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

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

Optimum Condition of Ni^{2+} Cation Desorption from Adsorbent Sulfonate-modified Silica gel-GPTMS

Desrike Kauri, Budhi Oktavia*, Trisna Kumala Sari, Miftahul Khair

Departement of Chemistry, Universitas Negeri Padang, Padang, Indonesia
*E-mail: budhioktavia@fmipa.unp.ac.id

Received: July 31, 2024. Accepted: September 28, 2024. Published: September 30, 2024

Abstract: Silica gel is a compound that has two active sides, namely silanol (S-OH) and siloxane (Si-O-Si), which are still less effective as adsorbents, so modification is carried out. Silica is modified by adding sulfonate compounds with the help of GPTMS bridging compounds. This modification aims to improve the absorption capacity of Nickel (Ni^{2+}) metal ions in the modified adsorbent, namely sulfonate-modified silica gel-GPTMS. The characterizations used are SSA (*Atomic Absorption Spectrophotometry*) to see the success of the adsorption and desorption process. This research is quantitative experimental research where the adsorption and desorption processes are carried out using the column method, where the adsorption process itself is carried out on the Ni^{2+} cation using silica gel-GPTMS Sulfonate adsorbent at an optimal concentration of 20 ppm and pH 3. Then, we continued with the desorption process, which aims to determine the optimum conditions of the desorption process, including determining the type of desorption agent (NaCl and $CaCl_2$) and concentration for the Ni^{2+} cation desorption process. Based on the results of the research conducted, the optimum condition of the type of desorption agent is $CaCl_2$ where the desorbed weight is 0.1527 mg, and the per cent desorption is 90.10%, the optimum concentration of CaCl2 is 0.025M with a desorbed weight of 0.1442 mg and a per cent desorption of 90.18%. Based on the experimental results, the sulfonate-modified silica gel-GPTMS adsorbent can still be used repeatedly for adsorption and desorption of Ni^{2+} cations at optimum conditions.

Keywords: Adsorption; Desorption; Ni^{2+} Cation; Sulfonate-modified Silica Gel-GPTMS.

Introduction

Silica gel is one of the largest minerals in Indonesia, It is an inorganic solid compound that can be used in the adsorption process as an adsorbent because it has silanol (-Si-OH) and siloxane (-Si-O-Si-) groups, which are active sides on its surface [1]. However, the binding capacity of silanol groups to metal ions tends to be limited, making its use less effective as an adsorbent for alkali and alkaline earth metals. Therefore, to increase its effectiveness, silica gel needs to be modified [2]. Silica gel was modified with monosodium salt of 4-amino-5-hydroxy-2,7-naphthalene sulfonic acid with the help of GPTMS (glycidoxypropyltrimethoxylane) bonding compound, which has epoxy groups to increase the adsorption capacity [3].

Nickel metal ions (Ni^{2+}) and their compounds have carcinogenic characteristics, which are one of the dangerous pollutants that can cause death in humans, lung cancer, nasal cavity cancer, and the potential for vocal cord cancer and environmental damage. Therefore, it is important to minimize or even remove the existence of these metals, and one of the methods that can be used is the adsorption method [4]. Adsorption using sulfonate-modified silica gel-GPTMS is an adsorbent to adsorb Ni^{2+} metal ions. The bonds that occur can be chemical and physical bonds between the adsorbent and the substance. The adsorption process depends on the effectiveness and characteristics of the adsorbent compound [5].

Adsorbents contacted with Ni^{2+} metal ions through the adsorption process with the column method are then followed by the desorption process. Desorption is a process where substances or molecules that have been absorbed (attached) to the surface of an adsorbent are released or removed from the absorbent [6]. Desorption aims to release the metals bound to the adsorbent using a desorption agent. This desorption agent is an eluent (mobile phase) on a chromatography column, which can be an acid, base and salt for recovery and regeneration of adsorbents that have been used [7].

Factors that affect the adsorption and desorption process include contact time and solvent (eluent) concentration, where the higher the eluent concentration, the more substances will be released during the desorption process. Other factors are the concentration of solutes in the sediment, speciation of solutes where the higher the number of cations desorbed in the eluent, the more cations are released, as well as organic or inorganic content in the sediment, temperature, sediment grain size, acid concentration (pH), and salinity [8].

