Adsorption of Lead Metal Ions In Solution With Diphenylcarbazide Modified Silica Gel

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ABSTRACT
Silica gel is one of the adsorbents whose surface is easy to modify and can be used in the adsorption of heavy metal ions. This study aims to modify silica gel with diphenylcarbazide and use it as an adsorbent for Pb²⁺ metal ions. The modification was carried out by impregnation of silica gel with diphenylcarbazide solution at a ratio of 1 gram of silica gel and 1 mmol of diphenylcarbazide. Characterization with IR spectrophotometry to analyze the functional groups formed on the modified silica gel and the initial silica gel, acid-base titration to determine the surface acidity, and methylene blue method to determine the surface area of the two silica gels. The results showed that the modification of silica gel with diphenylcarbazide had been successfully made, indicated by the appearance of the absorption band of the N-H group at ±3375.43 cm⁻¹, aromatic C-H at ±3032.10 cm⁻¹ and C=O at 1658.78 cm⁻¹, which are groups derived from diphenylcarbazide, and the absorption band of the Si-O-Si group at ±1203.58 cm⁻¹, the Si-OH group at 912.33 cm⁻¹, and the –OH group in the wave number range of 3600 -3400 cm⁻¹, which is the main group of silica gel. Diphenylcarbazide-modified silica gel experienced an increase in surface acidity from 0.5205 to 0.8133 mmol/g, and a slight increase in surface area from 46.1057 to 46.1613 m²/g. Adsorption of diphenylcarbazide modified silica gel on Pb²⁺ metal ions in optimum solution occurred at pH 3, contact time 10 minutes, and initial concentration of Pb²⁺ 300 mg/L, with an adsorption capacity of 52.6264 mg/g. The adsorption that occurs follows the Langmuir isotherm.

Keywords: Modified silica gel, Diphenylcarbazide, adsorption, Lead Metal Ions

INTRODUCTION
The presence of Pb metal in waters is a problem that needs special attention, because this heavy metal can adversely affect all organisms in the waters and can accumulate in the food chain (Ali et al., 2023; Pandey & Kumari, 2023; Saidon et al., 2024; Thanigaivel et al., 2023). Lead is highly toxic if it accumulates in the body. The effect of acute Pb toxicity is rarely found, but the influence of chronic Pb toxicity is often found especially in miners, painting,
printing and metal plating (Abed et al., 2023; Deng et al., 2022; Nakata et al., 2022). Lead can enter the human body through food, drink, and polluted air or dust. Lead can accumulate in the body and cannot be decomposed, so if Pb poisoning can have an impact on the kidneys, brain, reproductive system, liver, damage the nervous system, disrupt enzyme function and the rate of hemoglobin in the body becomes inhibited. Lead poisoning has been known since ancient Egyptian times and Greek physicians about 5000 years ago. Lead poisoning is one of the oldest diseases in the history of human civilization (Y.-G. Chen et al., 2021; Petrović, 2024; Rosselli et al., 2023; Xu et al., 2022). In recent years, lead poisoning has been recognized as one of the most serious environmental health problems worldwide, especially children living in developing countries (Adesogan et al., 2020; Imathiu, 2020; Workie et al., 2020). Lead can cause serious illness at a young age, especially in developing brains. Lead can reduce IQ levels, slow growth and damage the kidneys. Some cases of lead poisoning can lead to coma or death (Organization, 2002).

Given the negative impact caused by Pb metal, the presence of the metal as a pollutant in the environment needs to be minimized and even eliminated (J. Chen, 2020; Leach et al., 2020; Rosenkranz et al., 2021). Several chemical and biological methods have been tried to remove heavy metals contained in waste, including adsorption, ion exchange, and separation by membrane. One easy and environmentally friendly method to overcome the problem of heavy metals is the adsorption method. This method is widely used because it is safer, does not provide side effects that endanger health, and does not require complicated, cheap, and easy-to-work equipment. The performance of the adsorption method is affected by the type of adsorbent, adsorbate, pH, and contact time. One widely used adsorbent is silica gel (SiO2).

Silica gel is one of the inorganic solids that has active sites of silanol (Si-OH) and siloxane (Si-O-Si) groups on the surface as well as physical properties such as mechanical stability, porosity and surface area. The presence of an –OH group capable of forming hydrogen bonds with the same group of another molecule causes silica to be used as a desiccant and stationary phase in chromatographic columns or adsorbents for organic compounds. The adsorption process can occur due to interactions, both physically and chemically with the active surface and pores of the adsorbent (Abegunde et al., 2020; Baidya & Kumar, 2021; Gayathiri et al., 2022; Neolaka et al., 2023). Silica gels used as adsorbents of metal ions are generally first modified both chemically and physically (impregnation).

