Optimization of hexavalent chromium ion adsorption using natural silica modified with DMA (Dimethylamine) by batch method

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Abstract. Heavy metals are the most dangerous source of pollution for environmental systems because they have non-biodegradable, toxic, and even carcinogenic properties even in low concentrations (ppm). Usually metals are insoluble, precipitated, dissolved, absorbed, inorganic, reduced, oxidized, and free of metals. One of the heavy metals that can cause negative effects on humans and living things is chromium ion. One way to overcome chromium metal in waste is to absorb it with DMA modified silica adsorbent. The adsorption of chromium (VI) from aqueous solutions was examined at various pH, contact times, and initial Cr (VI) concentrations. Langmuir adsorption isotherm yields a regression coefficient R² = 0.9807. In the initial conditions Cr (VI) 100 mg L⁻¹, pH 2.0 with stirring for 90 minutes, the maximum adsorption capacity of Cr (VI) was 1,024 mg g⁻¹. In this study, researchers used natural silica modified with dimethylamine as an adsorbent for the adsorption of Cr (VI) ion, GPTMS (glycidoxypropyltrimethoxilane) as an intermediate or bridge connecting silica with DMA (modifying compound).

1. Introduction
Chromium metal has an important role in supporting various industrial sectors, such as in the metal industry, electroplating, tanning leather, dyes and various other sectors. However, waste disposal from the use of chromium can pollute the environment. Chrome is a heavy metal that has hazards to watch out for. In competition, Cr (VI) is very toxic, corrosive, carcinogenic, and has very high solubility. Chromium (VI) is found in two forms of ion species, namely as Cr₂O₇²⁻ anions (in acidic solutions) and CrO₄²⁻ anions (in basic solutions)[1]. Chromate ions are yellow, and dichromate ions are orange. one of the most important environmental problems to be aware of is the presence of heavy metals such as Cr (VI) in water, the presence of Cr (VI) in water can harm the environment, so it is necessary to overcome this metal [2] Currently, one of the cheapest and easiest methods to remove heavy metals of the aqueous solution is the adsorption of heavy metals by various adsorbents.[3]. Silica is an adsorbent that is often used in adsorption. Silica is a stable solid support under acidic conditions, porosity and specific surface area, also have high resistance to heat, but the effectiveness of silica adsorption on weak metal ions. This is caused by the low ability of oxygen (silanol and siloxan) as electron pair donors, resulting in weak metal ion bonds on the surface of silica [4].

The weakness of silica as an adsorbent can be corrected by several attempts, including by modifying the surface of silica [4]. Silica is often modified with organic groups formed to increase the ability of
adsorption. In 2009, Jiang et al succeeded in analyzing inorganic anions in seawater samples using silica which was modified with cetyltrimethylammonium ions as a stationary phase [5]. In 2013, Wang et al succeeded in absorbing chromium ions by using silica that has been modified with imidazole compounds [6]. In 2020, Oktavia and Kardi succeeded in making a monolith column with silica using dimethylamine (DMA) as a modifier and ethylene dimethacrylate as a crosslinker and its use in ion chromatography [7][8] 

In this study, researchers used natural silica modified with dimethylamine as an adsorbent for the adsorption of Cr (VI) ion, GPTMS (glycidoxypropyltrimethoxilane) as an intermediate or bridge connecting silica with DMA (modifying compound). Chromium (VI) is one of the priority pollutants in surface air and ground air, and is mainly present in the form of Cr\(_2\)O\(_7\)\(^{2-}\) anions (in acidic solutions) and CrO\(_4\)\(^{2-}\) anions (in alkaline solutions).

2. Experiment

2.1 Material
The materials used are natural silica, GPTMS, Dimethylamine, aquades, HCl, NaOH, K\(_2\)Cr\(_2\)O\(_7\), Ethanol and Methanol

2.2. Preparation of a standard solution of Cr (VI)
A standard concentration of 1000 ppm anion solution is made by dissolving K\(_2\)Cr\(_2\)O\(_7\) as much as 1 gram with a little distilled water, put into a 1000 ml measuring flask, add aquades to the mark mark. Stir until homogeneous and put in a reagent bottle. Solution work is prepared by proper dilution of standard solutions.

