Synthesis of thiazole silica hybrid from waste glass for adsorption of cadmium(II)

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Abstract. Synthesis of thiazole silica hybrid from waste glass to adsorption of cadmium (II) metal ion has been performed. The synthesis was done by attaching thiazole group through liaison compound γ-glycidoxy propyl tri-methoxy silane with silica gel obtained from waste glass. In this study, the effect of adsorption contact time and the concentration of cadmium (II) was studied to determine the reaction rate and the amount of adsorption thermodynamics. The existence of the cluster thiazole on silica gel indicated by IR spectra at wavelengths around 2576 cm\(^{-1}\) of mercaptan groups that previously did not appear on silica gel without modification. The synthesized TSH showed a high adsorption capacity of 9.363 mmol/g of Cd(II). The adsorption isotherm obtained with Langmuir isotherm model gives the negative values of \(\Delta G^\circ\), i.e. -15.488 kJ/mol for Cd(II), indicating the spontaneous process of adsorption. Kinetic studies showed that the adsorption of Cd(II) ion into TSH follows the pseudo-second-order kinetics.

1. Introduction
Glass has the main composition in the form of silica. Extraction of silica from the waste glass is one way to increase the economic value of the waste glass [1]. The extraction results can be used as a source of silica in the silica-based synthetic such as thiazole silica hybrid adsorbent. The investigation of adsorbent has been focused on synthesis and application. Thiazole silica hybrid can be formed by grafting and sol-gel methods [2-3]. Researches about sol-gel method besides the grafting one have been reported, i.e. preparing sulfonated-silica (osmosis) hydrogels [4], polyacrylate silica nanocomposite [5], and the hexagonal mesoporous silica modified with 2-mercaptothiazoline [6]. The sol-gel method has special quality because the formation of bonding at sol process. Therefore, in this study, the formation of thiazole silica was done using the sol-gel method. Thiazole-silica hybrid (TSH) is a product of silica and organic compounds containing thiazole groups. One advantage of the synthesis of silica materials via sol-gel process is the possibility to synthesize organic-silica hybrid materials in mild process condition and a low temperature. The paper reports the synthesis of TSH through the sol-gel process using silica precursor of sodium silicate solution extracted from waste glass, a γ-glisidoxypropyltrimethoxysilane bridge and mercaptobenzothiazole (MBT) as the active group source. The composition of TSH is elucidated based on FTIR spectra. A batch system was used in this experiment to evaluate parameters of the adsorption of Cadmium(II).

2. Experimental

2.1. Chemicals
The thiazole-silica hybrid was synthesized using Mercaptobenzothiazole (MBT), sodium hydroxide (NaOH), Potassium hydroxide, γ-glycidoxypropyltrimethoxysilane (GPTMS), hydrochloric acid (HCl) 37%, waste glass, aquabidest. The metal cations were from cadmium chloride hydrate (CdCl\(_2\).H\(_2\)O), dimethylformamide (DMF), asam sulfat p.a (H\(_2\)SO\(_4\)), etanol 96% (C\(_2\)H\(_5\)OH), sodium thiosulfat (Na\(_2\)S\(_2\)O\(_3\)). All other reagents unless silica, were of analytical reagent grade (Merck).
2.2. Procedure
The preparation of silica precursor was performed using a procedure reported by Kamath [7] with modification.

2.2.1. The Synthesis of thiazole silica hybrid. Synthesis TSH was performed by two-step processes, extraction of silica from WG and synthesis TSH. The sodium silicate were prepared by suspending 25 grams of fine glass powder in 125 mL of 5M sodium hydroxide (NaOH), stirred and heated on a sand bath with a Teflon container to boil for 4 hours. Subsequently, 150 ml of sodium silicate solution coupled with 6 M HCl to form silicate acid sol. Into the silicate sol is added to a solution of mercaptobenzothiazole (0.37 g MBT in 93 mL dimethylformamide (DMF) and 12.88 mL GPTMS) with stirring. The results obtained was aged for 24 hours, filtered, neutralized with distilled water, dried in an oven at a temperature of 100 ºC, and was analyzed by FTIR spectrophotometer.