Terrada et al. (1983) impregnated silica gel supporting solids, activated carbon and polytriflourochlooroethylene with impregnant materials 2,5-dimercapto-3,4-triadizole (DMT), 2-mercaptopbenzimidazole (MBT) for adsorption of Cu(II) in an aqueous medium. Adsorption of these metals is only effective at a certain pH for each type of ligand. Sudiarta et al (2013) modified silica gel from rice husk ash with diphenylcarbazone where the best modification was obtained at the ratio of mmol diphenylkarzon and gram silica gel is 1: 1, with a stirring time of 4 hours. The utilization of modified silica gel as an adsorbent has been reported to be widely
publicized. Giri et al (2014) utilize silica gel modified difelcarbazide as an adsorbent of metal Cr(VI). Diphenylcarbazide is one of the ligands that has been used to modify silica gels. This ligand belongs to the polydentate ligand group because it can provide more than two donor atoms electron pairs in the formation of bonds with metals (Bagheri et al., 2012).

**RESEARCH METHODS**

The chemicals used in the study were toluene, ethanol, diphenylcarbazide, silica gel 60, diethyl ether, sodium hydroxide, aquades, phenol phthalein indicator, hydrochloric acid, methylene blue solution, Lead nitrate, and nitric acid. The equipment used is laboratory glassware, Shimadzu/IR Prestige-21 FTIR Spectrophotometer, Shimadzu/UV-1800 UV-Vis Spectrophotometer, Shimadzu/AA-7000 Series atomic absorption spectrometer, magnetic stirrer, oven.

**Physical modification of silica gel with diphenylcarbazide**

Silica gel modification is carried out following the procedure that has been carried out by Sudiarta (2013) (Belyakova & Varvarin, 1999; Péré et al., 2005; Świtaj-Zawadka et al., 2004). A total of 0.24 g (1.0 mmol) of diphenylcarbazide is put into a mixture of 20 mL of toluene and 10 mL of ethanol and stirred until completely dissolved. A total of 1.0 g of silica gel was added to the solution and stirred with a magnetic stirrer for 4 hours. Silica gel modified diphenylcarbazide (Si-DPZid) is filtered, washed with 10 mL toluene, 10 mL ethanol and finally using 10 mL diethyl ether and dried at 60ºC in the oven. Si-DPZid adsorbents are characterized by FTIR to determine the change in functional group groups due to modification, acid-base titration to determine surface acidity and Methylene Blue adsorption method to determine the surface area of adsorbents.

**Si-DPZid Adsorption Study of Pb2+ Metal Ions**

Si-DPZid adsorption study on Pb2+ ions was carried out by bath adsorption method. A total of 0.1 g of adsorbent was interacted with 25 mL of Pb2+ solution in a 50 mL erlenmeyer glass then stirred with a magnetic stirrer for 30 minutes at a fixed speed. The effect of the initial pH of the solution on the adsorption power of Pb2+ on Si-DPZid was carried out in an acidic atmosphere, namely pH 1, 2, 3, and 4 using a solution of Pb2+ 200 mg / L. Variations in stirring time of 5, 10, 20, 30, 40, 50, and 60 minutes were carried out to determine the effect of stirring time on the amount of Pb adsorbent in the adsorbent at the optimum pH. The effect of the initial concentration of Pb solution on the adsorption power of Zi-DPZid was carried out with initial concentrations of 100, 200, 300, 400, 500, and 600 mg / L, interacted with adsorbents at pH and optimum stirring time.
RESULTS AND DISCUSSION

Physical modification of silica gel with diphenylcarbazide

The interaction that occurs in the silica gel modification process with diphenylcarbazide is likely through Van Der Waals forces. The attraction between the siloxane (Si-O-Si) and silanol (Si-OH) groups of silica gel having a negative dipole moment and the NH group of the diphenylcarbazide ligand having a positive dipole moment. Interaction can also be through hydrogen bonding between the H atom of the diphenylcarbazide with the O atom of silica gel, and vice versa. Modification of silica gel with diphenylcarbazide can add the active site of silica gel so that it can more effectively adsorb metal ions.

