Optimization of Nitrate and Nitrite Anions Adsorption on Modified Silica using Batch Method

Yuliana Arianti, Budhi Oktavia*
Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Padang, Padang, West Sumatra, 25173, Indonesia

*budhioktavia@fmipa.unp.ac.id

Abstract. Ammonia inorganic compounds are compounds that are often found because it is soluble in ground water which causes health hazards that are carcinogenic, mutagenic, tetratogenic and cause metamoglobinemia. Ammonia compounds that have negative effects on humans are nitrate and nitrite anions. Disposal of liquid waste and the use of fertilizers cause nitrates and nitrites to dissolve so that it has a negative impact on groundwater. One of the efforts to overcome nitrate and nitrite in waste is by adsorbing with adsorbent., where the adsorbent used is DMA modified silica. Characterization by adsorption of nitrites and nitrates from aqueous solution at various pH, concentrations, and contact times. The result showed that silica modification with DMA increased the adsorption capacity of nitrates and nitrites. The Langmuir isotherm yields a regression coefficient $R^2 = 0.9809$ for nitrate and $0.9469$ for nitrite. Nitrate adsorption capacity of $0.1669 \text{ mg g}^{-1}$ with an initial nitrate concentration of $60 \text{ ppm}$ at pH $8$ with stirring for $120$ minutes while the maximum adsorption capacity of nitrite was $0.1669 \text{ mg g}^{-1}$ with an initial nitrite concentration of $40 \text{ ppm}$ at pH $6$ with stirring for $120$ minutes.

1. Introduction

The rapid development of industry in Indonesia has resulted in many positive and negative impact, the negative impacts in the form of solid waste, air pollution and water waste [1]. Disposal of waste into waters without prior treatment causes pollution in the waters. This pollution is caused by improper waste handling. This also has an impact on water. Water has many roles in human life, such as in household needs, agriculture, fisheries, livestock, and industry. One of the water resources is ground water which is used as a source of drinking water because water treatment is relatively cheap [2]. Groundwater contains elements of organic compounds and inorganic compounds which are dangerous if their presence exceeds quality standards. This is due to human activities and natural factors. Several things affect the quality of groundwater, such as the use of nitrogen fertilizers and the decomposition of organic waste originating from animals and humans. Nitrogen compounds that pollute groundwater are nitrite ($\text{NO}_2^-$) and nitrate ($\text{NO}_3^-$) [3].

High concentrations of nitrite and nitrate anions in groundwater can cause health hazards, because these anions will from N-nitroso compounds which are carcinogenic and cause health problems such as methaemoglobinemia and stomach cancer [4]. Therefore we need a treatment for the waste. One of the processing methods that can be done by adsorption. Adsorption has advantages over other methods because of its low cost, low level of efficiency and easy [5]. Silica is one of the adsorben that is often used in adsorption. Silica is a solid that is stable under acidic conditions, has high mass exchange characteristics, specific porosity and surface area has high resistance to heat, but the effectiveness of the adsorption of silica against metal ions is weak. This is due to the low ability of...
oxygen (silanol and siloxane) as electron pair donors, resulting in weak metal ion bonds on the silica surface [6].

In 2020, Oktavia et al. research on monolith columns, where by making polymers in silica capillaries using several monomers such as (glycydyl methacrylate (GMA), azobisisobutyronitrile (AIBN) as an initiator, ethylene dimethacrylate (EDMA) as a crosslinker and porogen. 1,4butanadiol, 1-propanol, and water. Then after the polymer is formed, modification is carried out using Dimethylamine (DMA). Monolith columns are used to separate nitrate and nitrite anions [7]. In addition, polymer formation can be carried out using modifiers that another, namely Diethylamine. Where from these monomers can produce tertiary amine compounds as ion-exchange groups. Modification with monolithic columns is used as a separator in ion chromatography. Ion chromatography has developed into a good analytical technique for the separation of cations and anions [8]. Silica can bind inorganic compounds with the help of linking compounds. The bridging compounds used was dimethylamine (DMA) modified GPTMS (glycidoxypropyltrimethoxyl). GPTMS is compounds which has an epoxy group. This modified silica is used as an adsorbent for absorption of nitrite and nitrate anions. Dimethylamine acts as a functional group for anion exchange to separation anion [9].

2. Methods

2.1. Materials
The material used are natural silica, GPTMS, Dimethylamine, aquades, HCl, NaOH, NaNO\textsubscript{3}, NaNO\textsubscript{2}, Ethanol, and Methanol.

2.2. Tools
The tools used were electric oven, analytical balance, shaker (model: VRN-480), pH meter (H12211), glassware, filter paper, magnetic stirrer (MR Hei Standard), mortar and pestle, oven, spray bottle, sieve (BS410), spatula, volumetric pipette.

