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The adsorption isotherm and thermodynamic studies of rhenium onto mesoporous silica nanoparticles

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Abstract. In the case of mesoporous silica nanoparticle applications for nuclear medicine, for example in the case of nanoparticle labeling, it is often found cases of radiochemical impurities or low labeling efficiency which may be caused by the bonding properties that occur. In this work, the adsorption isotherm and thermodynamic studies of Rhenium onto mesoporous silica nanoparticles have been performed to determine the parameters associated with the surface properties of mesoporous nanoparticle silica for labeling purposes. Adsorption measurements were performed by a batch technique with the various initial concentration of rhenium solution (5, 10, 25, 50, 75, 100, 125, 150, and 200 ppm) and conducted with constant stirring for 20 minutes at 28, 35 and 45^{o}C, respectively. The results of the experiment were analyzed using UV-Vis spectrophotometer and through data calculations showed that the properties of rhenium adsorption onto silica mesoporous nanoparticles, among others, are exothermic (negative value of ΔH), spontaneous reactions (negative value of ΔG), and follow adsorption of chemisorption (ΔH value range -55,45 to -137,04 kJ/mol).

1. Introduction

Currently the use of mesoporous silica nanoparticles is being developed in the field of nuclear medicine for therapeutic and diagnostic purposes. Mesoporous silica has unique superior properties as a drug carrier such as high stability, biocompatibility, no apparent toxicity and large load capacity [1]. Research related to nuclear medicine uses a nanomaterial such as mesoporous silica nanoparticle which is an effective nuclear engineering innovation and is a new breakthrough for the development of the world of medicine and health in the world even more for Indonesia [2] [[3].

In the applications of mesoporous silica nanoparticle for nuclear medicine, particularly in radiolabeling of the nanoparticle, it is often found cases of radiochemical impurities or low labeling efficiency which may be caused by the bonding properties such as binding interference [4]. Therefore an investigation of parameters related to isotope exchange-based radiolabeling methods needs to be carried out as conducted by Hong et al [5].

The nanomaterial used is a type of silica-based nanomaterial M41S which will then be modified or functionalized with an amine group to bind beta (β) transmitter radionuclides. This type of nanomaterial can be synthesized by using silica precursors from rice husk ash or waste geothermal sludge [6]], [[7]], [[8]], [[9].

Radionuclide Beta transmitters which are also often used in therapeutic and diagnostic applications are Re-188 or Re-186 for example in radiosynovectomy applications[10]], [[11] In order to control radionuclides and keep it in the therapeutic site, a compound is needed to bind them or called a carrier [12]], [[13]. An ideal carrier for radiosynovectomy is a particulate or colloidal compound that can enter into synovial tissue, can form a stable complex (can bond strongly both in vitro and in vivo) [14]], [[15] with radionuclides used, easy to prepare with good repetition, not toxic, has the ability in terms of biocompatibility, is not allergenic, does not leak (leakage), can be degraded, and trigger radionuclide degradation in the body [16]], [[17]], [[18]], [[19]. As a carrier, this research will use a type of colloidal particulate based on ceramic material, one of which is known as the ordered mesoporous silica (OMS). More specifically the OMS used is the M41S. In order to chemically adsorb Re-188 particulates [20]], [[21]], [[22], the M41S material need to be modified. In this study, the modification is performed by adding an amine group to the M41S using *Post Synthesis Grafting* method [23]], [[24].

The least expected thing in the application of Radiosynovectomy is the weak bond between carrier and particulate so that the particulates are released in the body (leakage) and will spread to other tissues that should not be exposed to beta radiation. Of course this is very dangerous for patients who will carry out Radiosynovectomy therapy. The probability of leakage itself can be seen in terms of thermodynamic adsorption which will provide information about the chemical properties of M41S-NH_2 adsorption on Rhenium which will be described in the form of an isotherm adsorption curve. In this work, the adsorption isotherm and thermodynamic studies of Rhenium onto mesoporous silica nanoparticles need to be performed to determine the parameters associated with the surface properties of mesoporous nanoparticle silica for labeling purposes. Research on Rhenium adsorption with amine-group M41S was proposed in the Radiosynovectomy application simulation [23]], [[24].