The characterization of silica gel and diphenylcarbazide modified silica gel includes determination of surface acidity by acid-base titration, surface area by methylene blue method, and functional groups by FTIR analysis. Both silica gels have surface area and acidity as listed in Table 1.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Cal Surface Acidity (mmol/g)</th>
<th>Surface area S(m2/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica gel without modification</td>
<td>0.5205</td>
<td>46.1057</td>
</tr>
<tr>
<td>Silica gel modified diphenylcarbazide</td>
<td>0.8133</td>
<td>46.1613</td>
</tr>
</tbody>
</table>

Based on Table 1 it can be seen that there is an increase in surface acidity due to modification with diphenylcarbazide compared to without modification. The increase in surface acidity occurs due to the binding of diphenylcarbazide which carries the acid sites in silica gel. Modification of silica gel with diphenylcarbazide does not cause significant changes in surface area, only a slight increase in surface area. This indicates.

IR spectra of silica gelled modified diphenylcarbazide (Si-DPZid) in Figure 1 show that in addition to the appearance of the main functional groups of silica gel such as silanol in the wavenumber region 912.33 cm\(^{-1}\), siloxane at 1203.58 cm\(^{-1}\), and –OH at 3622.32 cm\(^{-1}\), vibration of the (N-H) group of amide at say wave 3375.43 cm\(^{-1}\), the aromatic (C-H) group in the wavenumber region 3032.10 cm\(^{-1}\) was also detected. The infrared spectral results show that silica gel modified diphenylcarbazide has been successfully made as evidenced by the detection of the functional groups mentioned above in the spectral results.
**pH Optimum Adsorpsi**

The effect of unmodified silica gel adsorption pH and diphenylcarbazide modified silica gel (Si-DPZid) on Pb$^{2+}$ ions shows that pH 3 is the optimum pH of Pb$^{2+}$ adsorption with unmodified silica gel adsorbent and diphenylcarbazide modified silica gel (Si-DPZid). At pH 1 and 2 the amount of Pb$^{2+}$ absorbed is less, this is because at pH 1-2 the adsorbent is surrounded by H$^+$ ions so that there is competition between Pb$^{2+}$ ions and H$^+$ ions. At pH 3 the amount of absorbed Pb$^{2+}$ ions reaches its highest point, after which a rise in pH causes a decrease in adsorption activity, which means silica gel is no longer able to bind Pb$^2+$ metal, even absorbed Pb$^{2+}$ is released. Thus, the optimum Pb$^{2+}$ adsorption pH occurs at pH 3 with an average absorption of unmodified silica gel of 19.1359 ± 0.2341 mg / g and in diphenylcarbazide modified silica gel (Si-DPZid) of 31.6325 ± 0.0313 mg / g. These results showed that diphenylcarbazide modified silica gel (Si-DPZid) absorbed more Pb$^{2+}$ metal ions than unmodified silica gel. The degree of acidity (pH) can affect the adsorption process. The pH of the solution can cause changes in the surface properties of the adsorbent, the properties of adsorbate molecules and changes in the composition of the solution. In addition, pH will also affect the metal species in the solution so that it will affect the interaction of metal ions with adsorbents (Riapanitra et al. 2006).

**Optimum adsorption time**

The variation in contact time of Pb$^{2+}$ ions with unmodified silica gel and diphenylcarbazide modified silica gel (Si-DPZid) is 5 - 60 minutes. The adsorption results of unmodified silica gel and diphenylcarbazide modified silica gel (Si-DPZid) to the contact time of Pb$^{2+}$ ions showed that the absorption of unmodified silica gel and modified silica gel to Pb$^{2+}$ ions increased in the first 10 minutes, then remained relatively constant as the adsorption time increased. The optimum adsorption process of silica gel without modification or diphenylcarbazide modified silica gel to Pb$^{2+}$ metal occurred at an adsorption time of 10 minutes with an average absorption capacity of 18.7289 ± 0.0793 mg / g, and 32.2304 ± 0.0992 mg / g. Fluctuations in the absorption of Pb$^{2+}$ metal against the contact time that occurs in the two silica gels indicate that the interaction force of Pb$^{2+}$ metal with the adsorbent is weak (physical interaction), where the metal that has been absorbed in the adsorbent is easily released back into solution. The saturation state is reached when the adsorbent reacted with the adsorbate passes its optimum time and the adsorbent is no longer able to absorb the adsorbate (Castellan, 1982). If the adsorbent is saturated, the adsorption time no longer has an effect. The optimum contact time of adsorption is achieved when there is a balance between the surface phase (adsorbate absorbed by the adsorbent) and the bulk phase (adsorbate remaining in solution). Under this condition the amount of adsorbate adsorbed by the adsorbent is fixed relative to the contact time.
Effect of initial concentration of Pb2+ with the amount of adsorbed Pb2+

