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Effect Type of Desorption Eluent and Concentration in Desorption of Zn^{2+} Cation from Sulfonate Modified Silica Gel-GPTMS (Glycydoxypropyltrimethoxysilane) Adsorbent

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ABSTRACT

Silica has silanol groups contained in it which have low binding ability because it has low acidity, resulting in low absorption effectiveness on silica. In order to improve the properties and to expand the field of utilization, a modification process is carried out on silica gel using GPTMS bridging compounds and sulfonate salts as modifiers. The study explains that $CaCl_2.2H_2O$ with a desorption percent of 97.25% has a greater ability than NaCl which is only 83.93% in the desorption of Zn^{2+} cations. The study also explains that the optimum concentration of $CaCl_2.2H_2O$ eluent in the desorption of Zn^{2+} cations is at 1mmol/L where the desorption yield is 93.74%.

Keywords: silica, GPTMS, sulfonate, ion exchange, zinc, sodium chloride, calcium chloride

1. INTRODUCTION

Silica found in nature has a high affinity for oxides and high electronegativity to other atoms making it difficult to obtain silica with high purity. The silanol group has a low binding ability because it has low acidity resulting in low absorption effectiveness on silica.[1] In order to improve the properties and to expand the field of utilization, a modification process is carried out on silica gel. This modification process basically changes the ≡Si-OH group into ≡Si-OM, where M is some species either simple or complex other than H. This modification aims to change the properties of silica gel so that it can be used in a wider range of applications, such as adsorption, heavy metal cation exchangers, and others.[2] Based on research conducted by Lessi et al., the use of bridging compounds in the binding of organic compounds on silica gel is more effective. The connecting compound that can be used as a silane reagent is glycidoxypropyltrimethoxysilane (GPTMS) which has an epoxy group.[3] Organic compounds used as modifiers in silica gel modification are 4-amino-5-hydroxy-2,7-naphthalenadisulfonic salt compounds forming sulfonate-modified Silica Gel-GPTMS.[1]

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Zn metal is in the form of ions in an acidic atmosphere, can form a precipitate in an alkaline atmosphere. Zn metal is an element that the body needs in small amounts because it has high toxicity, if its presence in the body exceeds predetermined levels it can cause dizziness, lethargy and digestive disorders. Adsorption is the process of agglomeration of dissolved substances in solution by the surface of an absorbent substance that makes the material enter and collect in an absorbent substance. In this process, there are two main components involved, namely adsorbent (absorbent substance) and adsorbate (absorbed substance), both of which often appear together with a process, so some call it sorption or desorption.[4]

One of the advantages of adsorption processes is the possibility of regeneration or recovery. Regeneration can be done through desorption methods, where the adsorbent that has been used can remove the adsorbed substance by contacting the adsorbent with a solution known as a desorption agent. Desorption agents can be acidic, neutral, or basic. By regenerating, the used adsorbent can be reused for the next adsorption process. This can reduce operational costs and protect the environment, as there is no need to use a new adsorbent each time.[5]

Desorption is the opposite of the adsorption process, where desorption it self aims to release ions attached to the adsorbent, through desorption studies, we can also find out the adsorption mechanism between cations and adsorbents,[6] therefore the adsorbent used can be used as an ion exchange resin. Desorption studies help in explaining the mechanism of ion removal and recovery (regeneration) of charged adsorbents.[7] Ion exchange is a process where the exchange of ions, either cations or anions that have the same charge, between insoluble solids in a solution.[8] Ions in solution can be easily exchanged by using ion exchange resins.[9]

2. EXPERIMENTAL

2.1. Chemicals, Equipment and Instrumentation

The tools used a magnetic stirrer, pH Meter, hot plate, oven, digital analytical balance, modified column, Atomic Absorption Spectrophotometer (AAS) type AA240, Fourier Transform Infrared (FTIR) type PerkinElmer Universal ATR and some glassware.

The materials used in this study were silica gel (Merck), GPTMS (Sigma A), nitric acid (Merck), 4-amino-5-hydroxy-2,7-naphthalenadisulfonic acid salt (Merck), $Zn(NO_3)_2$. $6H_2O$ (Merck), NaCl (Merck), $CaCl_2.2H_2O$ (Merck), Acetone (Smart-Lab), methanol (Smart-Lab), diethyl ether (Smart-Lab), sodium bicarbonate (Smart-Lab), and distilled water.

2.2. Research Procedure

2.2.1. Modification of Silica Gel with Sulfonate Salts

Weighed 25 grams of silica gel and then reacted with 25 mL of GPTMS and 87.5 mL of toluene. The mixture was shaken at 90°C for 24 hours. The silica gel-GPTMS obtained was then washed with 12.5 mL of methanol and then dried. A total of 23 grams of silica gel-GPTMS was reacted with 11.5 mL of monosodium salt compound of 4-amino acid, 5-hydroxy-2,7-naphthalendisulfonic acid in 0.1 M sodium bicarbonate solution for 20 hours. Then separate the solid and filtrate and wash with distilled water, acetone and diethyl ether. Dry in a desiccator, until silica gel-GPTMS-Sulfonate is obtained.