2. Experimental section

2.1. Materials

The materials used in this study are M41S material, rhenium solution (in form potassium perrhenate), 3-aminopropyltriethoxysilan (Sigma Aldrich), demineralization water, isopropyl alcohol (Merck), hydrochloric acid (Merck), stannous chloride (Sigma Aldrich), and toluene (Merck).

2.2. Post Synthesis Grafting

Grafting of amine functional groups in the M41S material was performed by the reflux method. M41S about 10 grams were dispersed into 150 mL of toluene and 3.2 mL of demineralization and stirred for 1 hour to form surface hydratation. APTES or 3 – Aminopropyltriethoxysilane solution (roughly equivalent to one monolayer 4 silanes/nm^2) about 10 mL was added to the mesoporous material mixture, refluxed for 4 hours, and cooled at room temperature. The resulted transplant was washed with isopropyl alcohol solution and dried. It is estimated that the amine group grafted on the final product is equivalent to 3 mmol/gram mesoporous material. M41S material (not been grafted) and M41S-NH_2 (been grafted) were characterized by Fourier-transform infrared spectroscopy (FTIR) spectrometer (Thermo Scientific Nicolet iS10).

2.3. Adsorption Studies

Adsorption measurements were performed by a batch technique. The concentration of rhenium in initial solution and in residual solution after adsorption was analyzed by UV-Vis spectrophotometer (UVmini-1240 Shimadzu).

2.4. Effect of Adsorption Time.

Effect of adsorption time was performed in acid condition by shaking 10 mg of M41S-NH_2 material (added stannous chloride) and rhenium solution (in the form of perhenate) 100 ppm at 28 °C for various adsorption time (5, 10, 15, 20, and 30 minutes).

2.5. Adsorption Isotherm and Thermodynamic Study.

Isotherm and thermodynamic study was performed in acid condition with various initial concentration of rhenium solution (5, 10, 25, 50, 75, 100, 125, 150, and 200 ppm) and the adsorption experiments were conducted with constant stirring for 20 minutes at 28, 35 and 45°C, respectively.

3. Results and discussion

3.1. Amine functional group characterization of material

M41S material is an adsorbent made from silica which has many advantages compared to other adsorbent materials. The amine group modification process was performed by the Post syntax grafting method by transplanting amine groups in the M41S material (Figure 1). NH_2 groups will be a negative ion substituent in the adsorption process, so the adsorbate bond chemically with the M41S material stably and desorption process can be avoided.