The desorption process follows a similar principle to ion exchange. Ion exchange is a mechanism in which ions from an electrolyte solution adhere to the surface of a solid material. In contrast, ions from the solid material are released into the solution. This process can only occur between ions of the same type and takes place over a short period as the solution interacts with the ion exchanger [9].

Eluents (mobile phase) used in the ion exchange of adsorbents containing Ni2+ metal ions have mostly been

How to Cite:
Kauri, D., Oktavia, B., Sari, T. K., & Khair, M. (2024). Optimum Condition of Ni2+ Cation Desorption from Adsorbent Sulfonate-modified Silica gel-GPTMS. *Jurnal Pijar Mipa*, *19*(5), 906–910. https://doi.org/10.29303/jpm.v19i5.7448

done. Several acids, bases, and salts are used, such as HCl [10], HNO_3 [11], NaOH [12], NaCl [13], and $CaCl_2$ [14]. In chromatography, resins are a group of strong or weak ion exchangers and can be acidic or basic. Resin is divided into two types, namely cation exchange resin and anion exchange resin. Resins are used in column chromatography as a stationary phase to remove cations or anions. A particular advantage of ion exchange resins is the reversibility of the reactions, which allows regeneration once the resin is saturated [15].

In this research, the column method carried out the desorption of Ni2+ cations from sulfonate-modified silica gel-GPTMS that had previously adsorbed Ni2+ cations. The eluents used previously were NaCl and $CaCl_2$ salts. This research aims to see the optimum conditions, including the optimum type of desorption agent and the optimum concentration in the desorption process of Ni^{2+} cations on sulfonate-modified silica gel-GPTMS. In addition, the stationary phase in column chromatography has a reasonably high price, so from this research, sulfonate-modified silica gel-GPTMS adsorbent can be used as a stationary phase in column chromatography. The advantage of this adsorbent is that it can be used repeatedly by utilizing the desorption process under appropriate conditions.

Research Methods

The equipment used includes an Atomic Absorption Spectrophotometer (AAS), magnetic Stirrer, hot plate, oven, analytical balance, reagent bottles, measuring flasks, beaker glass, stirring rods, measuring pipettes, measuring cups, spray bottles, thermometer, and desiccator.

Materials used in this study include silica gel, GPTMS, 4-amino-5-hydroxy-2,7-naphthalenedusulfonic acid monosodium salt, distilled water, $CaCl_2$, NaCl, sodium thiosulfate ($Na_2S_2O_3$), sodium bicarbonate, methanol, toluene ($C_6H_5CH_3$), diethyl ether, acetone, and $NiCl_2.6H_2O$.

In the sulfonate-modified silica gel-GPTMS process, 25 grams of silica gel were weighed, 25 mL of GPTMS and 87.5 mL of toluene were added and stirred at 90°C for 24 hours. Then washed using 12.5 mL methanol [14]. Weighing 23 grams of silica gel-GPTMS was reacted with 11.5 grams of 4-Amino-5-hydroxy-2,7-naphthalenedisulfonic acid in 3 M sodium bicarbonate solution as much as 23 mL and stirred for 20 hours. Then, it was filtered to separate the solid precipitate from the filtrate. The precipitate was washed using distilled water, acetone, and diethyl ether and stored in a desiccator for drying [2].

During adsorption, 0.1 gram of silica gel-GPTMS was modified with sulfonate and then put into the column as a stationary phase. Then, 20 mL of Ni^{2+} solution with a concentration of 20 ppm at pH 3, filter the solution, and AAS analyzed the filtrate

Then, in the desorption process, determine the type of desorption agent. A total of 10 ml of 0.05M NaCl solution flowed into the column containing silica gel-GPTMS, which already contained Ni2+ cations, to function as a Ni^{2+} cation desorption agent. A total of 0.1 gram of silica gel-GPTMS as stationary phase. Then, AAS analyzed the filtrate. A total of 10 ml of 0.05M $CaCl_2$ solution flowed into the column containing silica gel-GPTMS, which already contained Ni2+ cations, to function as a Ni^{2+} cation desorption reagent. A total of 0.1 gram of silica gel-GPTMS as stationary phase. Then, the filtrate was analyzed by AAS [21].