2.3. Preparation of 1M HCl solution
8.52 mL of 36% HCl solution pipette was put into a 100 mL volumetric flask after which aquades were added to the mark and put into a reagent bottle.

2.4. Preparation of 1M NaOH solution
Weigh NaOH powder as much as ± 4 g, put it in a beaker, add distilled water, stir until homogeneous, then put into 100 mL volumetric flask, add distilled water again until the boundary mark marks until homogeneous and put in a reagent bottle.

2.5. Silica Preparation
Blended natural silica (reduce particle size) with a smoothing machine at PT. Semen Padang, then carried out sifting with mesh in the Laboratory of SMK-SMAK Padang to get a particle size of 45µm. The 45µm 35 gram silica sample was soaked and stirred in 350 ml of 1M HCl for 24 hours. The pH is neutralized with aquades and dried in the oven for about 2 hours at 105°C.

2.6. Formation of Silica-GPTMS
Weigh 25 grams of activated silica and add 25 ml of GPTMS and 87.5 ml of toluene. The mixture is stirred at 90°C for 24 hours. Wash the mixture with 12.5 ml of methanol.
2.7. Modification of silica-GPTMS - Dimethylamine (DMA)
23 grams of silica-GPTMS modified with 11.5 ml in 11.5 ml ethanol. The silica is roasted for 4 hours at 80 °C. After being heated, rinse with methanol [6] [7].

2.8. Treatment research with a batch system

2.8.1. Effect of pH of solution. Chromate solution and dichromate 25 ml concentration of 125 ppm, each in a variation of pH 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 were put into the erlenmeyer contacted with Silica ± 1 g using a shaker for 120 minute speed of 150 rpm, then filtered with filter paper, the filtrate obtained measured by the concentration electronically. The optimum pH obtained is used for further research. The pH media was prepared by adding 1 M NaOH solution or 1 M HCl solution. The effect of pH variations was determined by the batch system adsorption method.

2.8.2. Effect of solution concentration. Chromate solution and 25 ml dichromate are adjusted to the optimum pH, each solution in a variety of concentrations of 25, 50, 75, 100, and 125 ppm is put into the erlenmeyer contacted with Silica ± 1 g using a shaker for 120 minutes speed 150 rpm, then filtered with filter paper, the filtrate obtained measured by electronically. The optimum concentration obtained is used for further research. The effect of concentration variations is determined by the batch system adsorption method.

2.8.3. Effect of contact time. Chromate solution and 25 ml dichromate are adjusted to the optimum pH, the optimum concentration is put into the erlenmeyer, contacted with Silica ± 1 g using a shaker with contact time variations of 30, 60, 90, 120, and 150 minutes speed of 150 rpm, then filtered with filter paper, the filtrate obtained measured by the electron concentration. The effect of contact time variations is determined by the batch system adsorption method.

2.8.4. Comparison of Sorption Capacity. Silica after activation, silica with the addition of GPTMS, modified silica each ± 1 g was contacted with 25 ml of chromate and dichromate solution at optimum pH, optimum concentration and optimum stirring time as the above determination results. The resulting filtrate was analyzed using spektronik to see the chromate and dichromate concentrations. The percentage of removal and absorption capacity of silica against harmful pollutants can be determined by examining the pollutant concentration before and after contact with the silica with spektronik.

\[
\text{% Removal} = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)
\]

\[
q = \frac{m}{V} \quad (2)
\]

Where \(C_0 (\text{mgL}^{-1})\) and \(C_e (\text{mgL}^{-1})\) are the liquid phase concentration of \(\text{Cr(VI)}\) at initial and at time, respectively, \(V (\text{L})\) is the volume of \(\text{Cr (VI)}\) solution and \(m (\text{g})\) is the mass of silica modified [2].
3. Results and Discussion

