Effect of Cellulose on The Characterization of Potassium Silica – Humate Composite Gel

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ABSTRACT

Potassium-Silica Humate Composite Gel or K-Si-Humate Composite Gel is a combined material of Potassium and Silica Humate derived from the extraction of raw materials for geothermal sludge and peat soil. This material is a multipurpose material, which can be used to improve soil aeration and as a fertilizer that can fertilize the soil because it contains humic acid. The purpose of this study was to examine the effect of cellulose content on the characteristics of the Potassium Silica-Humate composite gel. The manufacture of K-Si-Humate Composite Gel in this research by extracting potassium and silica from geothermal sludge and humic acid from peat soil, then the process of filtration and gel formation. The variable used is the addition of carboxymethyl cellulose content, namely Carboxy Methyl Cellulose (CMC). The best results from this study showed that with the addition of CMC, the highest silica content was 15.85%, and the highest potassium content was 89.88%.

Keywords: Potassium-silica humate composite gel, Carboxy Methyl Cellulose (CMC), geothermal sludge, peat soil

Introduction

K-Si-Humate Composite Gel is a composite gel consisting of humic acid and silica (SiO2) with KOH as the solvent. Humic acid is the main organic component in soil, peat, and coal which can bind metal ions to form complexes due to the presence of certain functional groups such as carboxyl, phenol, and mixed ligands. Humic acid as a precursor in the synthesis of adsorbents is still very limited, mainly due to the difficulty separating humic acid from the aqueous phase. Humic acid needs to be added with supporting materials. The supporting material used is silica. Silica has advantages in physical strength, easy-to-control structural parameters (surface area, pore size, particle shape), and stability (Prasetyo, 2016).

The process of forming potassium silica – humate composite by combining the two materials, namely Geothermal Sludge and peat soil, with one extraction with KOH solution, then adding cellulose as an adsorption center and citric acid for the gelling process. The addition of cellulose is needed because the resulting Silica-humate composite is less homogeneous, which functions as an adsorption center, which produces a hybrid material involving bound organic and inorganic phases (Evtuguin, 2009).

Silica (SiO2) is a metal oxide compound that is widely found in nature. According to its composition, silica can be divided into two, namely crystalline silica and amorphous silica. Crystalline silica has regularity in the arrangement of units, while amorphous silica has the same unit structure as crystalline but has a random arrangement of units (Kristiawati, 2018). The chemical properties of silica (SiO2) are relatively unreactive to acids except for hydrofluoric acid and phosphoric acid.
acid. Silica can react with bases, especially with strong bases, such as alkali hydroxides (Yansyah, 2015).

Silica has been widely used in industrial applications due to its unique properties and morphology, including its large surface area and pore volume and its ability to absorb various substances such as water, oil, and radioactive materials, as well as in the pharmaceutical industry. The most important property of silica is that it is a regenerated adsorbent (it can be reused as a drying agent). Its porous structure with a large silica surface area makes silica have a very large absorbing ability (Kristiawati, 2018).

Humic acid is one of the fractions of humic compounds, besides fulvic acid and humin (Furnata et al., 2017). Humic acid is a fraction of humic compounds that are insoluble at acidic pH (pH<2) but soluble at higher pH (Rahmawati, 2011). Humic acid is an organic substance found in soil and peat. Humic acid is a polyelectrolyte macromolecule material with functional groups such as –COOH, –OH phenolic and –OH alcoholate so that humic acid can bind to metal ions. These groups can experience proton release at a relatively high pH. The humic fraction can provide nutrients such as N, P, K, and S into the soil and C as an energy source for soil microbes. Currently, humic acid has been used to complement fertilizers that can increase the use of fertilizers and increase plant growth (Sembiring et al., 2015).

Geothermal mud as the main waste from PLTP has considerable potential in the industry, including as a source of silica. Almost all geothermal mud is white. Silica can be obtained by burning geothermal mud at a certain temperature to produce whitish ash containing silica as its main component. Geothermal mud that has undergone a combustion process will turn into geothermal powder. In general, the silica content in geothermal powders ranges from 75-85% (Adi, 2012).

