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Optimation of Adsorpsi and Desorpsi of Mn^{2+} Ions on Gel-GPTMS Silica (Glycidoxypropyltrimethoxysilane) Modified with Sulfonates

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Abstract: Silica gel is an adsorbent often used in chromatography columns as a resin or stationary phase. Silica gel has active groups on its surface in the form of silanol (-SiOH) and siloxane (-Si-O-Si-). The effectiveness of silica gel in absorbing heavy metal ions is very low, so modification is needed to increase the absorption capacity of silica gel to metal ions. The addition of sulfonate with the GPTMS linkage compound dose modification. Adsorption and desorption are two methods that can be used to separate manganese metal. This research aims to obtain the optimum desorption agent (NaCl and CaCl2) and the concentration of the AAS-characterised desorption agent. This study used the column method for the adsorption and desorption process. This study used the column method for the adsorption and desorption process. The column method is a technique used to separate certain substances from a mixture by utilizing the interaction between adsorbent and adsorbate. The results obtained optimum desorption agent $CaCl_2$ where the weight desorbed 0.1168002 mg with a percent desorption of 92.3%, the optimum concentration of $CaCl_2$ 0.05 M where the weight desorbed 0.132264 mg with a percent desorption of 95% Adsorbent characterization was conducted with FTIR and XRF.

Keywords: Adsorption; Desorption; GPTMS; Silica; Sulfonate; Manganese.

Introduction

Manganese (Mn) is a grayish-reddish metal found in nature in the form of compounds with various valences [1]. Manganese is the 12th most abundant element in the earth's crust. Its concentration varies among common rock types, about 0.1 to 0.2%. The highest quality manganese ore contains 40 to 45 % manganese [2]. Manganese is more reactive than other metals in group VII B. However, non-metallic elements are not so reactive; they often react upon heating. The results obtained in heating are such as Mn_3O_4, Mn_3N_2, $MnCl_2$, MnF_2 and MnF_3 [3].

Manganese is a harder mineral than iron, is also very brittle, white-grey, and has a melting point of approximately 125ºC. Due to pesticides and steel industry waste, heavy metal manganese (Mn) can damage water. The toxic properties of manganese are usually already visible in low concentrations. The limit of Mn concentration in water that is commonly used for daily needs is <0.05 mg/L. If the Manganese (Mn) content in drinking water is >0.5 mg/L, it can damage nerves, cause insomnia, and weaken the leg and facial muscles, which causes facial expressions to look stiff [1]. Electronegativity plays an important role in the adsorption process, which involves the formation of chemical bonds between heavy metals and active groups on the adsorbent. With an electronegativity of 1,55 and an ion size of 0.8 Å for Mn^{2+}, manganese metal in the form of Mn^{2+} is the most stable oxidation state18. Mn^{2+} ions oxidize faster in alkaline solutions because they belong to hard acids. Mn^{2+} ions can interact well with strong bases such as OH-, RNH_2, and R-OH [3].

Silica gel is one of the adsorbents that is often used in various analytical methods. Silica gel on its surface contains active groups in the form of silanol (-SiOH) and siloxane (-Si-O-Si-). Therefore, it is widely used for industrial purposes as a solid-phase liquid adsorbent in thin-layer chromatography [4]. Silica gel has many advantages, namely: inert, good adsorption, easy to modify to improve its performance, high thermal and mechanical stability, and can be used for preconcentration

Silica gel, also known as solid silica gel, is a form of synthetic silica made from sodium silicate ($NaSiO_2$). It is made through the agglomeration of a sodium silicate ($NaSiO_2$) sol similar to agar, which can be dehydrated to produce granules similar to inelastic glass or solids. These properties allow silica gel to be used as an absorbent, drying agent, and catalyst support. Silica gel prevents excessive moisture from forming before it does. Manufacturers know this, so they always use silica gel when shipping products in boxes [5]

One of the efforts that can be made to overcome the weaknesses of silica gel is the modification of silica gel. This modification is done on the silica surface to change its chemical composition. The -Si-OM group replaces the -Si-OH group during the modification process, where M has many species besides H, both simple and complex [6]

Modification on the surface of silica gel can use immobilization, which utilizes organic functional groups so that they can bind heavy metal ions [7]. Silica modification is done to increase the adsorption power of silica to metal ions using the active side on the surface of silica gel multiplied by O^- groups. Based on the provisions of Hard and Soft Acids and Bases, hard base adsorbents will have a high ability to adsorb metal ions that are hard acids. Sulfonate-modified silica gel, a rigid base, is expected to have better adsorption ability to metal ions [8].

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In this study, Silica gel-GPTMS was first prepared. GPTMS (glycidoxypropyltrimethoxilane) will be used as an intermediary or bridge between Silica gel and sulfonate groups. Silica gel that has bonded with GPTMS will be reacted with 4-amino-5-hydroxy-2,7-naphthalenadisulfonate so that it will produce Silica gel-GPTMS-Sulfonate.

