Jurnal Pijar MIPA
https://jurnalfkip.unram.ac.id/index.php/JPM

ISSN 1907-1744 (Print)
ISSN 2460-1500 (Online)

Optimation of Fe^{3+} Ion Desorption Using Sulfonate Modified Silica Gel-GPTMS

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Received: August 1, 2024. Accepted: September 15, 2024. Published: September 30, 2024

Abstract: Silica gel is one of the adsorbents widely used in adsorption, but silica gel has a low ability to absorb metals. Hence, modifications need to be made to improve it. Silica gel modified using sulfonate groups from monosodium salt compound of 4-amino-5-hydroxy-2,7-naphthalene disulfonic acid using GPTMS coupling compound for adsorption and desorption of Fe^{3+} ions by column method was carried out. The adsorption process of Fe^{3+} ions using silica gel-GPTMS-sulfonate has been carried out in previous studies and obtained an optimum state at pH 6 and a concentration of 20 ppm. After the adsorption process is carried out, the desorption process is continued with variations in the type of desorption eluent and concentration variations. The types of desorption agents are NaCl, $CaCl_2$, HCl, and HNO_3, with the optimum desorption agent being HNO_3 with a release of 0.077517 mg of Fe^{3+} ions from 0.1587403 mg of Fe^{3+} ions absorbed and a desorption percentage of 48.83%. The concentration variations are 0.5 M, 1 M, 2.5 M, and 5 M, with an optimum concentration of 2.5 M HNO_3 with a release of 0.098505 mg Fe^{3+} ions and a desorption percentage of 64.43%.

Keywords: Adsorption; Desorption; Ion Fe^{3+}; Silica Gel-GPTMS-Sulfonate.

Introduction

Iron (Fe^{3+}) ions are one of the heavy metal compounds that are very dangerous for the sustainability of living things if found in the surrounding environment that exceeds the threshold [1]. According to the Decree of the Minister of Health of the Republic of Indonesia NO.492/MENKES/PER/IV/2010 regarding the maximum threshold of iron metal levels in drinking water is around 0.3 mg/L and for the threshold of iron metal levels in waters is 1 mg/L [2]. Excess Fe ion content can be removed by ion exchange.

Ion exchange is a chemical reaction in which the freely moving ions of a solid substance, called an ion exchanger, are exchanged for different ions of the same charge in solution [3]. Ion exchange occurs in the adsorption process carried out by chromatographic methods. Separation using ion exchange chromatography on an open column has problems related to the amount of resin needed and its high price. Therefore, many researchers are researching the manufacture of polymer-based ion exchange resins, both organic and inorganic. This is expected to overcome these obstacles and make this separation technique more efficient and affordable for researchers in the future [4].

Silica gel is a supporting solid that is widely used as an adsorbent in the adsorption process because it has active sides such as silanol (-Si-OH) and siloxane (Si-O-Si) groups that can chemically bind to heavy metals [5]. However, because silanols and siloxanes cannot provide electron pairs as donors, the effectiveness of silica adsorption of metal ions is low [6], so modifications are made to silica gel using an organic compound, namely the monosodium salt of 4-amino-5-hydroxy-2,7-naphthalenadisulfonic acid with the connecting compound glycidoxypropyltrimethoxysilane (GPTMS).

This research uses silica gel-GPTMS-sulfonate as an adsorbent to adsorb Fe^{3+} metal ions. Adsorption is the mass transfer process on the surface of pores in adsorbent grains. Adsorption can occur due to surface energy and surface attraction forces [7]. When the adsorption occurs, the adsorbent will become saturated and cannot absorb the adsorbate anymore. To restore the function of adsorbents that have been saturated to absorb adsorbates again, it is necessary to carry out a regeneration process called desorption [8].

