Synthesis of Matrix Si-K-HAs Gel from Geothermal Sludge and Peat

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Abstract

The synthesis of matrix silica-potassium-humic acid gel (Si-K-HAs) has been performed successfully by gradual extraction and acidification method. The extraction was carried out in two stages: 1) extraction of humic substances from peat prepared by potassium hydroxide to produce potassium humate (K-HAs) solution, 2) extraction silica from geothermal sludge using K-HAs solution to produce Si-K-HAs solution. Acidification of Si-K-HAs solution prepared by citric acid (1-3N) to produce matrix gel of Si-K-HAs. The Si-K-HAs matrix gel products are characterized by Fourier Transform InfraRed (FTIR), X-ray fluroscence (XRF), and Brunauer–Emmett–Teller (BET) analysis. The acidification process was carried out in neutral to acid (pH 3-7) conditions and the results showed that at neutral pH no Si-K-HAs gel formed. IR spectra confirmed the presence of humic acid in the gel product, whereas XRF analysis confirmed the presence of potassium (K) and silica (SiO_2) in the gel product. The molar ratio of SiO_2:K_2O in the product is 0.9-0.3 in the pH range of 3-5. Si-K-HAs powder can be used as soil fertilizer especially for soils that lack silica, humic, and potassium nutrients or for future application development.

Keywords: *geothermal sludge; gradual extraction; humic substance; matrix gel*

INTRODUCTION

Indonesia has the largest area of peatlands in South East Asia, which are distributed in Sumatra, Kalimantan and Papua islands. However, the peat lands in Indonesia have been degraded rapidly by deforestation due to logging and agriculture, construction of drainages and forest fires (Siegert *et al.*, 2011). Peat land degradation often occurs due to land use for agriculture, plantation or for industrial development. The process of converting peat lands generally begins with deforestation followed by the draining of peat land. Peat lands could not be recovered

so that water released from peat lands will lose their ability to store water. The peat lands that have lost water are prone to fire in the dry season and prone to flooding in the rainy season.

Humic acid (HA) is a major component of humic substance (HAs), which is the main organic constituent of soil (humus), peat and coal. It is produced by biodegradation of dead organic matter. It is not a single acid but rather a complex mixture of many different acids that contain carboxyl and phenolic groups so the mixture behaves functionally as a two-base acid or, sometimes, as an alkaline acid. (Saito and Seckler, 2014). The macromolecular structure of humic substances (HAs), i.e. molecular size, shape, conformation, and weight is believed to control key physico-chemical reactions in aquatic systems. However, these properties of HAs are still deeply a matter of debate (Baalousha *et al.*, 2006). On the other hands silica has become important globally because it produces resistance to many plants against disease and pests, and can contribute to the decline of pesticide and fungicide applications. Silica is also now considered an environmentally friendly element. This research is an effort to provide a fire suppression material in peat soil as well as provide nutrients and silica elements that are useful for plant growth.

Hybrid organic/inorganic materials derived through sol-gel processing have been extensively studied and reviewed. These hybrid materials combine the properties of inorganic and of organic compounds in one material (Sandor *et al.*, 2016). Several studies on the synthesis of alkali-silica-humic acid have been carried out but have not involved gelation method. Most products are obtained through the process of mixing some raw materials to produce a solid fertilizer (Roger *et al.*, 1971) or as suport for immobilization of humic acid to silica gel (Sandor *et al.*, 2016; Alexander *et al.*, 2016; Prasety *et al.*, 2016). The gelation is that cluster grow by condensation of polymer aggregation of particulate until the clusters collide, then links form between the clusters to produce a single giant cluster that is called a gel (Brinker, 1990; Muljani *et al.*, 2014). The present study developed a gelation process to form a combined gel matrix of silica, potassium, and HAs. To support nutrients in gel matrix, potassium hydroxide is used as a solvent to form potassium silicate. Potassium silicate with a standard of fertilizer is known to be quite effective (Buck *et al.*, 2008; Muljani *et al.*, 2016). On the other hands potassium humates derived from lignite (Zhang *et al.*, 2015) are alkaline, rich in carboxylic and phenolic groups, aromatic in nature provide favorable conditions for biological activity, chemical reactions and physical improvement of soil (Shujrah *et al.*, 2010).