In previous studies, silica gel has been modified to increase its effectiveness in the adsorption process. In 2009, Jiang et al successfully analyzed inorganic anions in seawater samples using Silica modified with cetyltrimethylammonium ions as a stationary phase [9]. In 2013, Wang et al successfully adsorbed chrome ions using Silica that had been modified with imidazole compounds [10]. 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[11].

In this study, silica gel will be modified into silica-GPTMS-Sulfonate, which is expected to adsorb and desorb Mn^{2+} cations well. The principle of ion exchange is used in this study, where ions with a certain charge (either cations or anions) in solution are adsorbed on a solid material (ion exchanger) and replaced by other ions with the same charge in an equivalent amount released by the solid material. The atomic absorption spectrometry (AAS) method is an analytical technique used to determine the level of a metal in a compound by atomizing it first with a flame [12]. This AAS instrument is used to see the effectiveness of sulfonate-modified silica gel in adsorbing and desorbing Mn^{2+} ions at various variations of desorbing agents and concentrations. It is hoped that the results of this study can be used in the manufacture of resins to be applied to the High Ion Chromatography (HIC) method in the future.

Research Methods

Equipment and materials

The equipment that will be used in this research includes Atomic Absorption Spectrophotometry, a beaker, an erlenmeyer, a volumetric flask, a watch glass, a dropper pipette, a vaporizer cup, a spatula, a stirring rod, an analytical balance, a burette, stative and clamp, shaker, magnetic stirrer, filter paper, desiccator, hot plate, pH meter, oven, thermometer.

Materials that will be used in this research are Silica gel, Gptms, HCl, NaCl, $CaCl_2$, toluene, distilled water, methanol, sodium bicarbonate ($NaHCO_3$), sodium thiosulfate ($Na_2S_2O_3$), acetone, diethyl ether, sodium 4-Amino-5-hydroxy-2,7-naphthalenedisulfonate salt, and $MnCl_2 .4H_2O$.

Research Procedures

Reparation of Silica gel-GPTMS-Sulfonate

Silica gel was weighed as much as 25 grams, and then 25 ml of GPTMS was in 87.5 ml of toluene. The mixture was stirred for 24 hours at 90°C. Then the precipitate obtained was washed with 12.5 ml of methanol. Next, silica gel-GPTMS was reacted with monosodium salt of 4-amino acid, 5-hydroxy-2,7-naphthalendisulfonic acid in 0.1 M sodium bicarbonate ($NaHCO_3$) solution and then stirred for 20 hours. Then separate the resulting solid from the filtrate and washed with distilled water, acetone, and diethyl ether for 15 ml each.

Ion adsorption with silica gel-GPTMS-Sulfonate at optimum conditions

In the third stage, sample adsorption will be carried out using Silica gel-GPTMS-Sulfonate adsorbent using pH 4, and a concentration of 20 ppm. Adsorption will be carried out with a column system. Silica gel-GPTMS-sulfonate adsorbent weight of 0.1 g was used in the adsorption process. Filtrate adsorption was performed using the AAS method.[13]

1. Ion Desorption with silica gel-GPTMS-Sulfonate

a. Determination of Mn^{2+} cation desorption type
   - A total of 10 mL of 0.025 M NaCl solution was poured into the column containing sulfonate-modified silica gel-GPTMS containing Mn^{2+} ions. A total of 0.1 gram of silica gel-GPTMS as stationary phase.
   - A total of 10 mL of 0.025 M $CaCl_2$ solution flowed into the column, which already contained sulfonate-modified silica gel-GPTMS, which already contained Mn^{2+} ions. A total of 0.1 grams of silica gel-GPTMS was used as the stationary phase [14].

b. Determination of optimum concentration on desorption of Mn2+ ions

The sulfonate-modified silica gel-GPTMS, which already contained cations, was added to the column. Each salt solution with varying concentrations of NaCl and $CaCl_2$ (0.01 M, 0.025 M, 0.05 M, 0.75 M, 0.1 M) was added to each desorption type. Then, the filtrate was tested using AAS.

Results and Discussion

Modification of Silica gel

Silica gel is modified to increase the absorption of silica gel to metal ions. In this study, silica gel was modified to produce Silica gel-GPTMS-Sulfonate. This modification process requires a connecting compound because the binding of an organic compound on silica gel is not so effective [15].

Silica gel is reacted with glycidoxypropyltrimethoxysilane (GPTMS) as the connecting compound and toluene as the solvent. In the reaction between silica gel and GPTMS, the protons on the silanol group of silica gel will be released so that O^- on silica gel will bind to Si on GPTMS to form a siloxane bond (Si-O-Si). Furthermore, potentiometric titration is carried out to determine how much epoxy group content is contained in Silica gel-GPTMS [15].

