



Optimization of Cadmium Removal Using Tetraethylene Glycol-Modified Silica-Based Adsorbent via Response Surface Methodology

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Abstract

In solid-phase extraction for preconcentration, silica (Si) is the most commonly used as an adsorbent. However, the selectivity and effectiveness of silica gel adsorption on metal ions are low, so it needs to be modified to improve the adsorption capability. The modification was done using reflux and oven heating in the modification silica with 3-glycidoxypopyl trimethoxysilane (GPTMS) and tetraethylene glycol (TEG). A central composite design batch process determined the optimum conditions for cadmium adsorption. TEG-modified silica was successfully synthesized and characterized using FTIR spectroscopy, SEM, and elemental analyzers. Peaks of C-H and epoxy on FTIR spectra showed that Si-GPTMS was formed. The increase of %C and %H from the first to the second step indicated that Si-TEG was successfully synthesized. There was no significant difference in silica particle morphology on SEM before and after modification. The reflux method gave a higher yield compared to the heating method. The constant stirring by the magnetic bar and solvent cycle in the reflux method catalyzed the reaction. This study found that at pH 7, 30 mg of adsorbent weight at 35°C and 22 minutes of contact time were optimum Cd²⁺ adsorption conditions. As the weight of the adsorbent increases, the adsorption capacity decreases. Contact time and temperature have no significant effect on Cd adsorption by Si-TEG.

1. Introduction

Industrial and urban waste is one of the sources of heavy metal pollution in the environment. Some heavy metals have potency as contaminants and could affect human health, including cadmium (Cd), even at low levels. Cadmium is ranked in the top ten environmental toxicants. Mining, industry, wastewater, sedimentation, and agricultural activities are the primary sources of cadmium contamination [1]. In Indonesia, cadmium pollution has been recorded in several regions, for example, in the onion farming land at Brebes, Central Java, with a concentration of Cd of 1.83 ppm [2]. Long-term exposure to cadmium from polluted environments will accumulate and potentially cause various health problems, such as oxidative stress, oncogenesis, and cardiac inflammation [3]. Therefore,

heavy metal pollution must be determined and monitored in various sample environments.

The determination of heavy metals generally uses a flame atomic absorption spectrophotometer (FAAS). The FAAS detection limit for Cd(II) ions is about 0.021 mg/L, while according to Indonesian Government Regulation number 82, the year 2001, the limit for Cd ions in waters is 0.01 mg/L. So, it is necessary to concentrate on the solution to be analyzed or preconcentration. One of the preconcentration methods is solid-phase extraction (SPE), which uses adsorbent for separation. Adsorbent material needs to be studied for its characteristics and adsorption capabilities. As we know, silica gel is one of the most adsorbents used in many applications. Silica is widely used as an adsorbent in adsorption due to its several advantages, including being easy to produce, very

inert, hydrophilic, and high thermal and mechanical stability [4].

The low selectivity of silica adsorption to ion metals is a disadvantage of using silica as an adsorbent, caused by the direct bonding of oxygen. Some research improves the weakness by modifying silica surfaces using organic compounds containing ligands, which are specifically expected to interact with metal ions. Modifications need to be performed to increase silica adsorption capability. Several previous studies have reported the modification of silica-based solid-phase materials for the adsorption of Cd(II) ions, including the amino acid α -glycine [5]; Pyridine 2,6-diylbis (2,2 '(azamethane-1-ylidene) 4- bromophenol) (L); and silica-polyethylene glycol (PEG) [6]. Another adsorbent modification on silica could be used TEG (tetraethylene glycol).

TEG is an inert short-chain PEG that does not react with the analyte in the sample. The TEG -OH and ether groups allow non-covalent interactions between the adsorbent polymer and the target ion. Lin and Zhou [7] have reported that PEG chains are chemically bonded to the SiO₂ nanopowder, are highly hydrophilic on one side of the surface, and, on the other hand, have high chemical reactivity to SiO₂ nanoparticles with functional groups such as isocyanates and amines. Ethylene glycol polymer can trap cations through ion-dipole interactions between cations and oxygen atoms on the ethylene glycol chain.