2.3. Preparation of a standard solution of Nitrate and Nitrite
A standard concentration of 1000 ppm anion solution is made by dissolving NaNO\textsubscript{3} and NaNO\textsubscript{2} as much as 1.5 gram NaNO\textsubscript{2} and 1.38 gram NaNO\textsubscript{3} with a little distilled water, put into a 1000 mL measuring flask, add aquades to the mark. Stir until homogeneous and put in a reagent bottle. Solution work prepared by proper dilution of standard solutions.

2.4. Preparation of 1M HCl solution
8.52 mL of 36% HCl solution pipette was put into a 100 mL volumetric flask containing a small amount of distilled water after which aquades were added to the mark and put into a reagent bottle.

2.5. Preparation of 1M NaOH solution
Weigh ± 4 g NaOH powder put in a beaker, add distilled water, stir until homogeneous, and put into 100 mL volumetric flask. Add distilled water until boundary mark, and shake until homogeneous and put into reagent bottle.

2.6. Silica Preparation
Refined natural silica (reduce particle size) with a smoothing machine in PT. Semen Padang. Silica is sieved using a sieve at The Laboratory of SMK-SMAK Padang to get a particle size 45 µm. 35 gram of silica soaked and stirred in 350 mL of 1M HCl for 24 hours. The silica pH was neutralized using distilled water and oven dried for 2 hours at 105°C.

2.7. Formation of Silica-GPTMS
Weigh 25 gram of activated silica and add 25 mL of GPTMS and 87.5 mL of toluene, then stirred at 90°C for 24 hours. Solution washed with 12.5 mL of methanol.
2.8. Modification of silica-GPTMS with Dimethylamine (DMA)
Silica-GPTMS 23 grams were modified with 11.5 mL of DMA dissolved in 11.5 mL of ethanol (1:1 v/v). Then silica oven for 4 hours at 80 °C, rinse with methanol.

2.9. Treatment research with a batch system

2.9.1 Effect of pH. Nitrate and nitrite solutions 25 mL 50ppm concentration, each in a variation of pH 2,4,6,8,10, and 12 were put into the erlenmeyer contact with 1 gram silica using shaker for 120 minutes 150rpm of speed. Then filtered with filter paper, the filtrate obtained measured by concentration with spectronic. The optimum pH obtained is used for further research. The pH was prepared by adding 1 M NaOH solution or 1M HCl solution. The effect of pH variations was determined by batch system adsorption method.

2.9.2 Effect of solution concentration. Nitrate and nitrite solution 25 mL are adjusted to the optimum pH, each solution in variety of concentration of 20, 40, 60, and 80 ppm is put into the erlenmeyer contacted with 1 gram modified silica using shaker for 120 minutes 150 rpm speed, then filtered with filter paper, the filtrate obtained measured by spectronic. The optimum concentration obtained is used for further research. The effect of concentration variations is determined adsorption by batch method.

2.9.3 Effect of contact time. Nitrate and nitrite solution 25 mL are adjusted to the optimum pH, optimum concentration put into the erlenmeyer, contacted with 1 gram silica using shaker with contact time variation of 30 minutes, 60 minutes, 90 minutes and 120 minutes 150 rpm speed, then filtered with filter paper. The filtrate obtained measured by spectronics. The effect of contact time variation is determined adsorption by batch method.

3. Result and conclusion

3.1. Effect of pH on Adsorption of Nitrate (NO$_3^-$) and Nitrite (NO$_2^-$) anions using Natural Silica as Adsorbent.

pH is one of the factors that affect adsorption because pH affects the load of the active sites on the adsorbent surface due to protonation reactions, or deprotonation of the active adsorbent sites, pH also affects the adsorbate species in solution [10]. The variation of pH are 2,4,6,8, 10 and 12.
Based on the figure 2, it can be seen that the optimum pH obtained is at pH 6, the absorption obtained is equal to the absorption percentage of 13%. The absorption capacity increases from 0.013 to 0.073 with a decrease in the pH value from 12 to 6. Whereas in Figure 3 it can be seen that the optimum pH obtained is at pH 8, the absorption obtained is 0.06363 with an absorption percentage of 11%. The absorption capacity increases from 0.016 to 0.0636 with a decrease in the pH value from 12 to 8. pH is very necessary because at the time of adsorption there is a binding between the functional groups and the nitrite and nitrate anions which involves the H⁺ ion exchange process [11]. A good condition for adsorption is at a neutral pH around 6-8. This is because at low pH the H⁺ ion on the adsorbent surface increases, resulting in a strong electrostatic bond between the positive charges on the adsorbent surface. In addition, the dissolved organic matter in the waste is reduced [12]. While increasing the pH of the adsorption will decrease this because at high pH, the concentration of OH⁻ in the solution will increase, so that the cell surface slowly becomes negatively charged. At high pH conditions the adsorption ability is reduced and the strength to bind ions is getting smaller.