Silica from geothermal sludge is amorphous structure (Muljani *et al.*, 2014) and is known that amorphous silica soluble in alkaline but insoluble at low pH (Iller, 1978). Meanwhile, HAs are materials that are insoluble under acidic conditions (at pH < 2) but soluble at higher pH values, and humin is the humic susbstances fraction that is insoluble in water at any pH

(Stevenson, 1994). HAs extraction from some materials ie coal, soil, leaf and mine has been done using sodium hydroxide as solvent (Michael *et al.*, 2007; David *et al.*, 2014). HA can also be reduced from sodium-humic solutions by ion-exchange methods (Kurniati *et al.*, 2018). Each of the HAs from these ingredients has slightly different IR spectra characteristics (Yamaguchi *et al.*, 1998).

Based on the same solubility properties, HAs and silica allow to be extracted gradually or simultaneously. In gradual extraction, two extraction steps are carried out as follows: 1) extraction of HAs from peat using potassium hydroxide to obtain potassium-humic solution, 2) potassium-humic solution used to extract silica from geothermal mud. While for the extraction simultaneously is done by mixing peat and sludge materials and then extracting the mixture of both materials using alkaline hydroxide solution. No previous research information was found on peat and silica extraction either gradually or simultaneously.

The formation of hydrogel silica from sodium silicate by acidification and polymerization reaction is influenced by several factors such as silica concentration, pH, aging time, and acid concentration (Muljani *et al.*, 2014; Kalapathy *et al.*, 2002; Brinker, 1990). This research involves HAs in polymerization reaction to form silica-humic hydrogel. Types of acids ie organic acids or inorganic acids used as catalysts for hydrogel formation are generally less influential. Citric acid is generally used as a buffer solution to control the pH of the solution. Kalapathy *et al.* (2002) reported the preparation of silica gels by an improved method using citric acid and oxalate to control the pH of the solution. Citrate ions can react with many metal ions to form citrate salts. The acidity of citric acid is obtained from three hydroxyl groups which can release protons in solution. Elizabeth *et al.* (2010) reported that the precipitation of silica will occur in very acidic conditions. The form of the silica monomer in the solution is immediately polymerized to form the primary particles and subsequently flocculates. The acid-catalyzed mechanisms are preceded by protonation of OH or OR substituents attached to silica (Brinker, 1988). The gel is fragmented and the flocs densify until a suspension is obtained. Control of size and structure of the resulting aggregates were strongly influencing product properties (Quarzh *at al.*, 2010). Polymerization occurs when the concentration of silica exceeds 140 mg/l, but this can be prevented by the presence of humic acid. Humic substances and other organic acids are known to form complexes or chelates with silica (Tan, 2010). The present study was intended to form a gel matrix of a silica-potassium-humic substance (Si-K-HAs) by controlling the concentration of citric acid and pH value in the acidification and polymerization process. The acidification process in this study is carried out in neutral to acidic conditions because it is reported that the appearances of humic acid is generally at low pH (Baalousha *et al.*, 2006; Kurniati *et al.*, 2018).

MATERIALS AND METHODS
Sample Preparation

Geothermal sludge as a source of silica obtained from Dieng East Java, while peat as a source of HA obtain from Banjarmasin. Both raw materials are crushed to pass through a 100-mesh sieve. Potassium hydroxide (95.5%) as solvent and citric acid (high purity) for acidification process was obtained from chemical distributor CV Medica, Surabaya both in solid form. Subsequently the potassium hydroxide solution and citric acid solution were prepared by dissolution and dilution process using demineralized water. Provides a 2 N potassium hydroxide (KOH) solution and a citric acid solution of 1; 1.5; 2; 2.5; 3 N. To find out the presence of humic acid (HA) in peat is also carried out peat (15 grams) extraction using 300 ml KOH 2 N solution and acidification using citric acid (2 N) until it reaches pH 2 to form HA solids. The HA solid is then observed its morphology using SEM images.

Gradual Extraction and Acidification

Peat of 15 grams extracted using 300 ml KOH 2 N solution in an Erlenmeyer flask conducted with constant stirring using a magnetic stirrer to dissolve humic substances and produce a potassium humate (K-HAs) solution. The solution was then filtered through Whatman No. 41 ashless filter paper. The K-HAs solution subsequently used as a solvent for the extraction of silica from geothermal sludge (10 grams) at 100°C for 1.5 hours accompanied by stirring using a hot plate stirrer. The extraction of silica by K-HAs solution produces a filtrate of silica potassium humic substances (Si-K-HAs). The extraction of silica using K-HAs solution was produced filtrate silica potasium humic (Si-K-HAs) by filtration using Whatman No. 41 ashless filter paper.