Using NaOH and HCl as desorption agents in the desorption of Fe^{3+} ions from papaya seed adsorbents and obtained optimum desorption results using NaOH 0.2 M and HCl 0.15 M, namely 23.38% and 53.66%, and using HNO_3 as a desorption agent in the desorption of Fe^{3+} ions from Chealating disk adsorbents and obtained optimum desorption results using HNO_3 2 M, namely 99.1% [9][10] . In this study, the Fe^{3+} ion desorption process used eluents from salt solutions (NaCl and $CaCl_2$) and acid solutions (HCl and HNO_3) as desorption agents to desorb Fe^{3+} ions adsorbed on sulfonate-modified silica gel.

This research aims to provide information on the ability of the eluent desorption agent for Fe^{3+} metal ions on sulfonate-modified silica gel with GPTMS linking compound and the potential use of sulfonate-modified silica gel with GPTMS linking compound as a stationary phase or cation exchange resin in chromatography columns.

Research Methods

Tools and Materials

In this research, the tools used are beakers, volumetric flasks, vaporizer cups, spatulas, stirring rods, watch glass, thermometers, dropper pipettes, analytical scales, burettes, states and clamps, pH meters, magnetic stirrers, filter paper, desiccators, modified columns, spray

How to Cite:
Elvina, E., Oktavia, B., Nasra, E., & Zainul, R. (2024). Optimation of Fe3+ Ion Desorption Using Sulfonate Modified Silica Gel-GPTMS. *Jurnal Pijar Mipa*, *19*(5), 933–937. https://doi.org/10.29303/jpm.v19i5.7453

bottles, funnels, reagent bottles, volume pipette, suction bulb, and Atomic Absorption Spectrophotometer (AAS).

In this research, the materials used were silica gel (Merck), GPTMS compound ɣ-glycidoxypropyltrimethoxysilane (Sigma A), distilled water, methanol (Merck), diethyl ether p.a (Smart-Lab), acetone p.a (Smart-Lab), toluene p. a (Smart-Lab), sodium thiosulfate p.a 3 M (Merck), 4-amino-5-hydroxy-2,7-naphthalenedisulfonic acid (Merck), $FeCI_3.6H_2O$ (Merck), HCI p.a 37% (Merck), NaOH 1 M (Merck), NaHCO3, p.a 0.1 M (Smart-Lab), NaCl, $CaCl_2$, and HNO_3 p.a 65% (Merck).

Preparation of Silica gel-GPTMS-Sulfonate

As much as 25 grams of silica gel was added with 25 mL of GPTMS and 87.5 mL of toluene. Then, the mixture was stirred at 90ºC for 24 hours. The precipitate was washed with 12.5 mL of methanol and formed silica gel-GPTMS. The binding of sulfonate groups with silica gel-GPTMS was carried out by reacting 11.5 grams of salt from sulfonate groups, namely monosodium salt compounds of 4-amino-5-hydroxy-2,7-naphthalene disulfonic acid with 23 grams of silica gel-GPTMS and added 15 grams of 0.1 M sodium bicarbonate. Stirring for 20 hours until a solid was formed, the filtrate was separated and washed with distilled water, acetone, and diethyl ether. The next step was drying in a desiccator to produce silica gel-GPTMS sulfonate adsorbent [11].

Adsorption Process of Fe^{3+} Ions

Put 0.1 gram of silica gel-GPTMS-sulfonate into the column. Then, flowed 10 mL of Fe3+ ions with a concentration of 20 ppm, optimum pH 6 on the column using pressure to obtain a filtrate containing Fe3+ ions [12]. Some Fe^{3+} ions will be absorbed on silica gel-GPTMS sulfonate contained in the column, which will be used in the desorption process [12].

Determination of Fe^{3+} Ion Desorption Eluent Type

A 10 mL amount of NaCl or $CaCl_2$ HCl or HNO_3 solution with a concentration of 0.5 M was poured into the column filled with sulfonate-modified silica gel containing Fe^{3+} ions. The desorption eluent is flowed into the column with a flow rate of 1 mL/minute. The amount of sulfonate-modified silica gel used as stationary phase was 0.1 gram [13].

Determination of Optimum Concentration of Fe^{3+} Ion

Silica gel-GPTMS-sulfonate containing Fe^{3+} ions was added to the column, and then each desorption agent was added with varying concentrations of HNO3 (0.5 M, 1 M, 2.5 M, and 5 M). Then, the eluate resulting from the desorption process was measured and collected in a container for further processing in the analysis stage using an Atomic Absorption Spectrophotometer (AAS) instrument [13].