After obtaining Silica gel-GPTMS, the sulfonate salt can be reacted with Silica gel-GPTMS in sodium bicarbonate solution. Sodium bicarbonate serves as a solvent that can stabilize the pH during the reaction process, making the two materials mix and dissolve well to achieve a homogeneous reaction. The solution was stirred for 20 hours to maximize sulfonate groups' binding on the Silica gel-GPTMS's surface. In this process, the ring of the epoxy group will open so that it will form a partially positive C and negatively charged O. The O^- on the epoxy group will light up one of the protons on the amine group contained in the sulfonate salt, so that the N atom on the amine group will be negatively charged and bind to the positive partial C on Silica gel-GPTMS. The solution must be washed using distilled water, acetone and diethyl ether. Washing using three solutions aims to remove impurities based on their level of polarity after filtering and standing in a desiccator for 24 hours [15].

Adsorption

In this study, manganese ions were obtained from the manganese (II) chloride tetrahydrate compound; the analysis was carried out by utilizing sulfonate-modified silica gel as an adsorbent using the column method. Column method: the solution is contacted or flowed with adsorbents on a column with a specific flow rate to obtain optimal adsorption results [16].

In previous research conducted by Pratama Yuda (2023), namely silica adsorption, the optimum conditions for parameters were obtained, namely the optimum pH of 4 and a concentration of 20 ppm. Based on these optimum conditions, this research conducted adsorption of silica gel-GPTMS-Sulfonate by column method using these optimum conditions [13].

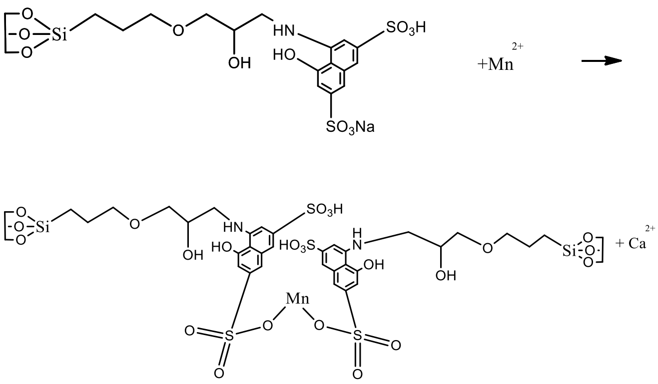

Figure 1. Adsorption reaction of Mn^{2+} on silica gel-GPTMS-sulfonate

Table 1. Adsorption of silica gel-GPTMS-Sulfonate by Column Method

C0 (mg/L)	C1 (mg/L)	Initial wight (mg)	Final weight (mg)	% adsorption
18.424	2.569	0.18424	0.0254331	86
18.424	2.946	0.18424	0.0291654	84
18.424	3.246	0.18424	0.0321354	82.5

Based on table 1. It is obtained that the absorption of manganese ions in the column method with the largest percentage is 86%, with the weight of manganese ions absorbed by 0.1588069 mg.

Desorption

Determination of Manganese Ion Desorption Type on Silica gel-GPTMS-Sulfonate

Desorption can be done by contacting the adsorbent with a desorption agent/solution. Desorption agents can be acidic, basic and neutral solutions [17]. The type of desorption is very influential in this desorption process because the type of solution to be used affects the size or size of the substance that has been absorbed to be rereleased so that the column can be reused or regenerated again. This study uses NaCl and $CaCl_2$ desorption.

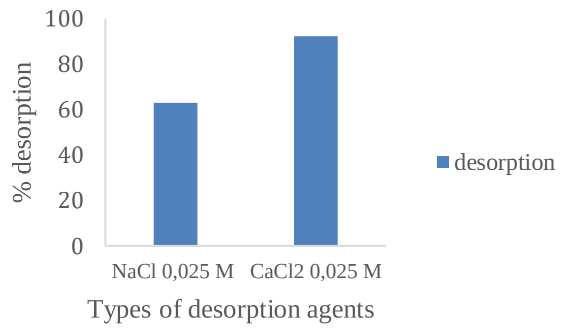

Figure 2. Variation of Desorption Agents

It can be seen from the table above that the best desorption agent is $CaCl_2$; this can be seen from the desorbed weight of 0.1168002 mg percent desorption obtained 92.3%. The NaCl eluent's desorbed weight was 0.00920304 mg, and the per cent desorption was 62.9%. Based on the study's results, it can be seen that the best desorption agent used to desorb Mn^{2+} ions is $CaCl_2$. This is proven by the theory that says that positive ion exchange resins that have the greatest to the smallest affinity for ion exchange are calcium (Ca^{2+}), magnesium (Mg^{2+}), ammonium (NH_4^+), potassium (NH_4^+), and calcium (Ca^{2+}).(NH_4^+), potassium (K^+), sodium (Na^+), and hydrogen (H^+) [18].

