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Article

The Effect of Resin and NH_4OH Addition in The Making of Ammonium Silica Fertilizer from Geothermal Sludge

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Abstract

Geothermal sludge is a waste product from geothermal where it contains SiO_2 which can be used as fertilizer. In this study, the making of silica ammonium fertilizer was carried out by taking salicy acid from geothermal sludge by extracting and adding resin which was then modified with NH_4OH addition. Extraction was done using 1000 ml of KOH 1 N to dissolve 60 grams of Geothermal Sludge. Resins are added with variations in resin weight, namely, 5, 10, 20, 30, and 40 grams. NH_4OH was added with variations in concentrations namely 3, 6, 9, 12 and 15% with a ratio of filtrate and NH_4OH solution of 1: 1. The resulting ammonium silica inorganic liquid fertilizer products were analyzed for free silica and ammonia levels. The results of this study indicate that the levels of free silica and ammonia are influenced by the weight of the resin used and the concentration of ammonium hydroxide mixed. From the results of the research, it was found that inorganic silica liquid fertilizer with the highest SiO_2 content in ammonium silica liquid fertilizer occurred when adding 20 grams of resin with the addition of NH_4OH with a concentration of 15% which was 1,831.87 mg / L while the highest NH_3 content in fertilizer liquid ammonium silica occurs when adding 40 grams of resin with the addition of NH_4OH with a concentration of 15% which is equal to 252,312.80 mg / L.

Keywords: Extraction, Geothermal Sludge, Resin, Ammonium Silica

1. Introduction

One effort to increase agricultural production is a program to increase cultivation. The thing that is most considered in efforts to increase agricultural production is fertilization. The use of fertilizer is one of the benchmarks of successful agricultural development because with fertilizer, increased agricultural production can be achieved. Inorganic fertilizer is a type of fertilizer that can help improve agriculture because inorganic fertilizer has the advantage of being absorbed faster than organic fertilizer.

Geothermal sludge is a waste product from Geothermal which is difficult to handle. Geothermal sludge contains silica which can be processed into fertilizer where silica is one of the nutrients needed by graminiae plants such as rice, sugar cane and corn which are silica accumulators.

Plants lacking Si cause the three plant organs above are less protected by a strong silicate layer, consequently:

- Leaves of weak plants droop, not productive to catch sunlight, so that plant productivity is low;
- Evaporation of water from the surface of leaves and stems of plants is accelerated, so that plants easily wither or are sensitive to drought;
- Leaves and stems become sensitive to pests and diseases;
- Easy to fall plants;
- The quality of grain is reduced because it is easily contact with pests and diseases

so that optimal plant results are not achieved, low yield stability (fluctuating) and low product quality.

The silica element is known as the beneficial element for rice plants. Si's main role is to increase productivity and strengthen plant growth so that it is resistant to pests. Increased silica uptake in rice is beneficial to protect plants from pests and diseases, can keep leaves upright, reduce water loss due to transpiration, increase plant tolerance to reduced osmotic potential pressure on medium roots, increase oxidation strength of rice roots and reduce excess iron uptake and manganese. [5]

Fertilizer is a material that is added to the planting media or plants to meet the nutrient requirements needed by plants so that they can produce well. In modern agriculture, the use of fertilizer material is absolutely necessary to spur expected crop production levels. Ammonium silica fertilizer is an inorganic fertilizer from a chemical process containing.

ammonium and silica which is designed to provide nitrogen and silica nutrients for plants. Ammonium is a form of nitrogen that can be absorbed both by plants from the soil, but is less good in sandy soils or in the low availability of organic matter. Nitrogen content in the form of ammonium (NH4) can be useful in alkaline soils (bases or pH <7). Ammonium fertilizers commonly found in the market are Ammonium ZA and Ammonium Urea.

Geothermal sludge has silica (SiO_2) content of 65-67% by weight [8]. In the use of various fields, most geothermal mud is drained first until the mud turns into geothermal powder. Geothermal powders are then screened until a geothermal powder size of 80-100 mesh is obtained [4].

Extraction is the separation of one or several materials from a solid or liquid with the help of a solvent. Extraction is also the process of separating one or more components from a homogeneous mixture using a liquid solvent as a separating agent. Separation occurs on the basis of the different solubility of the components in the mixture. To get silica from geothermal sludge, a liquid-liquid extraction process with a base solvent is used, namely Potassium Hydroxide (KOH).

The reactions that occur in the extraction process are as follows:

$SiO_2 + 2\ KOH \rightarrow K_2SiO_3 + H_2O$ (1)

The silica content contained in geothermal sludge will react with potassium hydroxide to produce a solution of potassium silica (K_2SiO_3) with a very high pH which is close to 14.