3.1. Effect of pH on Absorption of Chrome (VI) Using DMA Modified Natural Silica as Adsorbent

The influence of pH is an important parameter in the absorption of Chrome (VI). The effect of pH is very necessary because the binding between Cr (VI) involves the exchange of H\(^+\) ions. [9]. The present study carried out variations in pH from pH 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10. Good conditions for adsorption are at low pH [10], because at low pH the H\(^+\) ion at the surface of the adsorbent increases so as to produce, resulting in an electrostatic bond between the positive charge on the surface of the adsorbent with Cr(VI). Meanwhile, with increasing pH, the adsorption of Cr (VI) ions will decrease, because at high pH, the concentration of OH\(^-\) in the solution will increase, so that the cell surface slowly becomes negatively charged.

![Figure 2](image.png)

Figure 2. Effect of pH on absorption of dichromate anions using natural silica as an adsorbent (Condition: 25 ml 125 ppm dichromate solution, 1 g adsorbent, stirring speed 150 rpm, 120 minutes time).

The optimum pH results obtained at pH 2, the absorption obtained was 1.234 mg / g with a percentage of absorption of 40.76%. absorption capacity increases from 0.5115 mg / g to 1.234 mg / g with decreasing pH values from 10 to 2. In aqueous solution, hexavalent chromium is found in 2 species in chemical equilibrium

\[
2\text{CrO}_4^{2-} + H^+ \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + H_2O
\]

The predominant diagram shows that the equilibrium position depends on the pH value of the solution. When the pH value of the chromate solution is reduced (plus acid), the solution changes color until an orange color appears from the dichromate ion. When the hydrogen ions increase, the equilibrium shifts to the right. When excess hydroxide ions are added, the hydroxide ions will react with hydrogen and the equilibrium shifts to the left.

3.2. Effect of concentration on absorption of Cr (VI) Using DMA modified natural silica as adsorbent

Concentration is also an important parameter for the adsorption of Cr(VI) by adsorbents because the higher the concentration the higher the amount of Cr(VI) in solution so that the higher absorption occurs, but if the adsorbent has reached the saturation point then the absorption that occurs will tend to be constant [11], variations in concentration conducted in this study to do 5 variations of 25, 50, 75, 100, and 125 ppm at pH 2. The optimum results obtained are at a concentration of 100 ppm with an
absorption of 0.76375 mg / g with a percentage of absorption of 1.46%, the overall results can be seen in Figure 3 below.

![Figure 3](image)

**Figure 3.** Effect of concentration on absorption of Cr (VI) using natural silica as an adsorbent (Condition: 25 ml dichromate solution, pH 2, adsorbent 1 g, stirring speed 150 rpm, time 120 minutes)

The results obtained in Figure 3 can be seen an increase in absorption of CrO$_4^{2-}$ and Cr$_2$O$_7^{2-}$ from the concentration of 25 ppm to 100 ppm and at a concentration of 125 has decreased absorption. This can be related to the number of active sites in the adsorbent when the number of active sites that are in the adsorbent is greater than the amount of CrO$_4^{2-}$ and Cr$_2$O$_7^{2-}$ then the absorption that occurs will also be greater, when at a concentration of 125 ppm the number of metal ions absorbed will be the same as the number of active sides available, this will result in optimal absorption or also often called the equilibrium state [12] so that if the concentration is added it will not cause an increase.

The equilibrium between the adsorbent and adsorbate can be determined by the Langmuir isotherm. The langmuir isotherm, which states that adsorption occurs only in a single layer (monolayer) [13], which occurs on the surface, in figure 4 you can see the Langmuir isotherm curve.