After that, the optimum concentration of Ni2+ cation desorption is determined. Sulfonate-modified silica gel-GPTMS was added to the column containing Ni^{2+} cations. Then, 10 mL of salt solution with varying concentrations of CaCl2 (0.01M, 0.025M, 0.05M, 0.075M, and 0.1M) flowed into the desorption type. Then, the evaluation from the desorption process is calculated. Then, the filtrate was analyzed by AAS [21].

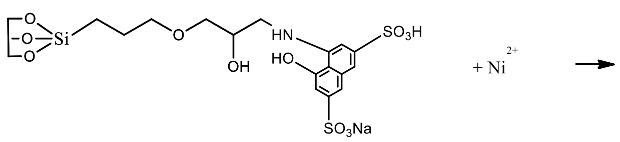
Results and Discussion

Silica gel is modified to improve its performance in the analytical field. In this research, the modification was carried out using the monosodium salt of 4-amino-5-hydroxy-2,7-naphthalene sulfonic acid and glycidoxypropyltrimethoxylane (GPTMS) as a linker, which aims to make the binding of organic compounds of sulfonate salts more efficient [2]. In this research, silica gel was added with the linking compound GPTMS and toluene, then heated at 90˚C for 24 hours. This heating aims to optimize the binding process of silane groups on silica gel. After that, the silica gel was washed with methanol to remove contaminants in the form of toluene and the resulting silica gel-GPTMS

Then, Silica gel-GPTMS was processed by adding sulfonate salt into sodium bicarbonate solution and stirring the mixture for 20 hours to ensure maximum sulfonate salt bonding. During this process, the epoxy ring on the silica gel-GPTMS opened up, resulting in a positive C atom and a negative O atom. The O atom of the epoxy group attacks the proton on the amine group of the sulfonate salt, making the N atom on the amine group negatively charged and binds to the positive C on silica gel-GPTMS, resulting in silica gel-GPTMS Sulfonate. The sulfonate group in this modified silica gel will be used as an ion exchange site in adsorption and desorption.

Adsorption

Previous research from Dwi Ramadhani in 2023 examined the determination of optimum conditions for the adsorption of Ni^{2+} cations and obtained an optimum pH at three and an optimum concentration of 20 ppm. Based on these conditions, the present study used the column method for the adsorption of silica gel-GPTMS Sulfonate. The solution containing Ni^{2+} cations flowed through the column, causing Ni^{2+} cations to bind to the adsorbent surface due to chemical and physical reactions [16]. The reaction for the adsorption of Ni^{2+} can be seen as follows.



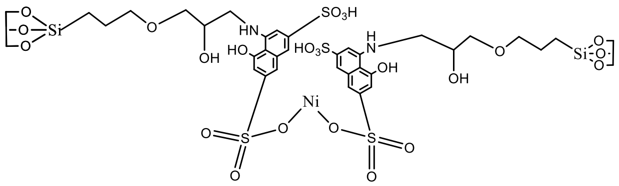


Figure 1. Adsorption reaction of Ni^{2+} on Silica gel-GPTMS Sulfonate

Table 1. Adsorption Data at Optimum Conditions

C0 (mg/L)	C1 (mg/L)	Initial weight (mg)	Final weight (mg)	% adsorption
18.945	1.428	0.1894	0.0139	92.61
18.512	1.512	0.1851	0.0148	91.96
18.512	1.600	0.1851	0.0155	91.61

The table shows that the adsorption of Ni^{2+} cations on silica gel-GPTMS Sulfonate using the column method resulted in the highest adsorption capacity of 1.7545 mg/g, with an absorption rate of 92.61% and an adsorbed weight of 0.1754 mg. The optimum absorption capacity is reached at pH three because the number of protons and OH in the solution is balanced so that Ni^{2+} ions can bond more effectively with sulfonate groups (SO3-) [2].

Factors that can affect the adsorption process are the adsorbent and adsorbate used, the concentration of each substance, the surface area of the adsorbent, pressure, solubility of the adsorbent, pH, temperature, and stirring speed [19]. The degree of acidity is a factor that affects the solubility of metal ions and active groups present in the adsorbent. This is because H^+ ions in the solution compete with cations to bind to the active groups on the adsorbent surface. In the effect of concentration, the higher the concentration used, the absorption of sulfonate-modified silica gel to cadmium solution increases until the active side of sulfonate-modified silica gel is saturated and cannot absorb [20].