Results and Discussion

Silica Gel Modification

Silica gel was modified to improve silica gel's ability to adsorb Fe^{3+} metal ions. Modification needs to be made to silica gel due to the low active side of silica gel (silanol and siloxane) as an electron pair donor, which results in weak bonding of metal ions on the silica gel surface [14]. Silica gel was reacted with GPTMS as a coupling compound and toluene as a solvent. The mixture of silica gel, GPTMS, and toluene was stirred at 90ºC for 24 hours to maximize the binding of silane groups on silica gel. Then, it was washed using methanol to remove impurities from toluene, and silica gel-GPTMS solids were obtained. 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) [15].

Silica gel-GPTMS was then modified using sulfonate groups from monosodium salt compounds of 4-amino-5-hydroxy-2,7-naphthalene disulfonic acid in sodium bicarbonate solution. Natirum bicarbonate acts as a solvent that can stabilize the pH during the reaction process, making the two ingredients mix and dissolve well to achieve a homogeneous solution. The solution was stirred for 20 hours to maximize sulfonate groups' binding on the silica gel-GPTMS surface. In this process, the epoxy group's ring will open to form a positive partial C and O, which will be negatively charged. O in the epoxy group will attack one of the protons in the amine group contained in the sulfonate salt so that the N atom in the amine group will be negatively charged and bind to the positive partial C on silica gel-GPTMS [15]. The solution obtained was washed using distilled water, acetone, and diethyl ether to remove impurities based on the level of polarity and dried in a desiccator to remove the moisture content of sulfonate-modified silica gel and keep it dry so that it is not susceptible to moist air. The following are the reactions that occur during the modification process to obtain Silica gel-GPTMS-Sulfonate:

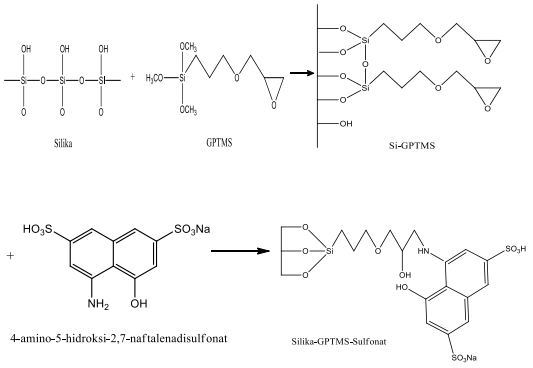

Figure 1. Silica gel-GPTMS-Sulfonate modification reaction

Adsorption of Silica Gel by Column Method

In this research, using the column method, adsorption was carried out by utilizing sulfonate-modified silica gel as adsorbent and Fe3+ ion as adsorbate. The column method is different from the batch method, wherein

the batch system, the adsorbent is mixed with the solution in one place (container) and stirred at a certain time and speed. In the column method, the solution is contacted or flowed with adsorbents in a column with a certain flow rate to obtain optimal adsorption results [16].

Several factors affect the silica adsorption process, including pH and solution concentration. In the effect of concentration, the higher the concentration of adsorbent, the better the absorption process [17]. The adsorption of Fe3+ ions using sulfonate-modified silica gel; optimum conditions were obtained at pH 6 and a concentration of 20 ppm [12]. Based on the optimum conditions obtained in the research, adsorption by the column method will be carried out using these optimum conditions and the following results.