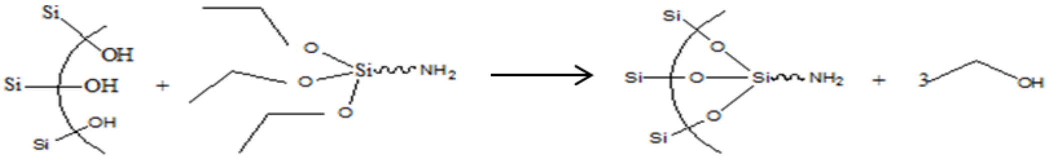

Figure 1. Reaction mechanism of amine grafting process onto M41S material

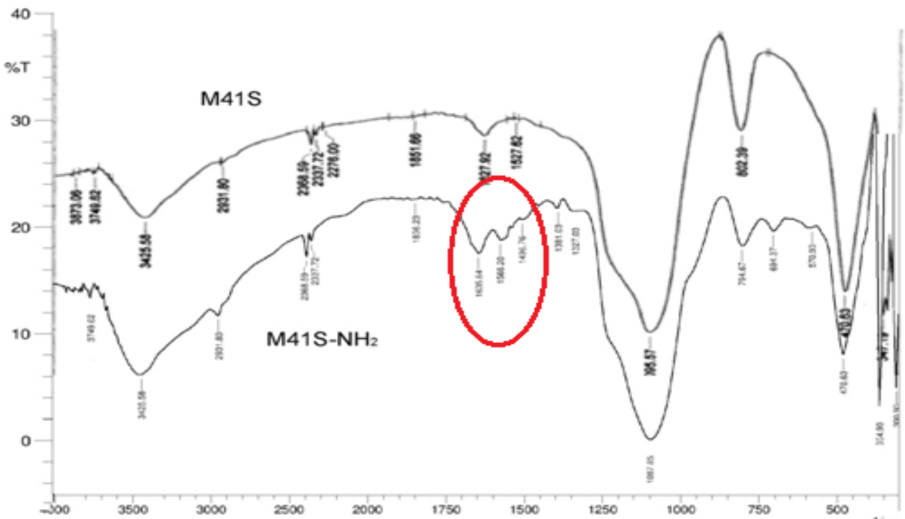

Figure 2. FTIR spectra of M41S and M41S-NH_2

The comparison spectra of M41S and M41S-NH_2 were performed using Fourier-transform infrared spectroscopy (FTIR) spectrometer in the wavelength range of 4000-400 cm^{-1} as shown in Figure 2. The presence of absorption of amine functional groups (NH_2) at 1566.2 cm^{-1} [25] is found in the FTIR spectra of M41S-NH_2 (Figure 2). The type of vibration of the secondary amine group (NH_2) is bending vibration. Unlike the spectra of M41S-NH_2, absorption of amine functional groups (NH_2) not be found in the FTIR spectra of M41S in Figure 2. Result in Figure 2 gives the conclusion if the amine grafting process onto M41S material was successfully performed and can be used for further Rhenium adsorption process.

3.2. Adsorption Study

3.2.1. Effect of Adsorption Time.In acid condition, Rhenium (VII) in the form of potassium perrhenate is reduced by the addition of $SnCl_2$ to Rhenium (V). Complex (clear yellow) reaction occurs during Rhenium (V) adsorption using M41S-NH_2 as shown in Equation 1. In this study, the correction factor was ignored because the risk of Rhenium left on the laboratory glasses wall was almost nonexistent. If there is any, the concentrations are very small and do not affect the amount of Rhenium left in the solution under equilibrium conditions. The effect of contact time of Rhenium adsorption onto M41S-NH_2 is shown in Figure 3.

$$\text{M41S-NH}_2 + KReO_4 + SnCl_2 + 6HCl \rightarrow \text{M41S-NH}_3ReOCl_4 + KOH + SnCl_4 + 2H_2O \quad (1)$$

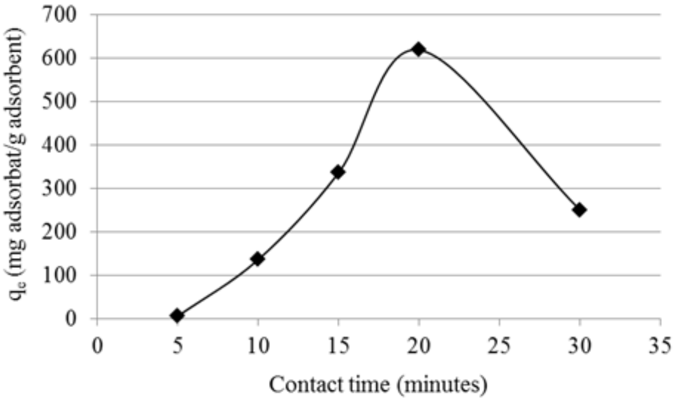

Figure 3. The effect of adsorption time to rhenium adsorption capacity onto M41S-NH_2

Result in Figure 3 shows as adsorption time increase, the amount of adsorbed Rhenium onto M41S-NH_2 increase till the equilibirum point at 20 minutes and decrease afterwards. Kinetics of adsorption of Rhenium (V) consisted of two phases: an initial rapid phase where adsorption was fast and contributed significantly to equilibrium uptake, and a slower second phase whose contribution to the total Rhenium (V) adsorption was relatively small. The first phase is interpreted to be the instantaneous adsorption stage or external surface adsorption. The second phase is interpreted to be the gradual adsorption stage where intraparticle diffusion controls the adsorption rate until finally the metal uptake reaches equilibrium. When equilibrium has achieved, there is no change in the concentration of the adsorbate in the sample or time when the adsorption rate is equal to the rate of desorption. Decrease in adsorption ability after equilibrium occurs because the adsorbed Rhenium anion will be released back into the sample solution called by desorption process. At the beginning of adsorption, the active site on the material surface of the M41S-NH_2 is completely open for Rhenium. This causes more Rhenium anions to be absorbed on the surface of the adsorbent. After the surface of M41S-NH_2 saturates with Rhenium, there is no increase in absorption, causing the Rhenium to escape and leave the surface of the adsorbent and the desorption rate tends to increase, so the Rhenium adsorption capacity onto M41S-NH_2 decreased afterwards.