The Si-K-HAs solution obtained as described above was use to produced Si-K-HAs gels. The solution was then titrated with citric acid under constant stirring and constant flow rate (0.7 ml/min) using syringe pump. 15 ml of the Si-K-HAs solution sample was titrated using citric acid at various concentration ie 1; 1.5; 2; 2.5, and 3 N until the pre-specified pH was reached ie 3; 4; 5; 6; and pH 7. After acidification, the solution is allowed for aging to form a solid gel for 48 h. The gel is then dried in the oven for 24 h at 100°C. The dried gel was subsequently crushed to obtained a powder of about 100 mesh. The experimental procedure for preparation Si-K-HAs matrix gel by gradual extraction and acidification methods precented as a stepwise schematic in Figure 1.

Characteristization

The composition of geothermal sludge and Si-K-HAs powder was analysed by X-ray fluorescence (XRF, Minipal 4, PANalytical). Functional group on products Si-K-HAs characterized by Fourier Transform Infrared (FTIR). The measurement were made with a Perkin Elmer spectrometer in the range of 400-4000 cm^{-1}. Nova 1200 gas sorption analyzer instrument used to characterized the nitrogen adsorption-desorption isotherms of the Si-K-HAs gels at 77 K. The surface area determined from the adorpstion-desorption isotherms by Brunauer-Emmet-Teller (BET) method while pore size, pore volume and pore distribution determined by desorption branch using Narret-Joyner-Halenda (BJH) method. Scanning Electron Microscopy (SEM) was used to observe the morphology of the samples.
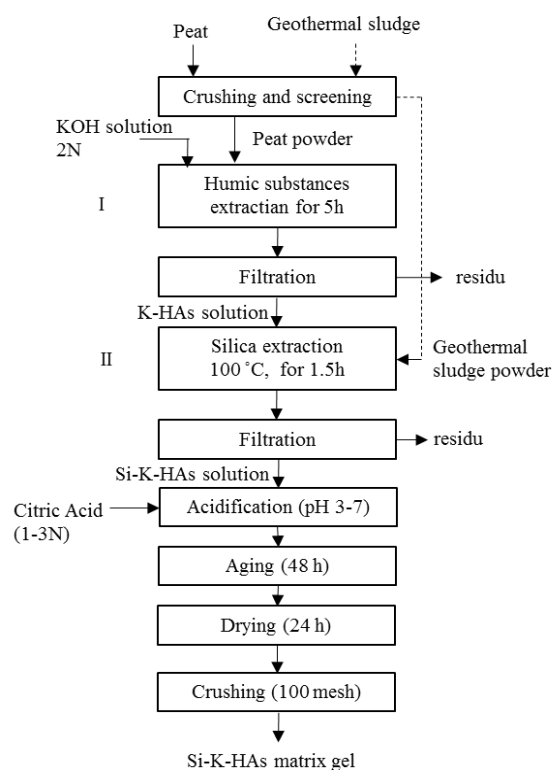

Figure 1. Schematic of experimental procedure for the preparation of Si-K-HAs matrix Gel

RESULTS AND DISCUSSION
Extraction of Silica and Humic Substance

The silica content of geothermal sludge characterized using XRF, was about 93 wt%. The extraction of peats using KOH 2 N solution yielded a K-HAs solution with a measured pH of about 13.3 using pH meters. The resulting filtrate is then used for the extraction of silica from geothermal sludge to produced Si-K-HAs solution. The results showed no residual solids in the silica extraction process indicated that all the silica (10 g) dissolved in the K-HAs as solvents (about 300 ml). The concentration of silica in Si-K-HAs solution is about 2.86 %w.

Figure 2 showed IR spectra on Si-K-HAs solution and K-HAs solution prepared by KOH 2 N solution. Wang *at al.* (2017) reported that the FTIR spectrum of coal and its derivatives can be divided into four regions: 900-700 cm^{-1} (aromatic substitution), 1800-1000 cm^{-1} (O-containing groups), 3000-2800 cm^{-1} (aliphatic structure), and 3700-3000 cm^{-1} (hydrogen bond regions). Inorganic silicates and