The adsorption ability of adsorbent material can be tested by batch and column systems. The batch system is a simple, inexpensive, and easy-to-perform adsorption test system. This study aimed to make TEG-bound silica-based adsorbents, characterize the material, and determine the optimal conditions for the variables pH, adsorbent weight, contact time, and adsorption temperature of Cd(II) ions by batch adsorption process using the response surface methodology (RSM).

2. Experimental

The adsorbent synthesis was carried out by reacting silica gel and PEGylating reagent. PEGylation is the process of adding an ethylene glycol polymer group to the silica molecule. The PEGylating reagent used was TEG. The adsorbent was characterized using FTIR spectroscopy, scanning electron microscope (SEM), and CHN elemental analyzers. This study optimized the synthesized material's optimum pH, adsorbent weight, contact time, and temperature using RSM batch adsorption.

2.1. Materials and Instruments

Silica gel (SG) 40-63 μm , N, N-dimethyl formamide, and CdCl₂ were purchased from Merck (Darmstadt, Germany), while 3-glycidoxypropyltrimethoxysilane (GPTMS), tetraethylene glycol (TEG), and molecular sieve 3 Å were obtained from Sigma Aldrich (St Louis, USA). The Cd ion level was determined by flame atomic absorption spectrophotometer (FAAS) AA-7000 (Shimadzu, Kyoto, Japan) at a wavelength of 228.8 nm. The solution's pH was measured using a pH meter HM-20S (TOA, Tokyo, Japan). Batch adsorption was carried out in a Unitronic ORP shaker water bath (JP Selecta, Barcelona, Spain). The

adsorbent's infrared spectra were recorded with an 8400S FTIR spectrometer (Shimadzu, Kyoto, Japan). Morphological and elemental analyses were performed with SEM SU3500 (Hitachi, Ibaraki, Japan) and MT-6 CHN Corder (Yanaco, Kyoto, Japan). The adsorbent was dried in the oven (Mettler, Schwabach, Germany).

2.2. Preparation of TEG-modified Silica

TEG-modified silica was synthesized using a procedure described by Linda *et al.* [8]. The synthesis used silica with a particle size of 40-63 μm and a pore size of 60 Å. Before use, the percentage of CHN in silica was measured. Synthesis methods used were reflux and oven heating. In the first stage reaction, 0.2 g of dry silica gel and 0.2 mL of GPTMS were added to 3.5 mL dry toluene in a stainless-steel column rinsed with acetonitrile. The reaction was conducted in an oven at 110°C for 20 hours. The column was shaken several times manually during the reaction. Silica gel reacted with GPTMS was washed with dry toluene and dried at 75°C for 4 hours.

In the second stage reaction, the dried silica-GPTMS was added with 3.5 mL N,N-dimethyl formamide (DMF), and 0.2 mL TEG in a stainless-steel column. The reaction was conducted in an oven at 120°C for 24 hours. The reaction product was filtered and washed with methanol to remove unreacted reagent residue. The reflux method was conducted with the same composition. However, a reflux system and a magnetic stirrer were used to react to the material. The first stage reaction was performed at 110°C for 20 hours with a stirring speed of 350 rpm. The second stage was done at a temperature of 120°C for 24 hours at a speed of 360 rpm.

2.3. Characterization of Si-TEG

The synthesized adsorbent was characterized using FTIR spectroscopy in the range 400-4000 cm⁻¹, SEM, and CHN elemental analyzers to estimate the structure and functional groups formed on the modified silica.