3.2.2. Adsorption Isotherm Study. The adsorption isotherm is the most important information, which indicates how the adsorbent molecules distribute between the liquid and the solid phase when the adsorption process reaches an equilibrium state [26]. Adsorption isothermal data are further analyzed by the Langmuir and Freundlich models. In general, there is no theoretical model to describe the adsorption isotherms of liquid/solid adsorption. Langmuir model is often used for monolayer adsorption occurred on a homogeneous surface with identical adsorption sites, which can be expressed by Equation 2 [27]. The empirical Freundlich model is appropriate for the adsorption occurred on a heterogeneous surface, which can be expressed by Equation 3 [28].

$$\frac{C}{q} = \frac{1}{q_m K_L} + \frac{1}{q_m} C \tag{2}$$

$$\ln q = \ln K_F + \frac{1}{n} \ln C \tag{3}$$

Table 1 lists the Langmuir and Freundlich parameters and the correlation coefficients (R^2). The adsorption isothermal data are well fitted by the Freundlich model with correlation coefficients higher than Langmuir model. In addition, the values of $1/n$ are smaller than 1, indicating that the adsorption process can proceed easily [29] and reaction tend to follow chemisorption [30]. As adsorption temperature increase from 28°C to 35°C, Freundlich constant value (K_f) increases from 1.035 to 1.081

and decreases when adsorption temperature at 45°C. These phenomena also can be figured out in Figure 4.

Table 1. Adsorption isotherm models of Rhenium onto M41S-NH₂

Temperature (°C)	Adsorption Isotherm Models					
	Freundlich			Langmuir		
	n	K_f (mg/L)	Error (%)	q_{max} (mg/g)	K_L (mg/L)	Error (%)
28		1.035	0.914		1.021	0.830
35	1,116	1.081	0.954	29,670	24.69	0.984
45		0.984	0.953		0.343	0.876

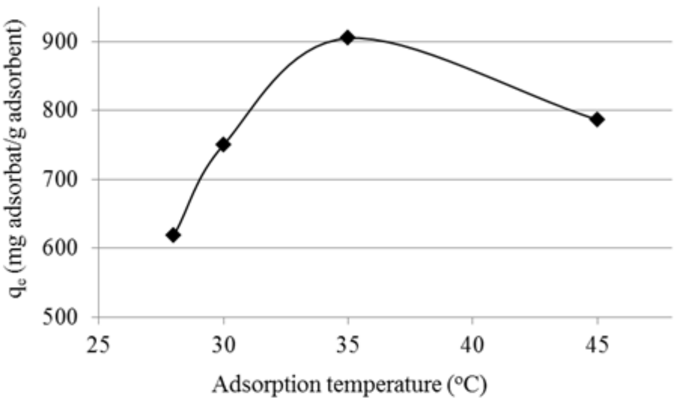

Figure 4. Effect of adsorption temperature to rhenium adsorption capacity onto M41S-NH_2

Result in Figure 4 shows Rhenium adsorption amount onto M41S-NH_2 increase by increase the adsorption temperature from 28°C to 35°C and decrease afterward from 35°C to 45°C. Increased adsorption ability with an increase in temperature shows an increase in ion affinity. Affinity is a measure of how strongly the adsorbate molecule is adsorbed towards the surface of the adsorbent. The increase in temperature causes the energy and reactivity of rhenium to increase so that more ions can pass through the energy level to interact chemically with surface sites. Besides that, the greater ion reactivity will increase the diffusion of ions in the pores of the adsorbent so that more ions are adsorbed on the surface [31]. Because the adsorption occurred on a heterogeneous surface (multilayer phenomena), the adsorbate in upper layer binds weakly and easy to lose as adsorption temperature increase. At high temperature, the particle moves faster because the reactivity of the particle is increase, so the adsorbate in upper layer tends to move from the layer (in solid) to liquid and the adsorption capacity onto M41S-NH_2 decreased called by desorption process.