Determination of the amount of Pb2+ adsorbed by unmodified silica gel adsorbent and diphenylcarbazide modified silica gel (Si-DPZid) was carried out at various Pb2+ concentrations, namely, 100, 200, 300, 400, 500, and 600 ppm. Adsorption is carried out at pH 3 with a contact time of 10 minutes. This concentration variation aims to determine the amount of Pb2+ optimally absorbed in each gram of unmodified silica gel adsorbent and diphenylcarbazide modified silica gel (Si-DPZid). Based on this study, it was found that the data from the analysis of variations in Pb2+ concentration on the amount of adsorbed Pb2+ there was an increase in the amount of Pb2+ absorbed along with variations in Pb2+ concentrations from 100 to 400 ppm in unmodified silica gel adsorbents, then after the concentration of 400 ppm decreased, then again increased at a concentration of 600 ppm, but the absorption was lower than the absorption capacity at a concentration of 400 ppm. Thus, the maximum adsorption process of silica gel without modification to Pb2+ ions occurred at a concentration of 400 ppm with an average absorption of 49.8455 ± 0.0371 mg / g.

While the modified silica gel adsorbent diphenylcarbazide (Si-DPZid) shows that there is an increase in the amount of Pb2+ absorbed along with variations in concentration from Pb2+ 100 ppm to 300 ppm, then after the concentration of 300 ppm decreases. The greater the concentration of Pb2+, the greater the amount of Pb2+ adsorbed on the surface of the adsorbent but will decrease when it has reached the optimum concentration. This is due to the interaction between the adsorbent surface and the adsorbate which is getting bigger due to the abundance of Pb2+ ions in the solution, so that if it has not reached the optimum state, the concentration of Pb ions dissolved in the solution is increasing, then the attraction between Pb2+ ions and the adsorbent surface is also getting bigger, but will decrease after reaching the optimum concentration. This is because the adsorbent is saturated and will come off because the bond is very weak. The amount of Pb2+ ions absorbed in the diphenylcarbazide modified silica gel adsorbent (Si-DPZid) with an optimum concentration of 300 ppm was 52.6264 ± 0.05549 mg/g. Sari (2015) with silica gel from rice husk ash modified diphenylcarbazide at a concentration of 300 ppm was able to absorb Cr (III) ions of 55.4857 mg / g at pH 4 and contact time 70 minutes.

According to Martell and Hancock (1996) in silica gel there are silanol groups (Si-OH) and siloxane (Si-O-Si) which are thought to play a role in the adsorption process of Pb2+ metal ions. The electronegativity of H, O, Si atoms, respectively by 2.2; 3.44; 1.9. Judging from the difference in the electronegativity value of each atom, the bond in the silanol group is more ionic than the bond in the siloxane group which tends to be more covalent. As a result, the H atom in the silanol group will be released and replaced by the electropositive logan Pb2+ ion. This interaction allows the adsorption of metal ions through ion exchange mechanisms. In solution Pb2+ can form Pb(OH)2 complexes. The interaction between hydrogen from the OH group at Pb(OH)2 with the active groups of silanol and iloxane in silica gel can allow adsorption
of Pb2+ metal ions through hydrogen bonding. This hydrogen bond does not only occur in the active group in silica gel, but can also occur in diphenylcarbazide ligands that have N atoms that have free electron pairs that can bond with hydrogen from the OH group in Pb(OH)2 (Martell and Hancock, 1996). Adsorption of Pb2+ ions to silica gel may also occur through the formation of complexes between the active groups of adsorbents as ligands with Pb2+ ions as the central atom. Based on hard and soft acid-base theory, Pb2+ ions are intermediate acid groups, then will react with hard alkaline adsorbents, these interactions can form complex compounds.