Peat soil is the soil from the geological process or the deposition and transportation process of peat. Peat is a brownish-black material that is formed under acidic conditions and anaerobic conditions of wetlands. Peat is formed from piles of dead plant remains, both weathered and not. The stockpile continues to grow because the decomposition process is hampered by anaerobic conditions or other environmental conditions that cause the low level of development of decomposing biota (Suwatno, 2010).

The physical characteristics of peat that need to be considered about peat soil conservation are water content and water holding capacity. The water content of peat soil ranges from 100-1.30% of its dry weight (13 times its weight), causing the Bulk density (BD) to become low. Bulk density is related to the level of maturity and mineral content, where the more mature and the higher the mineral content, the greater the BD and the more stable the peat soil (not easily damaged). The content and thickness largely determine the chemical characteristics of peatlands and the type of minerals in the substratum (at the bottom of the peat), as well as the level of peat decomposition. The mineral content of peat in Indonesia is generally less than 5%, and the rest is organic matter. The organic fraction consists of humic compounds around 10-20%, and most of the others are lignin, cellulose, hemicellulose, wax, tannin, resin, suberin, protein, and other compounds (Poeziya, 2014).

Peat soil has the following characteristics (Soesanto, 2014):
1. Areas with peat soils are often inundated with water.
2. Has a high salt content.
3. Thickness reaches more than half a meter.
4. Brownish black.
5. The decomposition of organic matter contained in it is not perfect.

Cellulose is a polysaccharide compound that is widely found in nature. Cellulose is an abundant natural polysaccharide used to synthesize silica biocomposites in various derivative forms, e.g., hydroxyethylcellulose and carboxymethyl cellulose. Cellulose added in this research is Carboxymethyl Cellulose or Carboxy Methyl Cellulose (CMC). Carboxy Methyl Cellulose (CMC) is a soluble
form of cellulose that has a carboxymethyl group (CH2COOH) on the glucopyranose monomer unit in bone cellulose (Ahmad et al., 2014).

The structure of CMC is a polymer chain consisting of cellulose molecular units. Each anhydroglucose unit has three hydroxyl groups, and some of the hydrogen atoms of these hydroxyl groups are substituted by carboxymethyl, with the degree of substitution abbreviated as DS. The number of hydroxyl groups replaced, or the DS value affects the viscosity and solubility properties of CMC in water. The CMC is often used as a DS value of 0.7 or about 7 carboxymethyl groups per 10 anhydroglucose units because it has good thickening properties (aqualone CMC Herculesincorporated). CMC is a long-chain polymer molecule whose characteristics depend on the chain length or degree of polymerization (DP). The DS value and DP value are determined by the molecular weight of the polymer. As the molecular weight of CMC increases, its nature as a thickening agent increases (Ahmad et al., 2014). The chemical properties of CMC are: 1) Easily soluble in cold water and hot water, 2) Stable to fat and insoluble in organic solvents, 3) Good as a thickening agent, 4) As an inert substance, 5) Acts as a binder.

Based on its properties and functions, CMC can be used as an additive in beverage products and safe for consumption. CMC can absorb water contained in the air where the amount of water absorbed and the rate of absorption depend on the amount of water content in the CMC and the humidity and temperature of the surrounding air. The permissible CMC humidity in the packaging should not exceed 8% of the total product weight (Kamal, 2015).

The process of forming the K-Si-Humate Composite gel goes through several stages of the process, namely:

a) Solid-liquid extraction or leaching: extraction from peat soil and geothermal mud using KOH solution to the K-Si Humate solution.

b) Filtration Process: The filtration process here separates from the sediment to get the filtrate of K-Si-Humate.

c) Gel formation: Before gel formation, the phytate was added with Carboxy Methyl Cellulose (CMC).

Solid-liquid extraction or leaching is the diffusion transfer of dissolved components from an inert solid into the solvent. This is a physical process because the dissolved components are returned to their original state without undergoing chemical changes. The factors that influence the leaching process are:

1. Particle size
   The smaller the size of the material, the greater the surface area of the material. The large surface area will increase the extraction rate. In this case, the capillary paths that must be passed by diffusion become shorter, thereby reducing the resistance.

2. Extraction time
   The longer the extraction time, the greater the amount of material extracted

3. Temperature
   In many cases, the solubility of the solute (in the extracted particles) in the solvent will increase with increasing temperature to give a higher extraction rate. The higher the extraction temperature, the higher the viscosity of the liquid phase and the greater the solubility of the extract in the solvent.