2.4. Optimization of Cd(II) Adsorption Using Response Surface Methodology

The fractional factorial response surface design with central composite design (CCD) optimization model in Minitab.v.18 software was used for optimization. The optimum condition was determined from the highest adsorption capacity value against four factors: pH, adsorbent weight, contact time, and temperature (Table 1). According to the order of the data matrix set, the batch method was carried out in the experiment by mixing 30-50 mg of adsorbent with 10 mL of Cd(II) solution in 50 mL Erlenmeyer. This mixture was contacted with a variation of 10-30 minutes at a temperature of 30-40°C and a pH 5-9 variation. The adsorption capacity was calculated using Equation (1) [9].

$$Q = \frac{(C_0 - C_e)V}{m} \quad (1)$$

Initial and equilibrium concentrations of Cd(II) are denoted by C₀ dan C_e, respectively. Adsorption capacity (mg/g) is denoted as Q. Solution volume (L) is denoted with V, and the weight of adsorbent (g) is denoted as m.

Table 1. The level of each independent variable

Independent variable	Variable code	Level				
		-2	-1	0	1	2
pH	X1	3	5	7	9	11
Weight of adsorbent (mg)	X2	20	30	40	50	60
Contact time (minute)	X3	0	10	20	30	40
Temperature (°C)	X4	25	30	35	40	45

The experimental design on CCD consisted of 2k fractional factorial with the nf experiment and 2k axial or star points with the nα experiment. The coefficients for four main effects, four quadratic effects, six interactions, and intercepts were estimated and resulted in the mathematical model (2).

$$Y = \beta_0 + \beta_1X_1 + \beta_2X_2 + \beta_3X_3 + \beta_4X_4 + \beta_{11}X_1^2 + \beta_{22}X_2^2 + \beta_{33}X_3^2 + \beta_{44}X_4^2 + \beta_{12}X_{12} + \beta_{13}X_{13} + \beta_{14}X_{14} + \beta_{23}X_{23} + \beta_{24}X_{24} + \beta_{34}X_{34} \quad (2)$$

Where, Y is the predicted response, β₀ is the intercept, β_i is the linear coefficient from i, β_{ii} is the quadratic coefficient of i, and β_{ij} is the interaction coefficient [10].

3. Results and Discussion

3.1. Silica-modified with Tetraethylene Glycol

The synthesis was conducted using silica particles ranging from 40 to 63 μm with a pore size of 60. Before utilization, the silica gel was heated at 110°C for 4 hours to activate it and eliminate the moisture trapped within the silica gel's pores, which may have accumulated during storage. After drying, the silica gel was reacted for 20 hours with GPTMS in dry toluene. GPTMS functions as a crosslinker that connects silica and TEG. GPTMS gives adaptability to the sol-gel arrangement much appreciated to one non-hydrolyzable epoxy gather, advances the coating attachment, and increases compatibility [11]. In the first stage of the reaction, the methoxy silane group in GPTMS hydrolyzed to form a silanol group (Si-OH) [12], resulting in a siloxane bond and leaving the epoxide in the terminal position. The remaining unreacted GPTMS was removed by washing the Si-GPTMS with dry toluene.

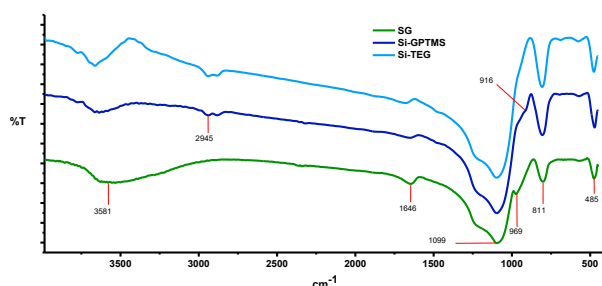


Figure 1. FTIR spectra of silica gel (SG), glycidoxypropyltrimethoxysilane (Si-GPTMS), and silica modified with TEG (Si-TEG)

Table 2. FTIR absorption characteristics of the main functional groups of silica material before and after modification with GPTMS and TEG

Functional group	Wavenumber (cm ⁻¹)	Reference
O-H (hydrogen bonding)	~3456-3425	Uda <i>et al.</i> [13]
O-H (water molecule)	~1632	Ying <i>et al.</i> [14]
Si-O-Si	~1012-1106	Sekar and Venkataprasad Bhat [15]
Si-OH	~1646	Yao <i>et al.</i> [16]
Si-O	~934	Sekar and Venkataprasad Bhat [15]
C-H	~2945	Ghanbari and Attar [17]
Epoxy	810-950	Ghanbari and Attar [17]

