Adsorption of Metal Ion Manganese (Mn) in Sodium Silicate Solution using Chitosan

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Abstract. High purity Silica precipitate is very potential materials which can be utilized for many applications for high grade silicon, filler, photovoltaic, catalytic chemical, etc. Indonesia has abundant natural resources including quartz sand as raw materials for making high purity silica precipitate. Silica precipitate is made by roasting quartz sand forming sodium silicate solution. In order to obtain high purity silica precipitate, purification of sodium silicate solution is needed. In this study, purification of sodium silicate solution is performed by adsorption process of metal ion manganese (Mn) using chitosan as adsorbent. The experiment was done using batch technique. The variation of adsorption process was performed to get optimum conditions such as sample concentration, adsorbent mass, contact time, pH and temperature. The adsorption of metal ions of Mn was analyzed by atomic adsorption spectroscopy. The result of experiment shows that the best mass of chitosan for Mn adsorption process is 0.2 grams which gives percentage adsorption of 56.63%. The optimum contact time is 30 minutes, it results percentage adsorption of 52.5%. The optimum pH 3 gives adsorption percentage of 58.67%. And the best temperature for adsorption is at 60 °C with the percentage adsorption of 65.72%. Adsorption mechanism of metal ion Mn follow the isotherm model of langmuir and freundlich with the linearity value of $R^2 = 0.99$ and 0.98 respectively.

1. Introduction
The increasing need for advanced technologies has an impact on the increasing need for pure materials [1]. One of these raw materials is high purity silica precipitate. This is a kind of very potential materials which can be utilized for many applications for high grade silicon, filler, catalytic chemical, as well as in silicon production for photovoltaic application [2].

Silica can be obtained from quartz sand which is abundant in Indonesia with distribution area covering Kalimantan, Bangka - Belitung Islands, west and north Sumatra, and several areas of Java Island [3]. This quartz sand usually has a high crystallinity and the purity is quite high even up to 90%. However, based on the results of material characterization, it turns out that natural quartz sand has several impurities such as iron, manganese, aluminum, boron, phosphorus, etc [4]. The presence of impurities can limit the applicability of quartz sand intended for photovoltaic (PV) application. The quartz sand containing 500-800 ppm of iron is ready to be used in the industry of glass [5], but for PV application, sand with Fe content <100 ppm is required [2]. So before using silica in the carboreduction process, it must be enriched for eliminating the impurities [1].
Several studies have been carried out to obtain high purity silica by eliminating the impurities. The physical purification of the sandstone process can be done by a mechanical grinding in a ball mill for several hours [6], magnetic separation [7-8], or flotation [9]. Purification of quartz sand has also been carried out chemically by acid leaching method [1], [10], percolation leaching using hydrofluoric acid and hydrochloric acid (HF and HCL) [2], acid leaching followed by alkali extraction of silica from diatomite [11]. However, these processes have not been able to provide optimal results because the impurity elements in silica are present in the form of complex crystal bonds with SiO₂ compounds. These complex bonds form very strong compounds in the quartz sand [3]. This causes impurities contained in the quartz sand are difficult to be separated using physical and chemical separation process when the silica is still in the crystalline form.

General method for producing silica can be carried out using an alkaline fusion method with the addition of sodium carbonate [12] or dissolution in alkaline media [4]. To obtain a more efficient separation of impurities, several studies have been carried out on the purification of sodium silicate solution as an intermediate material before silica precipitate is formed. The method used can be in the form of adsorption using Lewatit 207 resin to remove iron (Fe) and aluminum (Al) elements [12], Phosphorus elimination with Complexation using Chitosan-EDTA [13], also Iron and Boron elimination using complexation method [14].

In this study, the purification of silica from impurity metal ion Manganese (Mn) was carried out after a phase change of silica from crystalline to amorphous in the form of sodium silicate to facilitate the release of impurities from the SiO₂ complex bonds. The process of eliminating impurities use the adsorption method with chitosan made from crab shells as adsorbent. Parameters such as concentration of sodium silicate solution, mass of adsorbent, contact time, pH, and temperature were studied in detail to determine optimum conditions for purifying silica. In addition, adsorption isotherm was also studied to understand the adsorption mechanism.