Using the optimum conditions in the research conducted by Dwi Ramadhani in 2023, the percentage of adsorption is relatively constant and follows the results obtained.

Desorption

Desorption is the process by which substances or molecules that have been adsorbed (attached) to the surface of an adsorbent are released or removed from the adsorbent [6]. Adsorbed substances can be removed through several methods, such as heating, use of vacuum, washing with sorbents, pressing with additional sorbents, modification of environmental conditions, application of physical or chemical treatments, or extraction using solvents [17]

Adsorbed substances can be effectively removed using various methods, each suited to different scenarios based on the nature of the absorbent and the adsorbate. One common approach is heating, which involves raising the temperature to desorb the substances by breaking the bonds between the adsorbate and the adsorbent. Using a vacuum is another effective method; reducing the pressure around the adsorbent allows volatile compounds to be drawn off more easily. Washing with sorbents involves introducing materials that interact with the adsorbed substances to displace them from the surface, often employing specific solvents or reagents for selective removal.

The desorption agent type affects desorption effectiveness, as the solution determines how well the desorbed substance can be re-released. This allows the column to be reused or regenerated. In the Ni^{2+} cation desorption process, NaCl and CaCl2 salts were used to determine and compare which desorption agent is more effective in exchanging Ni^{2+} cations.

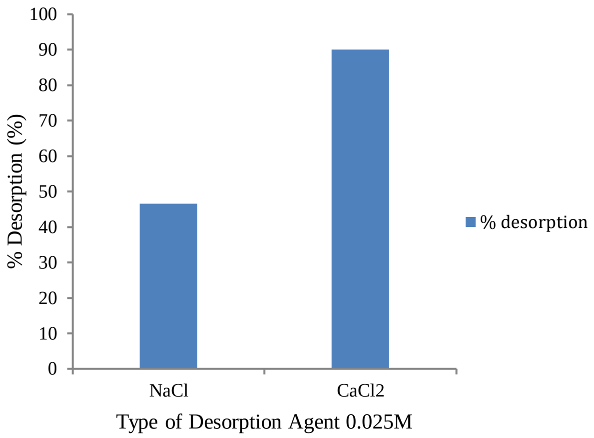


Figure 2. Type of Desorption Agent

The graph shows that the best desorption agent for Ni^{2+} cation is $CaCl_2$. This follows the theory that in cation exchange resins, the positive ions with the greatest to least affinity for exchange are calcium (Ca^{2+}), magnesium (Mg^{2+}), ammonium (NH_4^+), potassium (K^+), sodium (Na^+), and hydrogen (H^+) [18]. The charge of the exchanged ions influences the desorption process. Since Ca^{2+} has the same +2 charge as Ni^{2+}, it is more suitable to displace it than $Na^{+,}$ which only has a +1 charge. Therefore, the percent desorption with $CaCl_2$ is higher than NaCl, so $CaCl_2$ is more effectively used to desorption Ni^{2+} cations on silica gel-GPTMS Sulfonate. The ion exchange reaction between Ni^{2+} and Ca^{2+} in the desorption process is as follows.

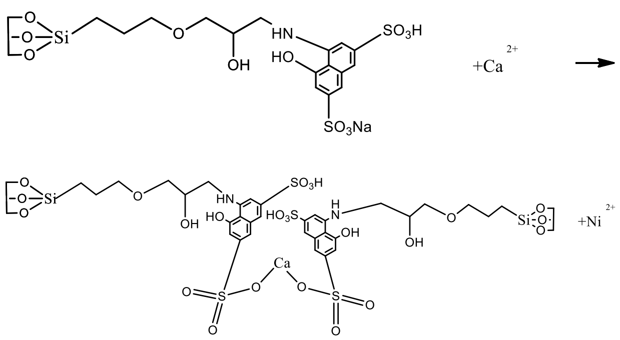


Figure 3. Desorption Reaction of Ni^{2+} on Silica gel-GPTMS Sulfonate

Concentration is a crucial factor in the desorption process as it affects the amount of Ni^{2+} cations released from the active side of the adsorbent. Concentration variation was conducted to observe the equilibrium conditions in the desorption process of metal ions on the adsorbent surface. In this study, the concentration variations tested were 0.01, 0.025, 0.05, 0.075, and 0.1 ppm. The effect of concentration variation on Ni^{2+} cation desorption on sulfonate-modified silica gel-GPTMS can be seen in the following graph.