The use of dry (anhydrous) toluene as a solvent aims to prevent side reactions that cause the opening of the epoxy ring to produce diol groups due to excess water content. In the reaction between GPTMS and silica, a small amount of water is an acid catalyst in the hydrolysis of GPTMS. Si-GPTMS was then reacted with tetraethylene glycol for 24 hours. The epoxy ring creates secondary alcohol, allowing the tetramer molecule to bond to the silica material.

3.2. FTIR Spectrum

Silica gel, Si-GPTMS, and Si-TEG were characterized using FTIR spectroscopy to see the functional groups formed in the modified material. The results of characterization (Figure 1) show differences in the spectral patterns of each material (Table 2). FTIR spectrum of SG showed the presence of Si-OH groups due to the broad absorption at 3500-3200 cm⁻¹, while the peak at 1646 cm⁻¹ indicated the presence of water adsorbed in the silica gel pores. Si-O-Si groups on silica are indicated by a peak at 1099 cm⁻¹. The peak at 1646 cm⁻¹ is the Si-OH group [16]. Corresponding to the stretching vibration of SiOH, the peak at 934 cm⁻¹ showed the sample's Si-O bonds [15]. The peak 811 cm⁻¹ is indicated by the presence of an epoxy group [17]. Si-O-Si and Si-O vibrations appear in the entire spectrum of the analyzed samples because these two groups are the main groups in the silica.

Silica reacted with GPTMS underwent some spectrum changes (Figure 1). The reduction in O-H absorption intensity at 3600-3200 cm⁻¹ indicates that the Si-OH group of silica has bound to GPTMS [17]. C-H stretching vibrations were indicated at the absorption at 2945 cm⁻¹, and the presence of epoxide groups in the sample was indicated at the absorption at 916 cm⁻¹ [17]. The absorption of epoxy and C-H groups proves that GPTMS has reacted with silica. No new groups were formed from the reaction between Si-GPTMS and TEG. However, from the results of the FTIR spectroscopic

characterization, it was seen that the epoxy peak at $\sim 916\text{ cm}^{-1}$ was no longer formed. This is presumably because the epoxy group has been opened by reacting with the alcohol group at the end of the ethylene glycol chain. In addition, there is an increase in the intensity of the O–H and C–H peaks in Si-TEG, which further confirms that Si-TEG has been formed.

3.3. Elemental Analysis

Elemental analysis was conducted with a CHN elemental analyzer to determine the percentage of elements in the adsorbent material. The determination of the element was carried out on silica gel before and after two reaction methods were modified, and the results are shown in Table 3. There is a small amount of carbon in the silica gel before being modified (0.37%); this occurrence could be attributed to residual impurities possibly lingering in the analytical sample container from previous measurements despite thorough cleaning with ethanol and heating.

The element H in SG is found on the surface of the silica gel, which contains a silanol group (Si-OH). The reaction was evaluated by increasing C and H elements because the silica molecule does not contain C. The increase in C and H elements in reaction steps 1 and 2 resulted from GPTMS and TEG molecules' binding to the silica molecule. The concentration of elements in the material is shown in Table 4.

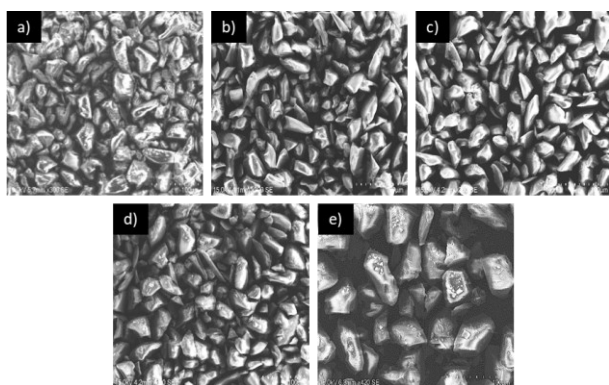


Figure 2. Particle morphologies of (a) silica gel (SG), (b) Si-GPTMS by heating method, (c) Si-TEG by heating method, (d) Si-GPTMS by reflux method, and (e) Si-TEG by reflux method