2. Experimental
2.1. Materials and chemicals
Natural quartz sand used in this research was from East Kalimantan, Indonesia. Sodium carbonate (Na₂CO₃), Sodium hydroxide (NaOH), and Hydrochloric acid (HCl) were of analytical reagent grade from Merck. For the absorbent we used chitosan made from crab shell. The crab shell itself was bought from local market in Banten, Indonesia.

2.2. Roasting of quartz sand
Quartz sand were washed using water to clean the soil and other soluble impurities, dried in an oven at 105 °C for 2 hours so that the washing water evaporates completely. A total of 165 grams of dry quartz sand were mixed with 135 grams of sodium carbonate in the mixing chamber. After obtaining a homogeneous mixture, the mixture was put into a graphite crucible then heated to a temperature of 1200 °C and held for 2 hours. The melted sodium silicate obtained from the roasting process was immediately removed and in its liquid state, it was poured from the crucible into the stainless steel pan. The melting sodium silicate was cooled with a fan cooler and the solid water glass was then collected. Cold water glass was crushed into powder. This powder was called Raw Sodium Silicate (RSS).

2.3. Preparation of sodium silicate solution
Raw Sodium Silicate (RSS) was weighed as much as 20 grams then dissolved in 200 mL of boiling water with a ratio of 1:10 (wt/wt) while stirring for 2 hours with a stirring speed of 300 rpm. The sodium silicate solution was then filtered with Whatman filter paper No. 40 so that it could be separated between the precipitate and the filtrate. Furthermore, quantitative analysis of the filtrate and residue was carried out to determine the impurity of the Mn metal using an Atomic Absorption Spectrophotometer (AAS).
2.4. Preparation of Chitosan
The preparation of chitosan was done through the stages of demineralization, deproteination, and deacetylation.

- Demineralisation
  Wet crab shells were washed, dried in the sun, milled, and sifted to get 100 mesh particle size. The fine shell was demineralized using a 1 M HCl solution with a ratio of the crab shell to HCl solution = 1:15 (wt/vol). The mixture of shells and HCl solution was stirred for 60 minutes without heating, decanted, washed with aquadest until the pH was neutral, filtered, and then the precipitate was dried to get shell powder.

- Deproteination
  This process was carried out at a temperature of 80-90 °C using 1 M NaOH solution while stirring for 3 hours. The ratio of shell powder : NaOH = 1:15 (wt/vol). Then the mixture was decanted, washed with aquadest until the pH was neutral, then filtered to get a precipitate called chitin.

- Deacetilation of chitin into chitosan
  Chitin was put into a 50% NaOH solution (1:15 wt/vol) at a temperature of 90 °C while stirring at a constant speed for 60 minutes. The mixture was filtered, the precipitate was washed with aquadest then added with a dilute HCl solution so that the pH was neutral and then dried to form chitosan.

2.5. Adsorption of Mn ion in batch system
0.2 grams of chitosan was mixed into 50 mL of sodium silicate solution with various process parameters including sodium silicate solution concentration, chitosan mass, contact time, pH, and temperature. The solution pH was adjusted using dilute solutions of HCl and NaOH. The adsorption process was carried out in a glass beaker reactor equipped with stirrer at a stirring speed of 300 rpm at room temperature for 30 minutes. The mixture was then filtered with Whatman filter paper No. 40.

The resulting filtrate was analyzed using AAS to determine the concentration of Mn metal ions remaining in the solution. The percentage of metal adsorbed was calculated by equation (1) as follows:

\[
\text{Percentage Adsorption} = \frac{C_0 - C}{C_0} \times 100 \%
\]

\(C_0 = \) initial concentration of metal ion (mg/L)
\(C = \) final concentration of metal ion after adsorption (mg/L)

The experimental parameters used in this study were as follow:

- Concentration of sodium silicate solution (3, 4, 5, 7, 10% by wt in aquadest)
- Chitosan with different masses (0.1; 0.2; 0.3; 0.4; and 0.5 gram)
- Contact time between chitosan and lartan sodium silicate (15, 30, 60, 90, and 120 minutes)
- pH of the solution (2, 3, 4, 5, 6, and 7)
- Temperatures (30, 40, 50, 60, 70, and 80 °C)

3. Result and Discussion
3.1. Effect of sodium silicate concentration on the Mn adsorption
Variation in the amount of metal ions adsorbed in the liquid phase is very important to optimize the absorption process and understand the absorption mechanism [15-16]. The results of adsorption of Mn metal ions by chitosan at various concentrations are shown in Figure 1 below. The higher the sample concentration, the more metal ions are absorbed by the chitosan. Adsorption increases with increasing initial metal concentration until saturation point of the active adsorption site is reached [16]. At a sample concentration of 3%, it is estimated that there are fewer metal ions in the sample, the metal that can interact with chitosan is also smaller. Then the saturation point of the active adsorbent is reached.
since the sample concentration of 5%, which is indicated by constant adsorption of Mn metal ions appears until the solution concentration is 10%.

![Figure 1](image)

**Figure 1.** Effect of sodium silicate concentration on the Mn adsorption percentage

According to the Langmuir isotherm theory, adsorption is thought to occur in a single layer. Once the adsorbate fills the layer, the absorbed molecules will not exceed the number of active sites on the adsorbent surface. When the active site of the adsorbent has not been saturated with adsorbate, the increased concentration of adsorbate exposed will increase linearly with the amount of adsorbed adsorbed. Furthermore, if the active site of the adsorbent is saturated with adsorbate, then increasing the adsorbate concentration exposed will not increase the amount of adsorbate adsorbed [17]. So the effective sample concentration that can be adsorbed by chitosan is 5%.

### 3.2. Effect of mass of chitosan on the Mn adsorption percentage

From the graph in Figure 2 it can be seen that the best mass for absorption of Mn metal ions is 0.2 grams of chitosan. The optimum absorption percentage of Mn was 56.63%. Higher adsorbent doses give more of the chelating active site exposed in solution, and metal ions can have more opportunity to join the active site that is still free [18]. The addition of chitosan mass to 0.3 grams did not show a significant correlation. According to Hargono et. al. [19] the decrease in absorption by chitosan is due to the solution becoming thick so that the stirring process is not perfect, as a result the percentage of absorption is decreased. Therefore, with only 0.2 grams of chitosan, the optimum adsorption percentage could be achieved.
3.3. Effect of time on the Mn adsorption

Data on the effect of time on Mn metal ion adsorption is presented in Figure 3 which shows a significant increase pattern from 15 minutes to 30 minutes then tends to decrease and is constant up to 120 minutes of processing. Increased adsorption activity due to availability of active binding sites on the sorbent [16]. After 30 minutes the adsorption process has reached an equilibrium condition with an optimum adsorption percentage of 52.50%. And after the optimum conditions were reached, the increase in contact time did not significantly increase the adsorption, indicating that the active site of chitosan was saturated with metal ions or equilibrium had been reached. This condition is in accordance with the results of previous studies by Saleh et. al. [16]. Another possibility that causes a decrease in adsorption activity occurs because the adsorption time is too long which can cause metal ions that have been bound by the adsorbent (chitosan) to be released or desorption occur.
3.4. Effect of pH on the Mn adsorption

pH is an important variable in the adsorption process because it greatly affects the solubility of metal ions in the solution, and these metal ions will replace some of the positive ions present in the active site of the adsorbent. pH also affects the degree of adsorbate ionization during the adsorption reaction [16]. Chitosan cannot dissolve in alkaline pH, so the adsorption is carried out at acidic pH to find out the optimum pH of the metal to be absorbed. In acid solutions, free amine groups are very suitable as polycations for chelating metals or forming dispersions because in the acid solution chitosan will become a polymer with a straight structure so it is very useful for flocculation, film forming or enzyme immobilization [20]. The optimum adsorption percentage results of manganese metal ions (Mn) by chitosan occurred at pH 3 according to the graph in Figure 4. The increasing in pH cause metal adsorption even tended to decrease until then it looked constant. According to Syahmani and Sholahuddin [21] states that the absorption capacity of a material is determined by its pH and the length of time it interacts characteristic for the material. The higher the pH, the smaller the resulting adsorption, because the possibility of Mn settling becomes Mn(OH)₂. Generally in acidic medium, metal (M) is present as free cation ion. But under neutral to alkaline conditions, cations will be hydrolyzed to form hydroxides, where most metal hydroxides are insoluble [22]. In several studies, increasing pH had no effect on metal ion adsorption activity [23], [24].

