------------|------------|
| 14 × 10$^{4}$         | 3 × 10$^{4}$           | 78.57%     |
| 14 × 10$^{4}$         | 2 × 10$^{4}$           | 85.71%     |

Based on the % adsorbed in Table 2 proves that silica xerogel can adsorb Co-60 so that its activity decreases. Based on calculations, the specific activity of Co-60 waste is 1143.58 Ci/g, when it is associated with the initial activity of the waste, there is 1.22×10$^{10}$ mg. If the adsorption process by the silica xerogel adsorption capacity is used, then 0.1 g of silica xerogel can adsorb 2.571 mg Co-60 or it should be adsorbed all of Co-60 in the waste. However, the results of the analysis showed that the remaining liquid still contained Co-60. This happens because in the liquid waste the primary coolant of the reactor also contains other elements such as Pb-212, Pb-214, Ru-2013, Eu-154, and K-40. These various elements were in competition with others, so that not of all Co-60 being adsorbed. If it was associated with the electronegativity value, the sequence of consecutive electronegativity values are 2.33; 2.2; 1.88; 1.63; and 0.82 for elements Pb, Eu, Co, Eu, and K, respectively. Elements that have greater electronegativity will be more easily adsorbed in this case by interacting with silanol groups in the silica xerogel.

4. Conclusions
The result of the experiments show that the adsorption of Co(II) on silica xerogel is more suitable following the Langmuir isotherm model with an adsorption capacity of 25.71; 26.25; and 26.81 mg/g each at a temperature of 30; 35; and 40 °C. The process of Co(II) by silica xerogel adsorption occurs spontaneously and is endothermic with a value of ΔH = 117.084 kJ/mol and ΔS = 35.582 kJ/K/mol, so that the value of ΔG in the studied temperature range is negative. The silica xerogel made from the rice husk ash can be expected to be one of an alternative Co-60 adsorbent.

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