The synthesis yielded greater quantities when using the reflux method aided by a magnetic stirrer than the oven heating method. However, this outcome may not signify significant differences as we did not replicate the material synthesis process. Using a magnetic stirrer in the reflux method results in constant stirring and is more efficient than the heating method, which requires manual stirring by occasionally shaking the reaction vessel. A solvent cycle in the reflux method also catalyzes the reaction, yielding a higher yield. The final results obtained have a higher percent yield than those reported [8].

3.4. Morphological Analysis of Particle Microstructure

Morphological analysis was done with an electron microscope to study the effect of modification on the microstructure of silica particles. SEM observed silica particles at magnifications of 300 times (Figure 2a-2d) and 420 times (Figure 2e). Silica with a 40–63 m and pore size of 60 Å has an irregular particle shape.

Silica morphology before and after modification (in the first and second steps) showed insignificant changes. This phenomenon is observed because the modification occurs in the silica pores. Differences were observed on the particle surface between the silica modified by the reflux and oven heating methods. The flakes on the silica surface modified by the reflux method in the first and second synthesis steps (Figure 2d-2e) are considered small fractions of the material due to the constant homogenization process by a magnetic stirrer.

3.5. Optimization of Adsorption Cd(II) with Si-TEG

The optimum condition of batch adsorption was determined using response surface methodology (RSM) with a central composite design. This study used a fractional factorial experimental design to review the effect of quantitative variables on a response variable and optimize the response variable. There were 30 treatments from randomization to the four factors used: pH (5–9), adsorbent weight (30–50 mg), contact time (10–30 minutes), and temperature (30–40°C). Treatments with six replicate at the center (treatments 4, 9, 13, 20, 24, and 28) were performed to determine reproducibility and experimental error (Table 5).

Table 3. Percentage of elemental weight to silica weight before and after modification with GPTMS and TEG

Element	Silica gel before modification (SG)	Reflux + magnetic stirring		Oven + manually shaking		Percent yield from Linda et al. [8]
		Stage 1 (Si-GPTMS)	Stage 2 (Si-TEG)	Stage 1 (Si-GPTMS)	Stage 2 (Si-TEG)	
%C	0.37	7.86	8.98	7.98	8.61	7.45
%H	1.27	2.58	2.72	2.62	2.69	1.64

Table 4. The concentration of elements in the material before and after modification with GPTMS and TEG

mmol/g	Silica gel before modification (SG)	Reflux + magnetic stirring		Oven + manually shaking		Linda <i>et al.</i> [8]
		Stage 1 (Si-GPTMS)	Stage 2 (Si-TEG)	Stage 1 (Si-GPTMS)	Stage 2 (Si-TEG)	
C	0.308	6.550	7.483	6.650	7.175	6.208
H	12.599	25.595	26.984	25.992	26.687	16.27