2.2.2. Adsorption of Zn^{2+} Cation on Sulfonate Modified Silica Gel-GPTMS

A total of 0.1 gram of silica gel that has been modified with sulfonate groups is added to the modified column, then a 20 ppm Zn^{2+} ion solution is flowed at an optimum pH of 6. Then the results of the elution process are filtered, the filtrate obtained is then measured by an Atomic Absorption Spectrophotometer (AAS).

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2.2.3. Determination of the optimum Desorption Eluent for Zn^{2+} Cation Desorption

First step is to take 10 mL of 5 mmol/L NaCl solution which serves as a desorption reagent for Zn^{2+} metal ions, then flow into the column. A total of 0.1 gram of sulfonate-modified silica gel as a stationary phase that has undergone an adsorption process with Zn metal using a flow rate of 1mL/min.

The next step is to take 10 mL of 5 mmol/L $CaCl_2$.$2H_2O$ solution which serves as a desorption reagent for Zn^{2+} metal ions, then flowed into the column, as much as 0.1 gram of sulfonate-modified silica gel as a stationary phase that has undergone an adsorption process with Zn metal using a flow rate of 1mL/min.

2.2.4. Determination of Optimum Concentration on Desorption of Zn^{2+} Cation

Varying the eluent concentration (0; 0.1; 0.5; 1; 3; 5) mmol/L on the optimum desorption eluent. Then calculate the eluate from the desorption process and collect it in a container and continue to the analysis stage using an Atomic Absorption Spectrophotometer (SSA) to see the concentration of Zn^{2+} that is desorbed.

3. RESULTS AND DISCUSSION

3.1. Analysis of Characterization Results

Analysis using FTIR is an analytical technique to observe the composition of chemicals based on functional groups in organic compounds and inorganic compounds. In this study, the functional groups contained in commercial Silica gel, Silica gel-GPTMS, and Silica gel-GPTMS-Sulfonate were analyzed using an FTIR instrument in the 4000-400 cm^{-1} wave range.

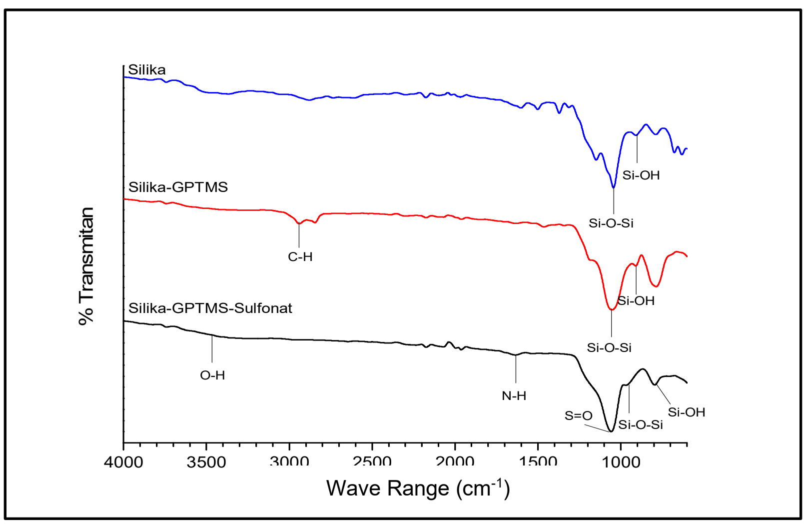

Figure 1. FTIR Spectra of Silica Gel, Silica-GPTMS, and Silica-GPTMS-Sulfonate

From the first FTIR spectrum produced above on commercial silica gel, there is a Si-O-Si group at wave number 1057 cm^{-1} and a Si-OH group at wave number 968 cm^{-1}. These two groups indicate that the group is the identity of silica gel.

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In the second FTIR spectrum of silica gel-GPTMS, we can see that there is a silanol group (Si-OH) seen at wave number 909 cm^{-1}, as well as a siloxane group (Si-O-Si) seen at wave number 1053 cm^{-1} which comes from the structure of silica gel (9). At wave number 2940 cm^{-1} there are vibrations (C-H) derived from propyl groups on GPTMS that have been bound to silica gel.[10]