![Figure 4. Effect of pH on the Mn adsorption](image)

3.5. Effect of temperature on the Mn adsorption

As can be seen in Figure 5, the optimum temperature for Mn adsorption at 60 °C resulted in an adsorption of 65.72%. The higher the temperature used, the faster the reaction takes place so that the greater the kinetic energy of the substance molecules and the motion of the substance particles (chitosan) will be faster. As a result, the frequency of collisions that occurs will be large. Thus, there will also be more successful collisions so that the samples reacting with chitosan will be more than the adsorption at low temperatures. This result is consistent with that gained by [25] for removal of Cd using electric arc furnace (WS-EAF) slag as adsorbent.
3.6. Comparison between synthetic chitosan and commercial chitosan

In this study, besides using self-made chitosan for adsorption, commercial chitosan was also used as a comparison. From the data obtained, the adsorption of Mn with synthetic chitosan was 65.72%, whereas with commercial chitosan it was only 56.48%.

Table 1. Adsorption of Mn with synthetic and commercial chitosan

| Sample          | Adsorption of Mn (%) |
|-----------------|----------------------|
| Synthetic chitosan | 65.72               |
| Commercial chitosan | 56.48               |

The adsorption with synthesis chitosan results was better than commercial chitosan. This is probably due to the difference in the basic ingredients of chitosan, where synthetic chitosan is made from small crab shells while commercial chitosan comes from shrimp shells. Synthetic chitosan has just been made, still fresh, so that its adsorption capacity is still optimal, while commercial chitosan has probably been made for a long time so that it can affect its adsorption ability. The last reason is the particle size, commercial chitosan has a larger particle size than synthetic chitosan.

3.7. Adsorption isotherms

Adsorption isotherms can be used to study the adsorption mechanism. Langmuir and Freundlich models are the most widely used ones because of their simplicity [16]. In the Langmuir isotherm, there is a one-layer chemical absorption, whereas in the Freundlich isotherm, the adsorption process is carried out by multiple layers of chemical absorption.

In Figure 6 (a), the Langmuir isotherm graph for the Mn metal ion has a correlation coefficient value \( R^2 = 0.99 \), while in Figure 6 (b) which is a Freundlich isotherm graph the Mn metal ion has a value of \( R^2 = 0.987 \). From these data, it turns out that the adsorption of Mn metal ions also occurs chemically. This shows that the adsorption of Mn metal ions with chitosan is more dominant following the Langmuir adsorption isotherm equation.
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4. Conclusion
In this study, manganese was successfully absorbed from sodium silicate solution using chitosan. The results showed that the best mass of chitosan for the Mn adsorption process was 0.2 grams with an adsorption percentage of 56.63%. The optimum contact time of 30 minutes resulted in an adsorption percentage of 52.5%. At pH 3, the adsorption percentage of 58.67% is the optimum result. The best adsorption temperature occurred at 60 °C with an adsorption percentage of 65.72%. The adsorption mechanism for Mn metal ions follows the Langmuir and Freundlich isotherm models with linearity values of $R^2 = 0.99$ and 0.98 respectively.

Acknowledgment
The experiments were carried out using facility of laboratory in Metallurgical and Material Research Center, Indonesian Institute of Sciences (LIPI). The authors would like to thank the Ministry of Research, Technology and Higher Education of the Republic of Indonesia through Program
Pengembangan Teknologi Industri (PPTI) scheme for funding the research Pengembangan Nano Silika Presipitat Sebagai Bahan Baku Industri Konstruksi.

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