4. Solvent
   The solution to be used as a solvent should be the best solution of choice, and its viscosity should be low enough to allow easy circulation. Usually, a pure solvent will be used initially. Still, after the extraction process ends, the solute concentration will increase. The extraction rate will decrease because the concentration gradient will decrease. After all, the solute becomes more viscous.

5. Fluid Stirring
   Stirring of the solvent is important because it will increase the diffusion process, thereby increasing the transfer of material from the particle surface to the solvent
Material and Methods

The research was conducted at the Research Laboratory of the Chemical Engineering Department, University of Pembangunan Nasional "Veteran" Jawa Timur, Surabaya. The tools used for this research are a series of extraction tools, namely Stirring Motor, Stative, Thermometer, Beaker Glass, and Electric Stove. The materials used are Geothermal Sludge from Dieng PLTPB, Peat Soil from Kalimantan, Potassium Hydroxide (KOH) from Utama Kimia, Demineralized Water, Carboxy Methyl Cellulose (CMC) from Utama Kimia, and Citric Acid (C₆H₈O₇) from Utama Kimia.

Extraction process from geothermal mud and peat soil. Silica extraction from geothermal mud was carried out by dissolving 10 grams of Geothermal Sludge powder in 400 ml KOH solution, stirring using a stirrer motor with a speed of 240 rpm at 100 °C for 1 hour. The resulting K₂SiO₃ solution was then cooled and filtered to collect the filtrate. Humic extraction from peat soil was carried out by dissolving 5 grams of peat powder in 400 ml KOH solution, stirring using a stirrer motor at 130 rpm at 100 °C for 2 hours. The resulting K-Humate solution was then cooled and filtered to collect the filtrate.

Adding Carboxy Methyl Cellulose (CMC) according to the run variables, namely 0.5 grams; 0.7 grams; 0.9 grams; 1.1 grams; 1.3 grams into the K₂Si-Humate solution, stir using a stirrer motor for 15 minutes (until the CMC dissolves), cool the solution. Then add 1 N citric acid until it reaches pH 7. then allowed to stand for 12 hours of gel maturation.

After the gel has formed, filter the solution and remove the residue. The residue is Cellulose–K–Si–Humate and K–Si–Humate gels. Then dried in an oven at 100 °C for 24 hours. Finally, grind the product using a grinder. Then do some analysis on the product with XRF.

Results and Discussion

The effect of the addition of carboxy methyl cellulose on potassium and silica content is shown in figure 1.

![Figure 1. The relation of carboxymethyl cellulose with the potassium and silica content](image)

From figure 1, we can see that the line graph shows that the effect on the highest potassium content is 89.88%. This result is in contrast to the more CMC added, the lower the potassium level. The addition of excessive cellulose can reduce the absorption power of the K-Si-Humate composite. Cellulose molecules more tightly cover the pores of the K-Si-Humate gel. So it is difficult for the citric acid solution to be absorbed, which causes the K content to decrease. However, this is also caused by too little weight of the extracted Geothermal Sludge. Then the effect on the highest Silica content is 15.85%. This shows that Carboxy Methyl Cellulose (CMC) 's increasing weight will
also affect the high silica content. This study obtained the highest value of the content of Potassium and Silica in the addition of CMC.

Conclusion
The effect of cellulose (CMC) content on the characteristics of the Potassium Silica – Humate composite gel is the more CMC added, the lower the potassium level. Still, it will affect the high silica content as well. However, adding CMC can reach potassium level at 89.88%, and Silica content is 15.85%.

References
Evtuguin, Dmitry, V., dkk. (2009). Preparation and properties of cellulose/silica hybrids composites. CICECO/Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
Prasetyo, E. (2016). Synthesis of humic acid-silica gel as a low cost adsorbent for uranium and thorium removal from wastewater. Division of Environmental Science Development Graduate School of Environmental Science Hokkaido University
Rahmawati, A. (2011). Pengaruh derajat keasaman terhadap adsorpsi logam kadmium(Ii) Dan Timbal(Ii) pada asam humat. Semarang:
IAIN Walisongo Semarang
Suwatno et al. (2010). Tinjauan mengenai gambut. (repository.unair.ac.id/25630/14/14.Bab202.pdf)