The factors that affect the extraction speed include:

- Particle Size
  Particle size will affect speed extraction. The smaller the particle size, the largest area between the solid and the liquid allows proper contact. The larger the particles, the liquid that will diffuse will require a relatively long time.
- Stirring Factor
  The faster the rotation speed of the particle stirring will be more distributed in the contact surface will be wider to the solvent. The longer the stirring time means the diffusion can continue and the duration of the stirring must be limited to the optimum price so that it can be optimum so that energy consumption is not too large. The effect of this stirring factor is only present when the dissolution rate is possible.
- Temperature
  In many cases, the solubility of the extracted material will increase and will increase the extraction speed.
- Solvents
  The choice of a good solvent is a solvent that is suitable for a viscosity low enough so that the circulation is free. Generally pure solvents will be used even though in extraction operations the concentration of the solute will increase and the speed of the reaction will slow down, because the concentration gradient will disappear and the liquid will be more viscous. [1]

Ion exchange is a method used to separate unwanted ions in a solution to be transferred to a solid medium called an ion exchange agent, where the ion exchange media release other ions into the solution.

The mechanism of the ion exchanger is called the ion exchanger. The mechanism of ion exchange occurs if a solution containing anions or cations is contacted with an ion exchange medium, anion exchange will occur with the reaction mechanism as follows:

- Anion exchange mechanism

$A^- + R^+ B^- \rightarrow B^- + R^+ A^-$ (2)

- Cation exchange mechanism

$A^+ + R^- B^+ \rightarrow B^+ + R^- A^+$ (3)

Information :
A = The ion to be separated (in solution)
B = Ion replaces ion A (on solid or ion exchange media)
R = The ionic part / functional group in the ion exchanger. [7]

Resins are high-polymerized hydrocarbon compounds that contain cross-linking bonds and clusters of ions to be exchanged. The resin requirements include:

- The resin must be sufficiently cross-linked, so that its solubility can be ignored.
- The resin must be hydrophilic to allow diffusion of ions through its structure at a measured rate.
- Must have enough ion exchange groups that can be achieved and must be stable.
- The resin that is swelling, must be denser than water. [2]

The resin used in making ammonium silica fertilizer is a cation resin containing a (H^+) group. Potassium (K^+) ions from the potassium silica solution (K_2SiO_3) have a very basic pH that must be broken down into Potassium (K^+) and Silica Oxide (SiO_3^{2-}). With the cation resin used, namely Dowex (charged Na^+), the reaction that occurs is as follows:

$Rc\ (2Na^+) + K^+ + SiO_3^{2-} \rightarrow Rc\ (K^+) + 2Na^+ + SiO_3^{2-}$ (4)

Factors affecting ion exchange:

- Type of resin
  In the study of Water Sorption Isotherms and Cation Hydration in Dowex 50W and Amberlyst-15 Ion Exchange Resins. [9]. The type of resin in the ion exchange process determines the mechanism. In that study it acts as a single ion solution, because the ionogenic groups are simultaneously inactive and unhygienic. So the view is to provide possible experimental evidence regarding the nature of ion-pair formation, ionic hydration, free water mobility. It has been shown previously that analyzing the Dowex 50W resin water highlight isotherms in different ion forms using the D'Arcy and Watt (DWE) equation provides a realistic and consistent hydration number with results obtained from other studies. Whereas in the same study the physical structure of macroreticular resin (ex-sufficient, Amberlyst-15) was basically different from gel type resins (Dowex 50W).
  Macroreticular resins have a gel phase, where ionogenic groups are located, and phases consisting of large pores. 9, 21-26. The gel phase usually has a higher crosslinking than conventional gel type resins. Large pores absorb more solvents (including nonaqueous solvents) than conventional gel type resins. Due to structural differences, the exchange kinetics and ion exchange options show variation compared to gel type resins. Measurement of hydrated porosity using mercury porous symmetry shows that about half of the total water in macroreticular resin is in the pores with the rest in the gel microspheres. [9]
- Contact time
  The effect of contact time on ion exchange shows that the percentage of metal ions adsorbed increases with increasing equilibration time but at a certain time it will stabilize and the reaction will go back and forth. Where the adsorbed metal ions will release again. [6]
- Effect of the amount of resin

The amount of resin is included in an important parameter to get quantitative absorption of metal ions. Increasing the amount of resin, sorption density, and number of metal ions per unit of mass adsorbed increases.

- Effect of pH
  In ion exchange resins, the equilibrium process that depends on the presence of cationic forms in the solution is determined by the pH of the solution which can affect loading efficiency. In addition, greater ion penetration into the resin may also occur which is influenced by the kinetic effect and competition with other ions present in the solution can also be observed. This is most likely due to a lower pH solution containing higher competition ion concentrations which marginally inhibits interactions with the

resin. In general, metal concentration and pH, have a strong effect on the distribution coefficient, Kd and can be used as a comparative measure of the efficiency of various exchangers. [3]

- Temperature
  The effect of temperature shows the effect of temperature on the distribution coefficient (Kd) for the exchange of metal ions to the resin. The distribution coefficient is defined as the ratio of the metal ion concentration to the resin in the aqueous solution. The Kd value for metal ions will increase with temperature and the reaction product is preferred at high temperatures. This is due to the endothermic ion exchange reaction of divalent cations.

The silica acid solution produced after the ion exchange process has a variable amount of silica content, determined by the amount of resin used. To make liquid ammonium silica fertilizer, an addition of ammonium hydroxide solution is carried out with various heavy concentrations. Ammonium Hydroxide solution is used to provide nitrogen nutrients in ammonium silica fertilizer. The higher the concentration of ammonium hydroxide added to the solution, the higher the free ammonia content contained in the solution of ammonium silica products.