**Determination of Adsorption Isotherms Pattern**

The type of adsorption that occurs in unmodified silica gel adsorbents and diphenylcarbazide modified silica gel (Si-DPZid) against Pb2+ can be determined by testing the Langmuir adsorption isothermic linear regression equation and the Freundlich isotherm equation. Langmuir adsorption isotherms assume that adsorbents have a homogeneous surface. Each adsorbent molecule can only adsorb one adsorbate molecule (monolayer). And Langmuir’s isothermic adsorption theory also applies to chemical adsorption, which is to form monolayer layers. The Freundlich adsorption isothermic assumption is that adsorbents have a heterogeneous surface. Each adsorbent molecule has a different absorption potential (multilayer). Freundlich’s adsorption isothermic theory applies to physical adsorption, namely forming multilayer layers.

The determination of Langmuir adsorption isotherms can be obtained by graphing adsorption isotherm patterns. The Langmuir adsorption isotherm pattern can be seen in Figure 1 and Figure 2.

![Figure 1. Langmuir adsorption isotherm pattern on silica gel adsorbent without modification](image-url)
Figure 2. Langmuir adsorption isotherm pattern on diphenylcarbazide modified silica gel adsorbent (Si-DPZid)

The determination of Freundlich adsorption isotherms can be obtained by graphing adsorption isotherm patterns. The Freundlich adsorption isotherm pattern can be seen in Figure 3 and Figure 4.

Figure 3. Freundlich adsorption isotherm pattern on unmodified silica gel adsorbent
Langmuir and Freundlich adsorption equation testing is proven by a good linearization graph and has a coefficient price $R^2 \geq 0.9$ (close to number 1). From the value of the correlation coefficient ($R^2$), it can be known which equation model can represent the reaction that occurred in this study. The isothermic pattern that occurs in the $\text{Pb}^{2+}$ ion adsorption process by silica gel without modification does not refer to the Langmuir isotherm pattern or the Freundlich isotherm pattern because it has an $R^2$ value that is not close to 1, but when compared between the two $R^2$ values obtained, it can be said that the $\text{Pb}^{2+}$ adsorption process on silica gel without modification is a Freundlich isotherm pattern because it has an $R^2$ value that is closer to 1, which is 0.738, while the $R^2$ value obtained in the Langmuir isotherm pattern is 0.2305.

In the Langmuir isotherm pattern, the adsorption process is monolayer, while in Freundlich isotherms it occurs in the multilayer adsorption process and the adsorption is physical (physisorption). The Freundlich adsorption isotherm pattern indicates that there are several layers that absorb $\text{Pb}^{2+}$ metal ions. Freundlich adsorption isotherms have several assumptions: adsorbents have a heterogeneous surface. Each adsorbent molecule has a different absorption potential (multilayer). This indicates that absorption is physically dominant, where $\text{Pb}^{2+}$ metal adheres to the Van der Walls force, which is a weak attraction between the adsorbate and the adsorbent surface on the silica gel pore wall. In adsorption physics, adsorbate is not firmly bound to the adsorbent surface so that the adsorbate can move from one surface to another, and the abandoned surface can be replaced by another adsorbate.

The adsorption process of $\text{Pb}^{2+}$ ions by diphenylcarbazide modified silica gel (Si-DPZid) is a Langmuir isotherm pattern that has an $R^2$ tending close to 1 which is 0.9206. Adsorption of
Pb2+ ions by diphenylcarbazide modified silica gel (Si-DPZid) according to the Langmuir isotherm pattern indicates that adsorption takes place only one layer (monolayer) and the surface sites are homogeneous because each active site absorbs only one molecule. Adsorption following Langmuir isotherm occurs chemically, where the adsorbent surface has a smaller adsorption capacity than Freundlich adsorption which is physically adsorbed.

CONCLUSION

From the results of the research that has been done, it can be concluded that the optimum pH of Pb2+ ion adsorption is achieved at a pH value of 3, both in silica gel without modification and silica gel modified diphenylcarbazide (Si-DPZid). The optimum contact time of Pb2+ adsorption occurs at minute 10, in both unmodified silica gel and diphenylcarbazide modified silica gel (Si-DPZid). The adsorption capacity by silica gel without modification reached 49.8455 mg/g at a concentration of 400 ppm, with an adsorption isotherm pattern following the Freundlich adsorption isotherm model (R2 = 0.738). Meanwhile, the adsorption capacity by silica gel modified diphenylcarbazide (Si-DPZid) reached 52.6264 mg/g at a concentration of 300 ppm, with an adsorption isotherm pattern in accordance with the Langmuir adsorption isotherm model (R2 = 0.9206).

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