Table 1. Adsorption Data of Fe^{3+} Ion by Column Method

C0 (mg/L)	C1 (mg/L)	Initial weight (mg)	Final weight (mg)	% Adsorption
16.570	1.428	0.1657	0.005544	96.57
16.570	1.512	0.1657	0.004910	96.96
16.570	1.600	0.1657	0.002247	98.64

Table 2 shows the results obtained from the absorption of Fe^{3+} ions using silica gel-GPTMS-sulfonate adsorbent in the column method, with the largest average absorption percentage of 98.64%. The percentage of Fe^{3+} ion adsorption using sulfonate-modified silica gel adsorbent obtained using the column method was higher than Fe^{3+} ion adsorption using unmodified silica gel adsorbent and sulfonate-modified silica gel using batch method. The adsorption results of Fe^{3+} ions obtained using unmodified silica gel and sulfonate-modified silica gel using the batch method were 52.92% and 95.76%. The following is a figure of Fe^{3+} ion adsorption reaction using silica gel-GPTMS-sulfonate adsorbent:

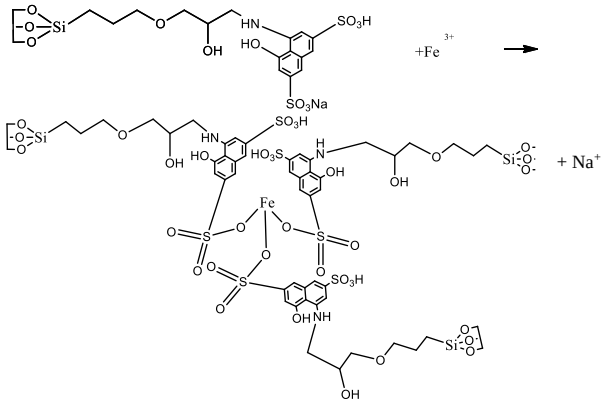

Figure 2. Fe^{3+} Ion Adsorption Reaction

Determination of Fe^{3+} Ion Desorption Eluent Type

Desorption can be done by contacting the adsorbent used with desorption agents in acidic, basic and neutral solutions. The desorption agent is very influential in the 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.

In this research, the desorption eluents used were salt solution (NaCl and $CaCl_2$) and acid solution (HCl and HNO_3). Salt solution can be a desorption agent because it does not damage the adsorbent and can exchange metal ions adsorbed on it. Acid solutions can also be used as a desorption agent because in an acidic medium, carboxyl, carbonyl, or hydroxyl groups on the adsorbent become protonated and attract positively charged metal ions, resulting in the release of metal ions into solution and protons (H^+) in solution replace metal ions on the adsorbent surface [9].

Desorption of Fe^{3+} ions by salt solution involves an ion exchange reaction between Na^+ ions from NaCl salt and Ca^{2+} from $CaCl_2$ salt with Fe^{3+} ions bound to $-SO_3^-$ functional group on the adsorbent and the acid solution involves an ion exchange reaction between H+ ions from acid with Fe^{3+} ions bound to $-SO_3^-$ functional group on adsorbent

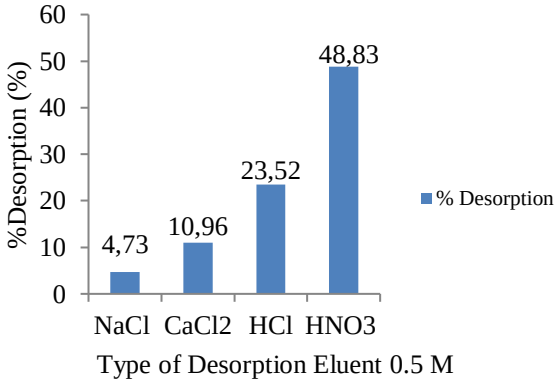

Figure 3. Type of Desorption Eluent

In Figure 2, it can be seen that the best desorption eluent is HNO_3. Based on the research that has been done, NaCl and $CaCl_2$ salt solutions are not effectively used as desorption eluents to desorb Fe^{3+} ions because they have a smaller affinity and charge than Fe^{3+} ions, making it difficult to release Fe^{3+} bound to the sulfonate group of silica gel-GPTMS-sulfonate and the desorption results are lower. However, between NaCl and $CaCl_2$, the $CaCl_2$ solution is more effective in desorbing Fe^{3+} ions. This happens when the affinity ion and charge of Ca^{2+} is greater than Na^+, which results in CaCl2 more effectively desorbing Fe^{3+} ions than NaCl. In acidic solutions, HNO_3 is more effective in desorbing Fe^{3+} ions than HCl, with 48.83% and 23.52% desorption yields. This is because HNO_3 is easier to release H^+ than HCl due to the higher stability of NO_3^- anion caused by resonance. In addition, NO_3^- does not form a strong complex with Fe^{3+}, so Fe^{3+} ions are more easily released from the adsorbent. In contrast, Cl^- forms stable complexes with Fe^{3+}, which can slow down or inhibit desorption. This makes HNO_3 have a greater tendency to release H^+ in the solution [18]. Therefore, HNO_3 was chosen as the Fe^{3+} ion desorption eluent in the next stage. The following is the Fe^{3+} ion desorption reaction using the optimum desorption eluent HNO_3:

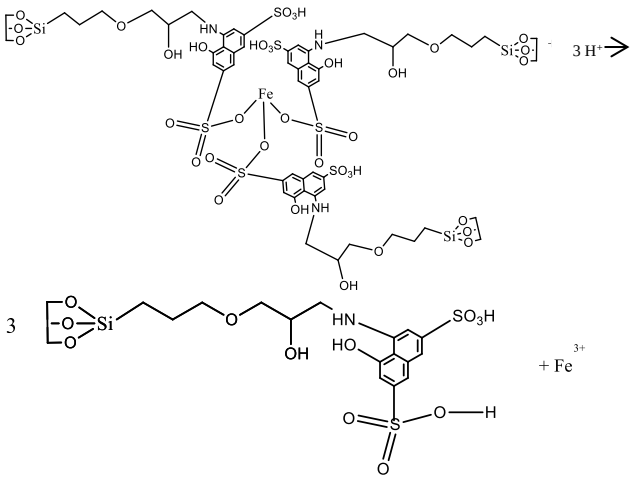

Figure 4. Desorption Reaction of Fe^{3+} Ion Using HNO_3

Determination of Fe^{3+} Ion Desorption concentration

One of the factors that affect the desorption process is the concentration of the desorption eluent. The lower the eluent concentration, the slower the desorption and requires more volume, while higher concentrations can damage the adsorbent structure [19]. The concentration variations used in this research are 0.5 M, 1 M, 2.5 M, and 5 M.

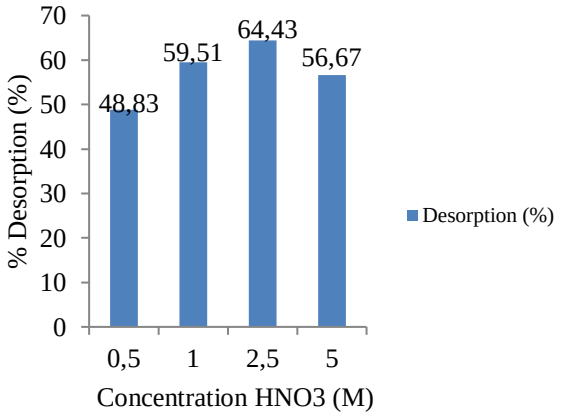

Figure 5. Variation of Concentration of Fe^{3+} Ion Desorption Eluent

In Figure 3, the optimum concentration obtained is HNO_3 2.5 M, with a percentage of 64.43%. The concentration of HNO_3 is directly proportional to the desorption percentage until it reaches the optimum point. The increasing concentration of HNO3 will increase the number of H+ ions, so the number of Fe3+ ions desorbed will increase.

At a concentration of HNO_3 5 M, the desorption result of Fe^{3+} ions decreased to 56.67%. Eluent concentrations that are too high can cause damage to the adsorbent structure, disrupting ion exchange [19]. The decrease in the percentage of desorption is also due to the active side of the adsorbent being saturated due to the equilibrium between Fe3 + ions and the adsorbent so that the desorption process decreases at too high a concentration [18][20].

Conclusion

Based on variations in the type of desorption eluent and variations in the concentration of desorption eluent that have been carried out in this study, the best type of eluent is HNO3 with an optimum concentration of 2.5 M. Percent desorption obtained is 64.43% as much as 0.098505 mg.

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