In the desorption process, the charge of the cation to be exchanged can affect the Mn^{2+} ion exchange process. Where the charge of Ca is the same as Mn, it is suitable to replace it, while Na only has 1 charge, so to exchange Mn2+, it takes 2 Na^+ molecules in the desorption process. So, the percentage of desorption using a CaCl2 desorption agent is higher than NaCl, and CaCl2 is used for the desorption of Mn^{2+} ions on Silica gel-GPTMS-Sulfonate.

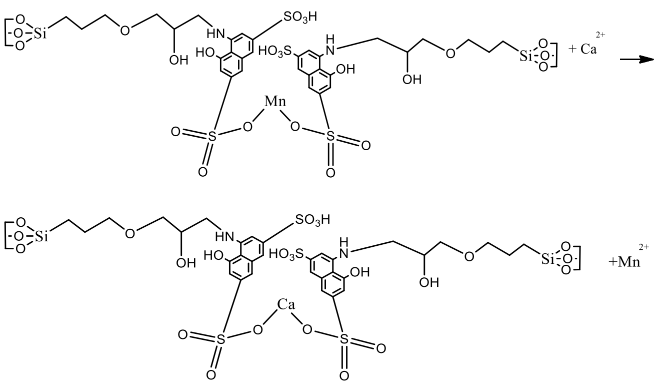

Figure 3. Desorption reaction of Mn^{2+} on silica gel-GPTMS-sulfonate.

Effect of Eluent Concentration Variation on Desorption of Manganese Ions on Silica gel-GPTMS-Sulfonate Adsorbent

The desorption process occurs when the absorption process has occurred maximally or the adsorbent has reached the saturation point and reached an equilibrium state so that it cannot absorb the adsorbent anymore. Desorption treatment is carried out using the optimum desorption agent obtained previously, $CaCl_2$. The $CaCl_2$ variations used in this study were 0.01 M, 0.025 M, 0.05 M, 0.75M, and 0.1 M. The results of desorption concentration research can be seen in the following table:

Table 2. Desorption using NaCl and $CaCl_2$

$CaCl_2$ solution concentration (M)	Weight adsorbed (mg)	Desorbed weight (mg)	Desorption Efficiency (%)
0.01	0.1463627	0.1339758	91.5
0.025	0.126523	0.1168002	92.3
0.05	0.1392148	0.132264	95
0.75 M	0.1588069	0.1450008	91.3
0.1 M	0.1521046	0.1369764	90

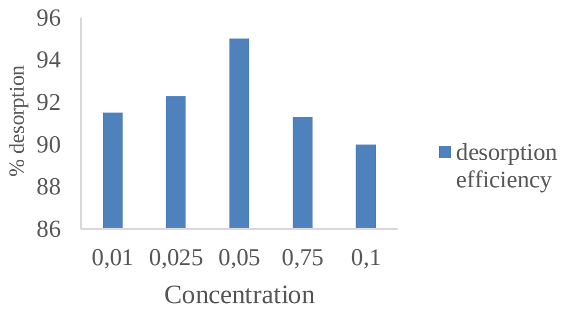

Figure 3. Variation of CaCl2 Desorption Agent Concentration

Based on the data above, the optimum concentration of $CaCl_2$ to desorb Mn^{2+} is 0.05 M, which is 95%. At concentrations of 0.75 M to 0.1 M, there was no significant increase in the percent desorption. This happens because $CaCl_2$ cannot be desorbed again with that concentration. According to (Patel, 2021), the eluent concentration is one of the parameters that affect desorption if the concentration is too high, it will cause damage to the adsorbent structure, making it difficult for ion exchange between CaCl2 and Mn2+, which has been bound to the adsorbent [19].

According to Stum and Morgan, Electrostatic force is caused by the attraction between oppositely charged ions. The electrostatic force has a strong bond, making the bond formed between metal ions and adsorbents difficult to release, and desorption is not maximized. The decrease in the percentage of desorption can be due to the active side of the adsorbent being saturated because there is an equilibrium between Mn^{2+} ions and adsorbents so that the percentage of desorption decreases [20]

Conclusion

Based on the research that has been done, the optimum type of Mn^{2+} ion desorption agent used is $CaCl_2$, which has a desorbed amount of 0.1168002 mg with a desorption efficiency of 92.3%. NaCl has a desorbed amount of 0.00920304 mg with a desorption efficiency of 62.3%. The optimum concentration of $CaCl_2$ desorption agent for the desorption of Mn^{2+} ions was obtained with a concentration of 0.05 M with a desorbed amount of 0.132264 mg with a desorption efficiency of 95%.

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