clay type materials have very characteristic spectra. There is a characteristic strong band centered around 1100 cm^{-1} which sometimes appears as one band and in other samples as multiple bands. There may also be bands due to associated water molecules around 3400 cm^{-1} and 1640 cm^{-1}. The absorption band centered at 1720 cm^{-1} (indicating acidic carboxyl groups) was clearly stronger for HAs from peat with higher degree of decomposition. As shown in Figure 2 the difference IR spectra K-HAs solution from the first extraction stage and the Si-K-HAs solution from the second extraction stage is the appearance of absorption at the wavenumber 1100 cm^{-1} indicating the vibration of siloxane (Si-O-Si).
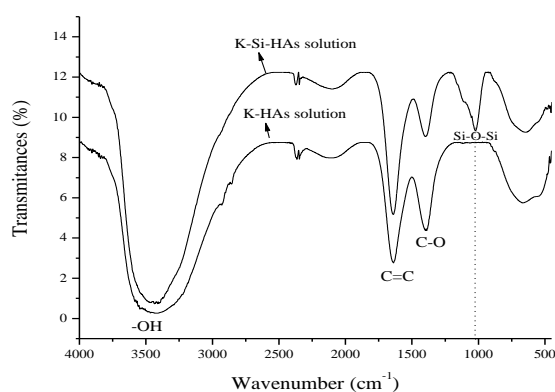

Figure 2. IR spectra of K-HAs solution and Si-K-HAs solution prepared by KOH solution.

Effect of Citric Acid Concentration

The Si-K-HAs solution produced from extraction process is then acidified with citric acid (1-3 N) to reach a pH that is adjusted in the range of 3 to pH 7. The presence of humic substances has no significant effect on the gel formation of Si-K-HAs during the polymerization process (aging). However, gel formation with the presence of humic substances is relatively longer than gel formation without the presence of humic substances as reported in previous studies (Muljani, 2014). The Si-K-HAs gel product is dark brown similar to humic acid color, but after the gel is dried (100°C) the brown color is uneven.

Figure 3 showed the IR spectra Si-K-HAs product in various citric concentrations. IR spectra were similar to each other in terms of the primary position of adsorption, but differences of various entities were apparent in the relative intensity of some bands, depending on acid concentracions.

To identify the presence of salt groups formed by the presence of potassium and citric acid can be explained as the following description. Carboxylic acid salts typically show a strong, characteristic asymmetric stretching absorption from the COO- group in the 1650-1550 cm^{-1} region. The corresponding symmetric stretching absorption occurs at around 1440-1335 cm^{-1}. For acid salts with a strongly electronegative group the asymmetric stretching absorption will shift to higher frequencies (around 1690 cm^{-1}). Fairly strong rocking

in and out of plane deformation absorptions are observed in the 770-400 cm^{-1} region.

(a)

(b)
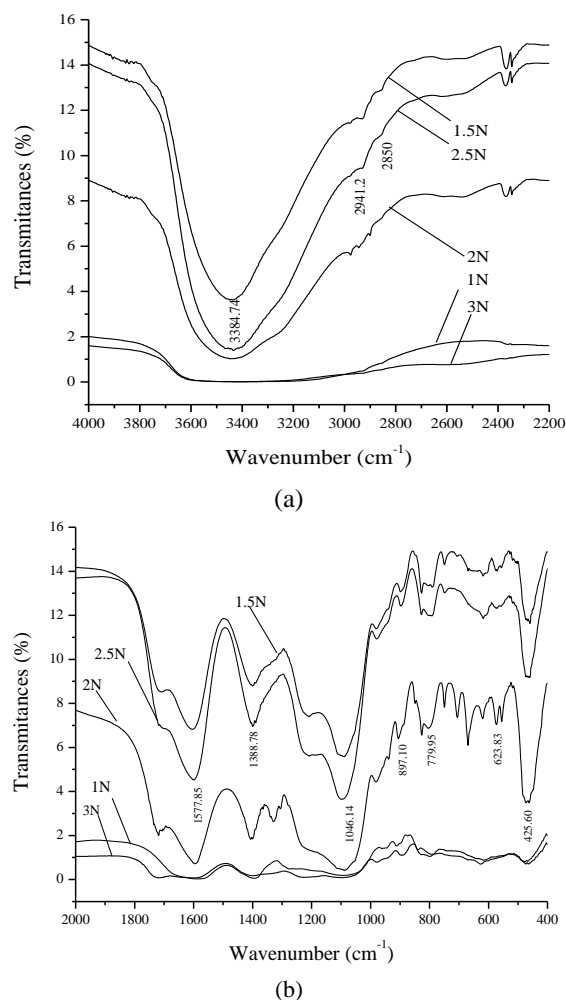
Figure 3. IR spectra Si-K-HAs gel on various concentration of citric acid at wavenumber a) 4000-2000 cm^{-1}, and b) 2000-450 cm^{-1}