Table 5. Data set matrix used in CCD

No.	Independent variable code				Independent variable randomization				Q (mg/g)
	X1	X2	X3	X4	pH	Weight (mg)	Time (minute)	Temperature (°C)	
1	-1	-1	-1	-1	5	30	10	30	0.4808
2	1	-1	1	1	9	30	30	40	0.9108
3	-1	1	1	-1	5	50	30	30	0.4129
4	0	0	0	0	7	40	20	35	1.0798
5	-1	1	-1	1	5	50	10	40	0.4097
6	1	-1	-1	-1	9	30	10	30	0.8110
7	-1	-1	1	1	5	30	30	40	0.5412
8	1	1	1	-1	9	50	30	30	0.4814
9	0	0	0	0	7	40	20	35	1.0806
10	1	1	-1	1	9	50	10	40	0.4937
11	1	-1	-1	1	9	30	10	40	0.8638
12	-1	-1	-1	1	5	30	10	40	0.4715
13	0	0	0	0	7	40	20	35	1.0805
14	1	-1	1	-1	9	30	30	30	0.8043
15	1	1	1	1	9	50	30	40	0.5613
16	1	1	-1	-1	9	50	10	30	0.5313
17	-1	1	-1	-1	5	50	10	30	0.4395
18	-1	-1	1	-1	5	30	30	30	0.6727
19	-1	1	1	1	5	50	30	40	0.4077
20	0	0	0	0	7	40	20	35	1.0798
21	0	0	0	-2	7	40	20	25	0.9960
22	0	2	0	0	7	60	20	35	0.5882
23	-2	0	0	0	3	40	20	35	0.0486
24	0	0	0	0	7	40	20	35	1.0804
25	0	0	2	0	7	40	40	35	0.8779
26	0	0	-2	0	7	40	0	35	0.9055
27	0	0	0	2	7	40	20	45	0.9196
28	0	0	0	0	7	40	20	35	1.0800
29	0	-2	0	0	7	20	20	35	1.3607
30	2	0	0	0	11	40	20	35	0.4684

Table 6. Analysis of variance (ANOVA) on the experimental design model on the optimization of Cd(II) adsorption on Si-TEG

Source	Degree of freedom	Number of quadrant	Mean of quadrant	F-value	P-value
X1	1	0.252	0.252	37.950	0.000
X2	1	0.471	0.471	70.890	0.000
X3	1	0.002	0.002	0.350	0.565
X4	1	0.001	0.001	0.100	0.755
X1 ²	1	1.541	1.541	231.75	0.000
X2 ²	1	0.092	0.092	13.900	0.002
X3 ²	1	0.170	0.170	25.580	0.000
X4 ²	1	0.106	0.106	15.970	0.001
X1*X2	1	0.043	0.043	6.410	0.024
X1*X3	1	0.002	0.002	0.290	0.600
X2*X3	1	0.009	0.009	1.340	0.267
X2*X4	1	0.006	0.006	0.920	0.354
X3*X4	1	0.000	0.000	0.000	0.973

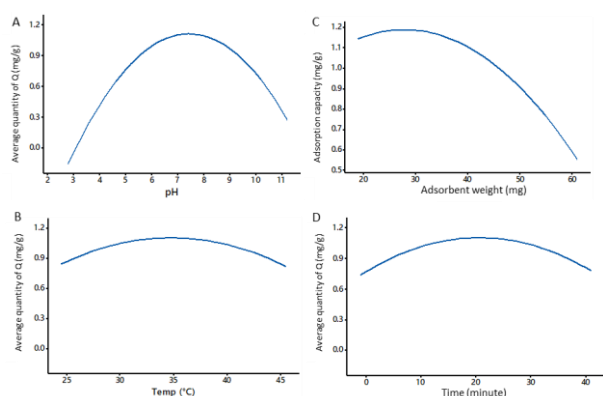


Figure 3. The effect of each variable on the adsorption of Cd(II) on Si-TEG: (A) pH, (B) temperature, (C) adsorbent weight, and (D) contact time

The effect of each factor on the adsorption capacity (Q) can be evaluated from Figure 3. pH and weight of the adsorbent have a significant influence on the response, which is indicated by the curved shape of the parabolic curve. The optimum condition for Cd(II) ion adsorption by TEG-modified silica was at pH 7, with an adsorbent weight of 30 mg. These results follow the reports of Dahaghin *et al.* [18] that neutral pH is a great condition for isolating metals because there is no need to change the pH in a real sample for analysis. Acid conditions will increase the number of protons that can protonate the ether group, while alkaline conditions will increase the number of hydronium ions that can precipitate Cd ions.