The third FTIR spectrum is the spectrum of the silica gel-GPTMS-Sulfonate analysis. The results of this analysis can be seen at wave number 909 cm^{-1} there are siloxane groups (Si-O-Si) and silanol groups (Si-OH) at wave number 789 cm^{-1} where both groups come from silica gel. At wave number 1043cm^{-1} there is a sulfonate group (S=O) derived from sulfonate salts bound to silica gel-GPTMS. The thing that strengthens the bonding of sulfonate salts on silica gel-GPTMS is the presence of OH groups at wave number 3365 cm^{-1} where this occurs due to the opening of ring on epoxy groups when reacting with sulfonate salts and the presence of primary amine groups (N-H) at wave number 1602 cm^{-1}, this primary amine band usually appears at a wavelength of 1620-1560 cm^{-1}.[1]

3.2. Determination of the Optimum Type of Desorption Eluent in Zn^{2+} Cation Desorption

Desorption process can be done if the adsorption process that occurs on sulfonate-modified silica gel has been maximized. In this study, two types of desorption eluents were used, namely NaCl and $CaCl_2.2H_2O$, to release the Zn^{2+} cation bound to the adsorbent.

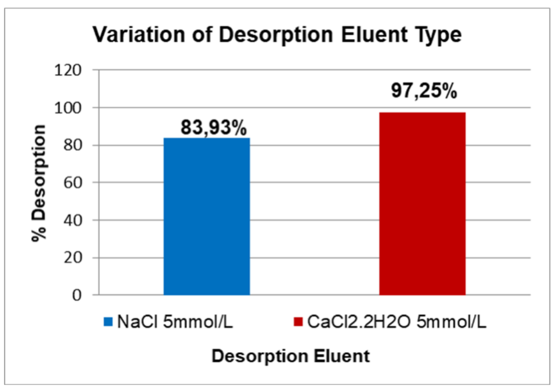

Figure 2. Graph of the Effect of Desorption Eluent Variation on Desorption Zn^{2+}

The results obtained can be seen in Figure that $CaCl_2.2H_2O$ has a stronger thrust than NaCl to release Zn^{2+} cations from sulfonate modified silica adsorbent, which $CaCl_2.2H_2O$ can desorb Zn^{2+} cations by 97.25% of those bound to the adsorbent. While the NaCl eluent is only able to desorb Zn^{2+} cations by 83.93% of those bound to the adsorbent. From these results it can be concluded that Ca^{2+} cations have greater affinity than Na^{+} cations to cation exchange resins. In research conducted by Wu. Et.all., namely the effect of salinity on metal desorption in the soil where $CaCl_2$ has a strong release power against Zn^{2+} cations compared to other salts.[11]

3.3. Determination of the Optimum Concentration of Zn^{2+} Cation Desorption

Desorption usually has several parameters to see its efficiency in the process of separating the adsorbate bound to the adsorbent, one of which is the concentration variation of the desorption eleunt. In this study, the concentration variation of $CaCl_2.2H_2O$ (0; 0.1; 0.5; 1; 3; 5) mmol/L was carried out as a desorption eluent.

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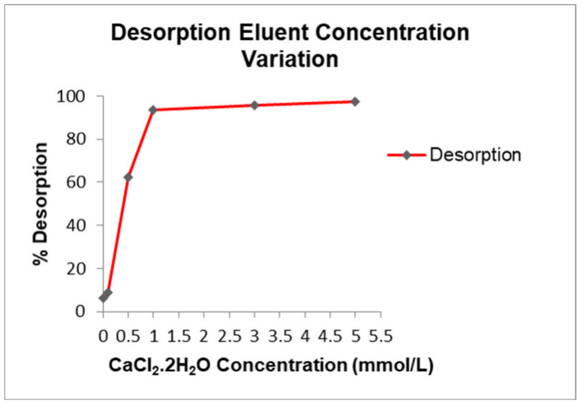

Figure 3. The CurveEffect of the Concentration Variation on Desorption Zn^{2+}

From the curve above, it can be seen that the increase in $CaCl_2.2H_2O$ concentration is directly proportional to the percent desorption of Zn^{2+} metal ions bound to sulfonate-modified silica adsorbent. A significant increase in desorption occurs up to a concentration of 1mmol/L $CaCl_2.2H_2O$, that is 93.74%. Furthermore, at the next concentration, the increase in percent desorption is not too far. This indicates that the reaction between the eluent and adsorbent is balanced, so that there is no difference in desorption results that are very far. By increasing the concentration of desorption eluent will cause the number of protons (Ca^{2+}) from $CaCl_2.2H_2O$ that will release Zn^{2+} metal ions bound to sulfonate modified silica gel so that the resulting percent desorption becomes greater.[12]

4. CONCLUSION

Desorption of Zn^{2+} metal ions on silica gel-GPTMS-sulfonate increased. From the results of this study, it is concluded that the desorption of Zn^{2+} ions on silica gel-GPTMS-sulfonate can be desorbed optimally using $CaCl_2.2H_2O$ desorption eluent and at an eluent concentration of 1mmol/L with a resulting desorption percent of 93.74%.

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