2.2.2. Adsorption Process. The metal salt of CdCl$_2$.H$_2$O was used as the source of metal ions. Cd(II) solutions (1000 mg/L) was prepared by dissolving appropriate amounts of metal salt in a double distilled water. The working solution was prepared by diluting the stock solution to appropriate volumes. All the adsorption experiments were conducted batch wise [8]; the sorption equilibrium was obtained by shaking 0.1 g of TSH in 20 mL of aqueous solution containing cadmium ion for 2 hours. Adsorption experiments were carried out in an incubator at a temperature of 25˚C. After 2 h was shaken, the mixture was aged for 24 h, the solution was filtered, and the cadmium ion concentrations in the aqueous solutions were measured. Initial and equilibrium cadmium ion concentrations in the aqueous solutions were determined by using flame atomic absorption spectrometer. Initial pH of the solutions was adjusted to the desired pH by adding nitric acid to the medium to maintain a constant pH. Experiments were repeated three times in each case. The amount of adsorbed cadmium ion was calculated from the difference between metal concentration in the aqueous solution before and after equilibrium and the certain weight of the dry TSH.

3. Result and Discussion
Silica hybrid material is a material modification of silica gel with organic compounds through chemical bonds. This material has advantages in applications, such as adsorbents, catalysts, and ion exchange. The ability of silica hybrid materials depends on the success of the synthesis of these materials. One indication was done by the characterization of the products [9]. The synthetic procedure was based on the production of the new sylilant agent named TSH (Figure 1) from the reaction between mercaptobenzothiazole (MBT) and γ-glycidoxypropyltrimethoxysilane (GPTMS) according to Eq. (1). This reaction is analog with the synthetic procedure of the reaction between 2-mercaptothiazoline (MTZ) and 3-chloropropyltrimethoxysilane (SiCl) to produce SiMTZ has reported by Evangelista et al. [6]. The final silica modified with MBT was produced by ordered polymerization of Si-thiazole according to equation (2a and 2b).
Figure 1. The reaction equation (1) between $\gamma$-glycidoxypropyltrimethoxysilane (GPTMS) to produce Si-SH and (2) polymerization of Si-SH, sodium silicate, and hydrochloric acid to produce TSH.

From infrared spectra (Figure 2) obtained for solid samples, it was possible to conclude the successful of the thiazole attachment onto silica gel due to the presence of three well-defined peaks at 2576 (S-H stretching), 1050 (C-H aromatic), and 910 cm$^{-1}$ (for asymmetric C-S stretching) in TSH spectrum [10-11]. However, Si-O stretching asymmetric and symmetry of Si-O-Si that appears in silica gel and TSH at about 1080 to 1100 cm$^{-1}$ and 750 to 790 cm$^{-1}$, respectively. The binding of organic compounds on the silica gel is also characterized by the emergence of the peak at about 750, 1050 and 3040–3060 cm$^{-1}$ of TSH in a CH bonds aromatic bending, CH bending aromatic, and C-H stretching aromatic, respectively [12-13]. While sequentially it can be said that peaks at ~910 and 1450–1490 cm$^{-1}$ for C-C stretching aromatic asymmetric C-S stretching. However, the silica hybrid, TSH, presented a characteristic peak at 2962 cm$^{-1}$ is assigned to C-H stretching of sp$^3$ carbon and confirm the presence of the organic group attached onto silica surface and peak at 3450 cm$^{-1}$ was characteristic for –OH.
Figure 2. FT-IR spectra of Silica gel (SG), Mercaptobenzothiazole (MBT) and Thiazole Silica Hybrid (TSH).

3.1. Kinetic studies
Chemical kinetics gives information about reaction pathways and times to reach equilibrium. Adsorption kinetics shows a large dependence on the physical and/or chemical characteristics of the sorbent material. The study of adsorption dynamic describes the solute uptake rate, and this rate controls the habituation time of adsorbate uptake at the solid-solution interface (Figure 3).
Various models have been described reaction sequence kinetic adsorption system is based on the concentration of the solution [6]. In this study, an absorption kinetics batch Cd (II) ion with TSH has been studied in terms of first-order kinetics, the second-order kinetic, pseudo-first-order kinetics, and the pseudo-second-order models (Table 1). Pseudo-second order kinetics models are given in the equation (1) [9][14][15].

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}
\]

Where \(k_2\) is the rate constant of pseudo-second-order reaction (g.mg\(^{-1}\).min\(^{-1}\)), \(q_e\) and \(q_t\) are the amounts of solute adsorbed at equilibrium and at any time (mg.g\(^{-1}\)), respectively. Plot the straight line of \(t/q_t\) against \(t\) is used to obtain constant pseudo-second-order reaction. Here, the initial absorption rate follows equation (2).

\[
k_c = k_2q_e^2
\]

The greatest value of the correlation factor \(R^2\), obtained from the field of pseudo-second-order kinetics are given in Table 1. These results indicate that the adsorption of Cd (II) ion to the following TSH also pseudo-second-order kinetics model. Expression levels of pseudo-second order is used to describe physisorptions involve valence forces through the sharing or exchange of electrons between the adsorbent and adsorbate. In recent years, the expression level of pseudo-second-order has been widely applied to adsorption of pollutants from aqueous solutions [9].