3.2. Effect of concentration on Adsorption Nitrate and Nitrite anions using DMA Modified natural Silica as adsorbent.

Variation in concentration were 20, 40, 60, and 80 ppm of the solution with adjusted optimum pH.
Based on the figure 4 it shows an increase in silica nitrite anion absorption after modification from a concentration of 20 ppm to 40 ppm and at a concentration of 60 ppm - 80 ppm the absorption has decreased. The optimum results obtained were at a concentration of 40 ppm with absorption of 0.1669 mg / g with a percentage of 41.97%. The results obtained from Figure 5 show an increase in silica nitrate anion absorption after modification from a concentration of 20 ppm to 60 ppm and a concentration of 80 ppm has decreased absorption. The optimum results obtained were at a concentration of 60 ppm with an absorption of 0.093 mg / g with a percentage of 11.87%. This can be related to the number of active sites that are on the adsorbent, when the number of active sites in the adsorbent is greater than the amount of anions, the greater the absorption that occurs. When at a concentration of 80 ppm the number of ions absorbed will be the same as the active side available, this causes optimal absorption or is often called an equilibrium state [13]. So that the concentration added will not cause an increase. The equilibrium between the adsorbent and the adsorbate can be determined by the Langmuir isotherm. Langmuir isotherm states that adsorption occurs only in a single layer (monolayer) [14].
Based on Figure 6, it is obtained that the $R^2$ value obtained meets the Langmuir isotherm equation, the results obtained from $R^2$ are 0.9469, with a value equilibrium capacity of 1.01822 mg / g. whereas based on Figure 7, it is obtained that the $R^2$ value obtained fulfills the Langmuir isotherm equation. The results obtained from $R^2$ are 0.9809, with a value equilibrium capacity of 1.2971 mg / g. The greater the $K_I$ value, the greater the adsorbent affinity for the dye [15].

3.3. Effect of Contact time on Adsorption of Nitrate ($NO_3^-$) and Nitrite ($NO_2^-$) anions using Natural Silica as Adsorbent

Contact time is an influencing factor in the adsorption process. The contact time aims to determine the length of time required for the adsorbent to optimally absorb nitrate and nitrite anions. Determination of the optimum capacity at the time of stirring was carried out with variations from 30, 60, 90 and 120 minutes with a pH of 6 for nitrite and pH 8 for nitrate with a concentration of 40 ppm for nitrite and 60 ppm for nitrate. The longer the contact time, the greater the absorption of the anions [16].
Based on Figure 8, it is found that the optimum contact time for the adsorption of nitrite anions on silica increases with increasing stirring time, the optimum stirring time is 60 minutes with an adsorption rate of 0.211 mg/g with a percentage of 50%. The optimum time is the time of equilibrium between the adsorption and desorption rates [15]. Based on figure 9, it can be seen that the optimum contact time for the adsorption of nitrate anions is 90 minutes with a pH of 8 at a concentration of 60 ppm with an adsorption rate of 0.065 mg/g. The longer the rebellion, the better the adsorption power [17]. The duration of contacting produces a large anions adsorption because the anion that bind to the more anions that will bind to the active site of the adsorbent. However, prolonged exposure can result in decreased adsorption because the active side of the adsorbent is completely bounds, so that it cannot bind anymore and when the saturation point is 90 minutes and 120 minutes the adsorption will tend to be constant, this is because the active side has bind to the anion is saturated and not can bond again [18].

4. Conclusion
Affect the adsorption process of nitrate and nitrite anions using silica as adsorbent. The optimum conditions are at pH 6 for nitrite and pH 8 for nitrate, while the optimum contact time is 60 minutes for nitrite and 90 minutes for nitrate. The maximum absorption capacity obtained using silica before modification and dimethylamine modified silica as adsorbent at the maximum concentration for nitrite 40 ppm and 60 ppm for nitrate.
Acknowledgment
The author thanks the Directorate of Research and Community Service at Padang State University, facilities and support. Thank you to Chemistry Laboratory, Faculty of Mathematics and Natural Science, Padang State University for their facilities and support. The final manuscript of this publication was presented at Webinar SEMIRATA 2020 on The 4th International Conference on Mathematics, Science, Education and Technology (ICOMSET) in conjunction with The 2nd International Conference on Biology, Science and Education (ICoBioSE) virtually at UniversitasNegeri Padang, Padang City, Indonesia on September 19th, 2020.

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