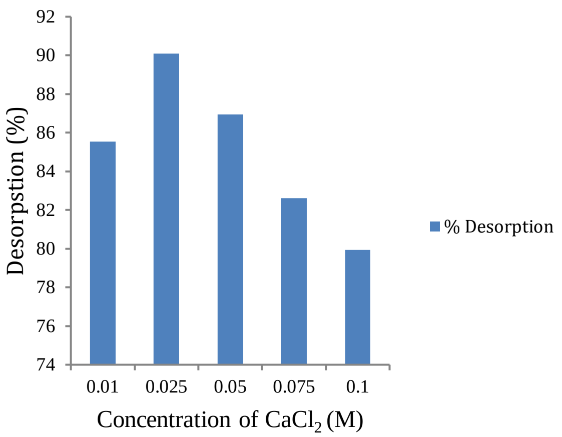


Figure 4. Concentration Variation of Desorption Agent

Based on the data obtained, the optimum concentration of $CaCl_2$ to desorb Ni^{2+} cations was 0.025 M, where the efficiency reached 90.10%. At higher concentrations, i.e., between 0.05 M and 0.1 M, the desorption percentage had no significant increase. This may be due to the inability of Ni^{2+} cations to desorb at these concentrations. Eluent concentration is one of the important parameters in the desorption process [10]. If the eluent concentration is too high, it may damage the adsorbent structure, inhibiting ion exchange between Ni^{2+} and Ca^{2+} cations bound to the adsorbent, resulting in a decreased desorption percentage

In addition, at $CaCl_2$ concentrations of 0.05 M to 0.1 M, there has been an equilibrium between Ni^{2+} cations and the adsorbent, so high $CaCl_2$ concentrations can no longer effectively release Ni^{2+} cations from the adsorbent.

Conclusion

The optimum condition obtained in determining the type and variation of desorption agent concentration is to use $CaCl_2$ with a percent desorption of 90.1% when compared to NaCl with a desorption percent of 46.53%. And eluent at a concentration of 0.025M with percent desorption of 90.18%. It can be applied directly to the chromatography column after obtaining the optimum conditions for Ni2+ desorption on silica gel-GPTMS Sulfonate adsorbent.

References

[1] Kristianingrum, S., Siswani, E. D., & Fillaeli, A. (2020). Pengaruh jenis asam pada sintesis silika gel dari abu bagasse dan uji sifat adsorptifnya terhadap ion logam tembaga (II). *Sumber, 2(1),* 7.

[2] Azmiyawati, C. (2004). Modifikasi Silika Gel dengan Gugus Sulfonat untuk Meningkatkan Kapasitas Adsorpsi Mg (II). *Jurnal Kimia Sains dan Aplikasi*, *7(1)*, 10-16.

[3] Fitriningsih, A., & Oktavia, B. (2023). Optimasi Adsorpsi Ion Co2+ Menggunakan Silika Gel-GPTMS (Glycidoxyproyltrimethoxysilane) Dimodifikasi dengan Sulfonat. *Jurnal Pendidikan Tambusai*, *7(3)*, 24102-24110.

[4] Rahayu, P., & Khabibi, K. (2016). Adsorpsi Ion Logam Nikel (II) oleh Kitosan Termodifikasi Tripolifosfat. *Jurnal Kimia Sains dan Aplikasi*, *19(1)*, 21-26.

[5] Kristina, D., Etika, S. B., Nasra, E., & Oktavia, B. (2022). Pengaruh Kecepatan Pengadukan dan Waktu Kontak Terhadap Penyerapan Fenol Menggunakan Adsorben C-SinamalKaliks [4] Resorsinarena Hasil Sintesis Limbah Minyak Kayu Manis (Cinnamomum burmanii). *Periodic, 11(3)*, 48-52.

[6] Yanti, D. R., & Oktavia, B. (2022). Desorpsi Nitrat (NO3-) dari Silika Gel Termodifikasi Dimetilamina (DMA) menggunakan Eluen Asam. CHEDS: *Journal of Chemistry, Education, and Science, 6(2)*, 82-89.