Dou *et al.* [10] stated that solution conditions that are too acidic could also increase ether cleavage into smaller fragments. The value of Q decreases as the weight of the adsorbent increases. This is because there has been an imbalance between the amount of adsorbent and adsorbate. The optimum adsorption temperature was obtained at 35 °C and a contact time of 22 minutes. However, the temperature and time variables on the

adsorption of Cd(II) by Si-TEG did not have a significant effect, which was indicated by the shape of a sloping parabolic curve. The three-dimensional curve used to evaluate the interaction between two different variables on Cd(II) adsorption capacity by Si-TEG is shown in Figure 4. The conditions that produce the optimum adsorption capacity are at the top of the curve. A more curved curve indicated that the interaction between the variable pH and adsorbent weight had a significant effect.

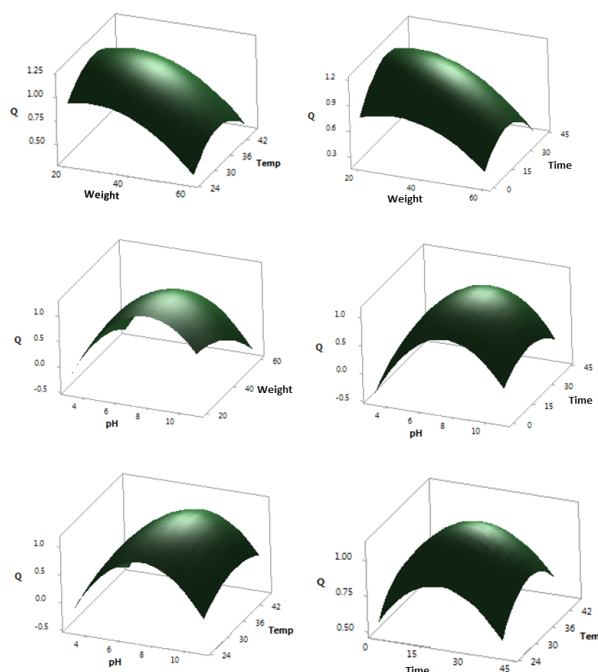


Figure 4. Three-dimensional plot to evaluate the effect of interaction between different variables on adsorption capacity: (A) Interaction between weight and temperature, (B) weight and time, (C) pH and weight, (D) pH and time, (E) pH and temperature, and (F) time and temperature. The unit for each parameter follows the same unit in Figure 3

Table 7. Comparison of the adsorption capacity of cadmium by various types of adsorbents at optimum conditions

Adsorbent	pH	Initial concentration	Weight of adsorbent (mg)	Time (minute)	Temperature (°C)	Q (mg/g)	Reference
Chitosan	6		50	40		1.0080	Rahmi <i>et al.</i> [19]
Fe ₃ O ₄ @SiO ₂ .HO-S	6	0.002	20	720	25	0.56	Zhao <i>et al.</i> [20]
Ferromanganese binary oxide-biochar composite	6	0.01		120		101.00	Zhou <i>et al.</i> [21]
Fe ₃ O ₄ @SiO ₂ .HO-S	6	0.002	20	720	25	0.80	Zhao <i>et al.</i> [20]
Natural zeolite from Aceh, Indonesia	6		1000	40		0.5379	Raziah <i>et al.</i> [22]
Silica	6		300	10	28	0.3518	Indriyani <i>et al.</i> [5]
Si-TEG	7		30	22	35	1.2236	In this study

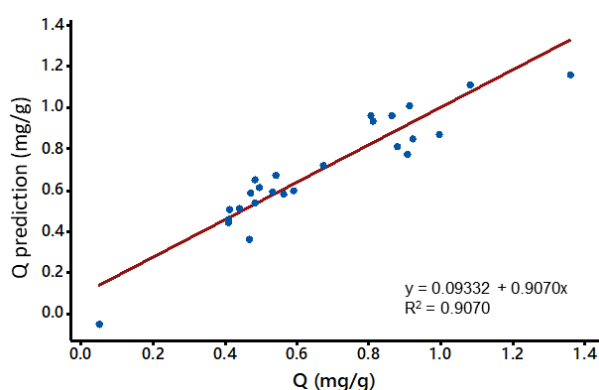


Figure 5. The relationship between the predicted Q and the experimental Q results in the optimization process of Cd(II) adsorption on Si-TEG