2. Material and Method

Geothermal powders that have been dried are uniform in size using 100 mesh screening. Furthermore, an analysis was conducted to determine the initial levels of SiO_2 in geothermal powders. A total of 120 grams of geothermal powder with a size of 100 mesh was dissolved in KOH concentration of 1N as much as 2000 ml.

The solution is heated at 100OC for 1 hour at a processing speed of 200 rpm. Then the pH is checked, the filtered solution where the filtrate will be used for the next step.

A total of 300 ml of filtrate was taken to be added with cation resin (Dowex) with a variation of resin weight of 5, 10, 20, 30 and 40 grams. Ion exchange is carried out by stirring for 1 hour in the stirring tank at a speed of 200 rpm. Then the solution is filtered to separate the resin from the filtrate which will be used at a later stage.

The filtrate from the ion exchange results added to the ammonium hydroxide solution with variations in the concentration of the solution, 3, 6, 9, 12 and 15%. The product solution was then analyzed to determine the levels of free SiO2 and NH3 by spectrophotometric methods.

3. Results and Discussion

The process of making ammonium silica fertilizer is used as the main ingredient of geothermal sludge as a source of silica. Based on the results of the initial material analysis, it was found that the silica content in the geothermal sludge was 34.98 %.

In the process of silica extraction used a potassium hydroxide solvent so that a solution of potassium silica is obtained. With the ion exchange process, potassium levels are lowered to produce a silicic acid solution.

Then do the addition of ammonium hydroxide to produce ammonium silica fertilizer. The addition of resin and ammonium silica turned out to affect the solution of ammonium silica fertilizer products, which are as follows:

Effect of resin on SiO_2 levels in product solution.

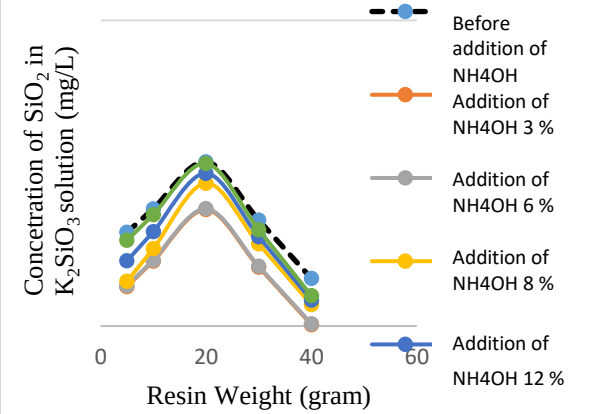

Fig 1. Effect of the addition of NH_4OH to SiO_2

In Figure 1 Effect of the addition of NH_4OH on SiO_2 levels in product solutions with variations in the weight of the resin, it can be seen that the weight of the cation resin used in the ion exchange process affects the concentration of SiO_2 in the K_2SiO_3 solution.

This is because the K_2SiO_3 solution inserted in the resin column experiences an exchange between the impurities cation of K_2SiO_3 solution

with H + from the resin which has a lower conductivity than the impurity cation of K_2SiO_3 solution so that the concentration of SiO_2 increases in addition of resin 5, 10 and 20 grams. Ion exchange resins have an ion exchange capacity which depends on the total number of active groups of ionic compounds in the weight of the material and the more the number of ions, the greater the capacity. However, in conditions where the resin has been saturated, that is, when the entire resin molecule has bonded with impurity ions, the resin will experience a reversible reaction.

Therefore the concentration of SiO2 decreases with the addition of 30 and 40 grams, this is likely due to the back and forth reaction in the K2SiO3 solution.

$$Rc\ (H^+) + K_2SiO_3 \Leftrightarrow R\ (K^+) + 2\ H^+ + SiO_3^{2-} \quad (5)$$

Effect of Addition NH_4OH to NH_3 levels in solution products with variations in resin weight, it can be seen that the addition of NH_4OH with different concentrations affects the NH_3 content in the product solution. In the research it can be seen that the effect of the addition of NH_4OH is the same for each variation of resin weight, ie the higher the concentration of NH_4OH added, the higher the NH_3 content contained in the product solution.

4. Conclusions

The quality of Ammonium Silica fertilizer is influenced by the weight of the resin used and the concentration of ammonium hydroxide added. Ion exchange resins have an ion exchange capacity which depends on the total number of active groups of ionic compounds in the weight of the material and the more the number of ions, the greater the capacity. So that in a condition where the resin has been saturated, that is, when the entire resin molecule has been bound to the impurity ions, the resin will experience a reversible reaction. In the research, the highest SiO2 content in ammonium silica liquid fertilizer occurred during the ion exchange process using 20 grams of resin with the addition of NH4OH with a concentration of 15%, amounting to 1,831.87 mg / L. While the highest NH3 content in liquid ammonium silica fertilizer occurred during the ion exchange process using as much as 40 grams of resin with the addition of NH4OH with a concentration of 15%, amounting to 252,312.80 mg / L.

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