### Table 1. Adsorption kinetics models for Cd(II) ion onto TSH*

| Kinetics models     | Cd(II)     | Rate constant (k) | \(R^2\) |
|---------------------|------------|-------------------|---------|
| First order         | -0.003 min\(^{-1}\) | 0.958             |
| Second order        | 0.00003 min\(^{-1}\) | 0.966             |
| Pseudo-first order  | -0.001 min\(^{-1}\) | 0.958             |
| Pseudo-second order | 0.076 min\(^{-1}\) | 0.999             |

*at \(C_0=25\) mg/L, pH 6.0; TSH= 0.1 g; temperature 25ºC

### 3.2. Thermodynamic studies

Isotherm data analysis is important to develop an accurate equation is the result and can be used for design purposes. In order to investigate the adsorption isotherms, two equilibrium isotherms were analyzed: Langmuir and Freundlich. Constant parameter equation for this process of adsorption isotherms calculated by linear regression of isotherm equation. Constant parameters and correlation coefficients (\(R^2\)) are summarized in Table 2.

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**Figure 3.** The sorption of Cd(II) ion onto TSH.

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Table 2. Adsorption isotherm models for Cd(II) ion onto TSH*

| Parameter                  | Cd(II) |
|---------------------------|--------|
| Langmuir parameter        |        |
| $q_m$ (mmol/g)            | 9.363  |
| $K_a$ ($\times 10^4$ mg/g) | 1052.434 |
| $\Delta G^\circ$ (kJ/mol) | -15.488 |
| $R^2$                     | 0.991  |
| Freundlich parameter      |        |
| $N$ (mmol/g)              | 2.242  |
| $K_F$ (mg/g)              | 21.184 |
| $R^2$                     | 0.970  |

*at $C_0=25$ mg/L, pH 6.0; TSH= 0.1 g; temperature 25ºC

Langmuir adsorption isotherm has been successfully applied to many real absorption process [9][16-18]. It predicts the maximum adsorption capacity adsorbent monolayer and also determine whether the adsorption is profitable or not. Langmuir (Ce/qe vs Ce) field of Cd (II) were found linear for the entire concentration range studied and the correlation coefficient is very high. The maximum adsorption capacity was determined as 9.363 mmol/g for Cd(II) (Table 2).

The Freundlich isotherm is known to describe the adsorption isotherm initial relationship [19]. Satisfactory empirical isotherm can be used in adsorption from aqueous solution. The Langmuir and Freundlich isotherms constants are shown in Table 2. Thermodynamic considerations adsorption process necessary to conclude whether or not this process is spontaneous. The Gibbs free energy change, $\Delta G^\circ$, an indication of the spontaneity of chemical reactions and, therefore, is an important criterion for spontaneity. The reaction occurs spontaneously at a certain temperature if $\Delta G^\circ$ is a negative quantity. Free energy of adsorption, calculates based on adsorption equilibrium constant $K_a$ is given by the following equation Gibbs (3)[16]

$$\Delta G^\circ = -RT\ln K_a$$ (3)

The $\Delta G^\circ$ which is the standard free-energy change (J / mol), R the universal gas constant (8.314 J / Molk), and T is the absolute temperature (K). The $\Delta G^\circ$ parameters for adsorption process using the $K_a$ of the Langmuir isotherm shown in Table 1. The calculated $\Delta G^\circ$ give a negative value for the adsorption of Cd(II) onto TSH, confirmed the feasibility of the process and the spontaneous nature of adsorption.

4. Conclusion

Synthesis of thiazole silica hybrid can be done through the sol-gel process. The presence of the thiazole modifier on the surface of silica gel was evidence using FTIR. The TSH can be used to absorb cadmium ion from the aqueous solution. The kinetics of adsorption processes fit a pseudo-second-order kinetic model. The thermodynamic parameter, $\Delta G^\circ$ has been evaluated from adsorption equilibrium constant based on a Langmuir, isotherm model. The negative values of $\Delta G^\circ$ indicate the spontaneous nature of adsorption Cd(II) onto TSH.

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