The carboxylic acids are tremendously more acidic than the very weak organic acids (alcohols). As a result, the aliphatic carboxylic acids readily form the carboxylate ion in aqueous solutions. A water soluble organic compound that dissolves in cold, dilute aqueous potassium hydroxide is almost always a carboxylic acid. When ionization of the acid occur giving rise to the R-COO$^-$ group, resonance is possible between the two -CO groups. As a result, the characteristic acid group absorption around 1700 cm^{-1} disappears and is replaced by two bands; the first occurs between 1615-1550 cm^{-1} and the second in the 1400-1300 cm^{-1} region. These absorptions correspond to the asymmetric and symmetric vibrations of the R-COO$^-$ group. Of these two bands, the band around 1600 cm^{-1} is most indicative since the symmetric absorption occurs in the crowded fingerprint region.

As shown on Figure 3a the strong absorption peak at the wavenumber 3384 cm^{-1} shows the vibration of the –OH indicates the bands due to associated water

molecules. The absorption at wavelengths of 2941.2 cm^{-1} and 2850 cm^{-1} identified the weak absorption due to the vibration of CH$_3$- and CH$_2$- group, respectively. Figure 3b showed the split of IR spectra in the range of 2000 to 450 cm^{-1} wavenumber. The adsorption band around 1620 cm^{-1} is indicated of the existence of carboxylate group with streching of CH bonds observed aroud 2940 cm^{-1}, also indicated of interaction between silica and these groups. The absorption band at wavenumber 1637.43 cm^{-1} is interpreted as -C=C- which hydrogen bonds. The presence of a C-O vibration from -COOH is identified by the appearance of absorption at wave number 1261.12 cm^{-1}. Humic acid has a characteristic that is the appearance of spectra at wavenumber around 950-1000 cm^{-1}. All results presented above were obtained for silica gels produced at a gelation pH of 4.

Figure 4 showed SEM images for Si-K-HAs gel prepared by citric 2.5 N (pH 4) and typycal morphologi of HA solid prepared by KOH 2 N. It appears that the Si-K-HAs gel particles are more dense than the humic acid particles, indicating that the humic substance is involved in forming the matrix with silica during the gelation process.
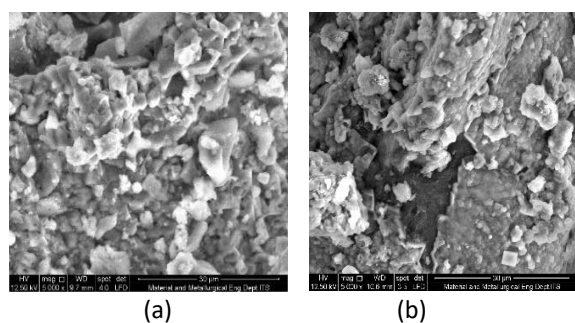

(a)   (b)

Figure 4. A typical morphology of a) the Si-K-HAs gel prepared by citric acid and b) HA solid prepared by KOH 2 N

Effect of Gelation pH

As previously described, the acidification of the Si-K-HAs solution with citric acid is carried out until it reaches the adjusted pH. Furthermore, to investigated the effect of gelation pH, 2.5 N citric acid was used for the acidification process. The results showed that the gelation time was different for each gelation pH. The higher of the gelation pH, the faster gelation time ie from 20 h (pH 3) to about 30 min (pH 5). Typically polymerization for the pH gelation 7 particles rapidly forms aggregate or floculates very rapidly (Iler, 1978; Brinker, 1990; Muljani *et al.*, 2014), but the result showed that flocculation has not yet occurre d until reach 60h gelation time. The observations at pH 6 showed that aging for 60 h the solution formed a fragile and weak solid wherein some solutions remained liquid. While at pH 7 the gel has not formed until it reaches 60 h aging time. The observation at this pH refers to the amount of citric acid added insufficient so that the salt formed is also small where this causes the low viscosity of the solution.