3.3. Adsorption thermodynamic

Thermodynamic analysis is performed to determine enthalpy (ΔH), entropy (ΔS) and free energy of the specific adsorption (ΔG). The value of ΔH and ΔS were calculated from slopes and intercepts of linearized curve of Ln D_c with the reciprocal of temperature, $1/T$ (Figure 5), by using the relation in Equation 4. The value of ΔG is calculated from Equation 5 [32]. The thermodynamic values are given in Table 2.

$$\ln D_C = \ln\left(\frac{q_e}{C_e}\right) = -\left(\frac{\Delta H}{R}\right)\frac{1}{T} + \frac{\Delta S}{R} \tag{4}$$

$$\Delta G = \Delta H - T\ \Delta S \quad (5)$$

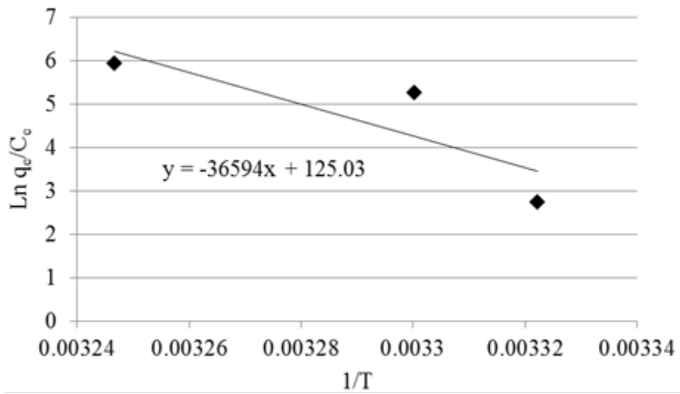

Figure 5. Plot of Ln K_d versus 1/T for Rhenium adsorption onto M41S-NH_2

Table 2. Adsorption thermodynamic parameters of Rhenium onto M41S-NH_2

Temperature (°K)	ΔH (kJ/mol)	ΔS (J/molK)	ΔG (kJ/mol)
301	-55,45		-67,79
303	-117,94	0,04	-130,37
308	-137,04		-149,66

Result in Table 2 shows the ΔH value at various temperatures is negative value which indicates the exothermic reaction during adsorption process. In addition, the ΔH value in Table 2 is in the range of -40 to -800 kJ/mol. According to that ΔH value, Rhenium adsorption onto M41S-NH_2 follows chemisorption process which involves a chemical reaction between M41S-NH_2 and Rhenium. The value of ΔG is a thermodynamic parameter that can be used to find out how the process of chemical reactions occurs in this case adsorption reaction between Rhenium and M41S-NH_2 material. Negative value of ΔG in Table 2 indicates the adsorption reaction takes place spontaneously. Decreasing of ΔG value by increasing the adsorption temperature show that the adsorption is more favorable at high temperature [33].

Entropy or ΔS is a quantity that is often said to be an irregularity in a reaction. Entropy is the ratio of heat transferred during the reaction process in an absolute temperature system. Entropy only depends on the initial state and the final state of the system, without depending on the trajectory of the process. The smaller the entropy value, the more stable the process of running the reaction. The value of ΔS obtained from adsorption of rhenium with M41S-NH_2 is 0.04 which indicate the adsorption reaction is quite stable.

4. Conclusion

The amine grafting process onto M41S material was successfully performed with the presence of absorption of amine functional groups (NH_2) at 1566.2 cm^{-1} using FTIR. Freundlich model is suitable for adsorption equilibrium of Rhenium (V) onto M41S-NH_2 than Langmuir model. In addition, the properties of Rhenium adsorption onto M41S-NH_2, among others, are exothermic reaction (negative value of ΔH), non-spontaneous reactions (negative value of ΔG), and follow adsorption of chemisorption (ΔH value range -40 to -800 kJ/mol).

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