The R² value of 0.9070 (Figure 5) indicates a good relationship between the predicted and experimental Q results in the optimization process. Modifying silica with TEG will produce functional groups as ether chains that can form complexes with metal ions (Figure 6) through ion-dipole interactions [23]. Two possible interactions may be formed between Si-TEG and Cd(II). First, ethylene glycol chains can form a helical structure and coordinate with cations (Figure 6a) through ion-dipole interactions [24]. Second, ethylene glycol chains can trap cations similar to crown ether molecules (Figure 6b) but with a more flexible shape, and the size of the trapped cations may be less significant. Ethylene glycol polymers can form helical conformations. PEG molecules form helical in the temperature range of 25–40°C [25].

The quadratic relationship between responses and variables is expressed in the regression equation. The positive sign of the coefficient (β) in the regression equation indicates that the effect of the variable on the response is synergistic, while the negative sign indicates the antagonistic effect. The Q value in various experimental conditions can be predicted based on the following regression equation with a coefficient of determination (R²) of 0.9649 (Equation 3).

$$Q = -6.20 + 0.913 \text{ pH} + 0.0549 \text{ weight} + 0.0409 \text{ time} + 0.1554 \text{ temp} - 0.05926 \text{ pH} \cdot \text{pH} - 0.000581 \text{ weight} \cdot \text{weight} - 0.000788 \text{ time} \cdot \text{time} - 0.002489 \text{ temp} \cdot \text{temp} - 0.00258 \text{ pH} \cdot \text{weight} - 0.00055 \text{ pH} \cdot \text{time} + 0.00236 \text{ pH} \cdot \text{temp} - 0.000196 \text{ weight} \cdot \text{time} - 0.000014 \text{ weight} \cdot \text{temp} + 0.000092 \text{ time} \cdot \text{temp} \quad (3)$$

The feasibility of the model used was tested by analysis of variance (ANOVA) (Table 6). Variables with a calculated P-value <0.05 indicate a statistically significant effect [26]. ANOVA test using Minitab revealed that pH and weight of the adsorbent played a significant role as independent variables and quadratic variables; contact time and temperature played a significant role as quadratic variables. The interaction between pH and weight on Cd(II) adsorption on Si-TEG had a significant effect.

A comparison of the adsorption capacity of Cd at optimum conditions with initial concentrations of 1–10 ppm by various types of adsorbents is shown in Table 7. TEG-modified silica has a reasonably high capacity than some other adsorbents. Silica has a lower adsorption capacity than Si-TEG; thus, modifying silica can enhance its adsorption capacity.

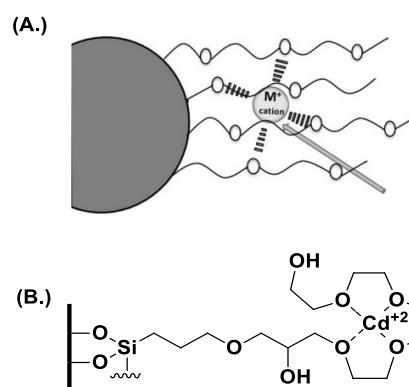


Figure 6. Prediction of interactions formed between Si- TEG and Cd(II) ions: (A) helical chains and (B) resembling crown ether [23, 24]

4. Conclusion

TEG-modified silica has been successfully synthesized and characterized using FTIR spectroscopy, SEM, and elemental analysis. The presence of C-H and epoxy peaks in the spectra indicated the formation of Si-GPTMS. Moreover, the observed rise in %C and %H during the second reaction step signified the formation of Si-TEG. Synthesis by reflux method gave more yield compare to the heating method. The optimum conditions for Cd²⁺ adsorption were obtained at pH 7, and the adsorbent weight was 30 mg at a temperature of 35°C and a contact time of 22 minutes. The adsorption capacity decreases as the adsorbent weight increases. Contact time and temperature did not significantly affect the adsorption of Cd by Si-TEG.

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