[7] Manuhutu, J., Nuryono, N., & Santosa, S. J. (2018). Desorpsi Ion Emas (III) Dalam Sistem Multilogam Au/Ni/Ag Dengan Menggunakan Variasi Tiourea-HCl. *Molluca Journal of Chemistry Education (MJoCE), 8(1),* 56-63.

[8] Maslukah, L., Zainuri, M., Wirasatriya, A., & Widiaratih, R. (2020). Studi kinetika adsorpsi dan desorpsi ion fosfat (PO42-) di sedimen perairan Semarang dan Jepara. *Jurnal Ilmu Dan Teknologi Kelautan Tropis, 12(2),* 383-394.

[9] Ahsanti, H., Slamet Mulyati, S., & Yulianto, B. (2021). Pengaruh Variasi Berat Resin Ion Exchange Terhadap Penurunan Ph Air Limbah Produksi Di Pt. Xyz. Jurnal Kesehatan Siliwangi, 2(2), 427-430.

[10] Patel, H. (2021). Review on solvent desorption study from exhausted adsorbent. *Journal of Saudi Chemical Society, 25(8)*, 101302.

[11] Miner, L., & Beauchemin, D. (2020). Inductively coupled plasma mass spectrometry coupled to cation exchange chromatography for the determination of trace nickel in alkaline electrolyte. *Journal of Analytical Atomic Spectrometry, 35(7),* 1295-1299.

[12] Bakkaus, E., Collins, R. N., Morel, J. L., & Gouget, B. (2006). Anion exchange liquid chromatography–inductively coupled plasma-mass spectrometry detection of the Co2+, Cu2+, Fe3+ and Ni2+ complexes of mugineic and deoxymugineic acid. *Journal of Chromatography A, 1129 (2),* 208-215.

[13] Abesekara, M. S., Kosvinna, K. N. R., & Amarasinghe, B. M. W. P. K. (2020). Adsorption and desorption studies of Ni2+ ions on to coconut shell char. *In IOP Conference Series: Earth and Environmental Science (Vol. 427, No. 1, p. 012005)*. IOP Publishing.

[14] Bolisetty, S., Peydayesh, M., & Mezzenga, R. (2019). Sustainable technologies for water purification from heavy metals: review and

analysis. *Chemical Society Reviews, 48(2),* 463-487.

[15] Wu, L., Yue, W., Zheng, N., Guo, M., & Teng, Y. (2022). Assessing the impact of different salinities on the desorption of Cd, Cu and Zn in soils with combined pollution. *Science of the Total Environment, 836*, 155725.

[16] Maregianti, M., Wardani, G. A., & Wulandari, W. T. (2022, January). *Adsorpsi Senyawa Antibiotik Tetrasiklin Hidrolirida Menggunakan Limbah Serbuk Gergaji dengan Metode Kolom*. In Prosiding Seminar Nasional Diseminasi Hasil Penelitian Program Studi S1 Farmasi (Vol. 1, No. 1).

[17] Sati, B. N. (2023). Desorpsi Anion Kromat dari Silika Gel Termodifikasi Dimetilamin (DMA). CHEDS: *Journal of Chemistry, Education, and Science, 7(1),* 35-39.

[18] Shahab, A., & Setiorini, I. A. (2023). Efektifitas Volume Resin Ion Exchanger Terhadap Kapasitas Pertukaran Ion Dan Waktu Jenuh Pada Unit Demin Plant Di Pt Pln (Persero) Updk Keramasan. *Journal of Innovation Research and Knowledge, 2(9),* 3791-3802.

[19] Widayatno, T. (2017). Adsorpsi logam berat (Pb) dari limbah cair dengan adsorben arang bambu aktif. *Jurnal teknologi bahan alam, 1(1),* 17-23.

[20] Sy, S., Kurniawati, D., Lestari, I., Harmiwati, H., & Kasman, M. (2018). Pengaruh pH dan dosis adsorben dari limbah lumpur aktif industri crumb rubber terhadap kapasitas penyerapan ion Cd (II) dan Zn (II). *Indonesian Journal of Industrial Research, 8(2),* 95-104.

[21] Marlina, D., Oktavia, B., Benti, S., & Aini, S. (2023). Penentuan Kondisi Optimum Desorpsi Anion Nitrat (NO3-) pada Silika Mesopori Termodifikasi 54 Dimetilamina (DMA). *Periodic, 12(2),* 16.