![Figure 4](image)

**Figure 4.** Langmuir Isotherm

In order to obtain information about the properties and the mechanism of the sorption process, the langmuir (Eq.(3)) dan freundlich (Eq (4)) models were used in this study to characterize adsorption isterm, respectively.

\[
\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{k_1q_mC_e} \tag{3}
\]
\[ \log q_e = \log k_f + \frac{1}{n} \log C_e \]  

(4)

Where \( q_m \) (mg/L) is maximum adsorption capacity, \( C_e \) is the equilibrium concentration of Cr (VI) in solution, \( k_l \) (L/gr) is the langmuir constant. The parameters of \( k_f \) ((mg/g)/(mg/L)) and \( n \) are the constans freunlich model, respctively.

The values of corelation coefisient (R2) for langmuir model is 0.9807 and freunlich model is 0.8808 respectively. It can be seen that langmuir model represent a good fit with the experimental data [2].

3.3. Effect of contact time on absorption of Cr (VI) using DMA modified natural silica as adsorbent

Stirring time aims to determi ne the amount of time needed for adsorbent to adsorb \( \text{CrO}_4^{2-} \) and \( \text{Cr}_2\text{O}_7^{2-} \) so that it can bind \( \text{CrO}_4^{2-} \) and \( \text{Cr}_2\text{O}_7^{2-} \) optimally. Determination of the optimum capacity of the effect of the stirring time is done with variations of 30, 60, 90, 120, and 150 minutes with a pH of 2, a concentration of 100 ppm. The longer the contact time the greater the absorption of \( \text{CrO}_4^{2-} \) and \( \text{Cr}_2\text{O}_7^{2-} \), the effect of the time of contact / stirring by the adsorbent on the \( \text{CrO}_4^{2-} \) and \( \text{Cr}_2\text{O}_7^{2-} \), can be seen from figure 5.

![Figure 5](image)

**Figure 5.** Effect of contact time on absorption of dichromate anions using natural silica as an adsorbent (Condition: 25 ml of 100 ppm dichromate solution, pH 2, adsorbent 1 g, stirring speed 150 rpm)

In figure 5, it can be seen that the optimum contact time is 90 minutes with the absorption rate of 1.025 mg / g, the percentage of absorption is 39.41%. The absorption capacity of \( \text{CrO}_4^{2-} \) and \( \text{Cr}_2\text{O}_7^{2-} \) to silica increases with increasing stirring time, Absorption of \( \text{CrO}_4^{2-} \) and \( \text{Cr}_2\text{O}_7^{2-} \) increases due to \( \text{CrO}_4^{2-} \) and \( \text{Cr}_2\text{O}_7^{2-} \) which binds to the adsorbent the longer the time, the more anion of \( \text{CrO}_4^{2-} \) and \( \text{Cr}_2\text{O}_7^{2-} \) which will bind to the active side of the adsorbent to the saturation point when it is at the saturation point which is 120 to 150 minutes of absorption will tend to be constant this is because the active site has been bound to anion chromate (\( \text{CrO}_4^{2-} \)) and dichromate (\( \text{Cr}_2\text{O}_7^{2-} \)) has been saturated so that it cannot bind again[14].

3.4. Comparison of adsorption capacity of silica, silica-GPTMS, silica-GPTMS-DMA under optimum conditions

Comparison of the adsorption capacity of silica, silica-GPTMS, silica-GPTMS-DMA at optimum conditions can be shown in figure 6 below:
Figure 6. Comparison of silica-GPTMS, silica-GPTMS-DMA adsorption capacity (condition: 25 ml of 100 ppm Cr solution, pH 2, 1g adsorbent, 90 minutes stirring time, and 150 minutes speed)

The figure above shows that silica-GPTMS-DMA increases the adsorption capacity for chromate and dichromate anions, the adsorption capacity of chromate anion and silica-GPTMS-DMA dichromate is higher than silica-GPTMS and silica activation.

4. Conclusion
Modified DMA silica can be used as an adsorbent to absorb Cr (VI) ions with the optimum capacity obtained at a pH of 2, a solution concentration of 100 mg/L, for 90 minutes of stirring time. The maximum absorption capacity obtained from the absorption of Cr (VI) ions by using modified DMA silica as biosorbent is 1.024 mg/g, increasing from 0.65 for silica before modification.

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