Figure 5 showed the IR spectra of Si-K-HAs product prepared by citric acid at pH 3 to 6. As shown in Figure 5a the absorption at wavenumbers 3346.50 cm^{-1} and 3388.50 cm^{-1} indicated the presence of O-H vibration. The weak absorption at wavenumber 2365.60 cm^{-1} shows -OH vibration, while absorption at wavenumber 1637.55 cm^{-1} shows vibration C = O as shown in Figure 5b. IR spectra were similar to each other in terms of the primary position of adsorption, but differences of various entities were apparent in the relative intensity of some bands, depending on pH value. At pH > 5 there is almost no visible absorption, this indicates a gel matrix formed predominantly of potassium.
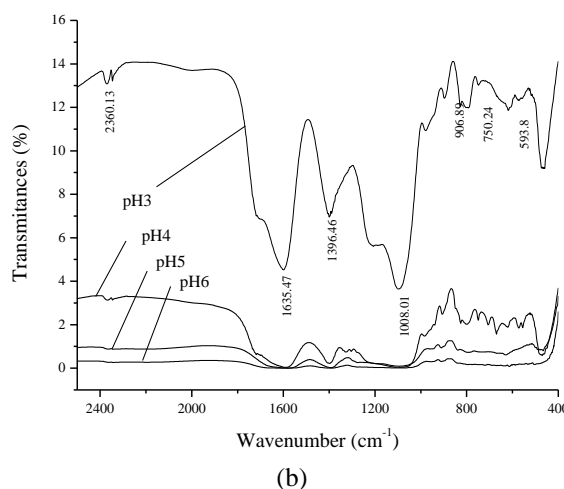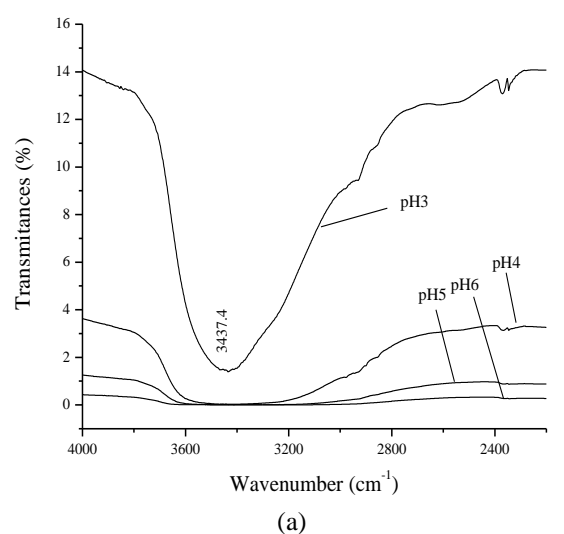

(a)

(b)

Figure 5. IR spectra Si-K-HAs gel on various pH value at wavenumber a) 4000-2200 cm^{-1}, and b) 2500-450 cm^{-1}

Table 1 corresponds to Figure 6 shows some of the components contained in the Si-K-HA (matrix gel) product. An increase in pH value from pH 3 to 5 causes an increase in K$_2$O concentration from 49 to about 72% but instead decreases SiO$_2$ concentration from 47 to 25%. The result is that the SiO$_2$:K$_2$O molar ratio in the gel matrix product decreases from about 0.95 to 0.35 as the pH increases from 3 to 5. The level of acidity or pH

value adjusted in the acidification process indicates a significant effect on the characteristics of Si-K-HAs products.

Table 1. SiO_2:K_2O molar ratio in matrix gel product

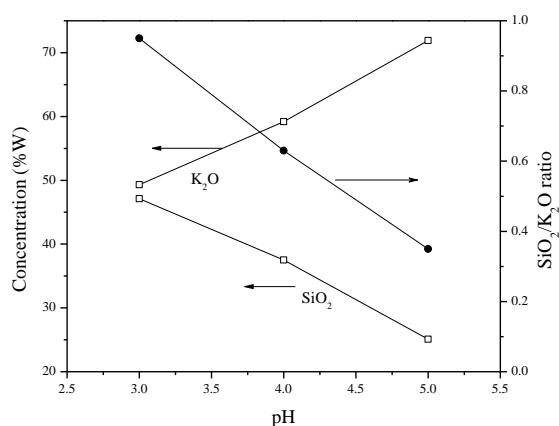| pH	SiO_2 (%)	K_2O (%)	SiO_2:K_2O
3	47.1	49.3	0.95
4	37.5	59.2	0.63
5	25.1	71.9	0.35

Figure 6. Effect of pH on SiO_2 an K_2O composition in Si-K-HAs gel prepared by citric acid
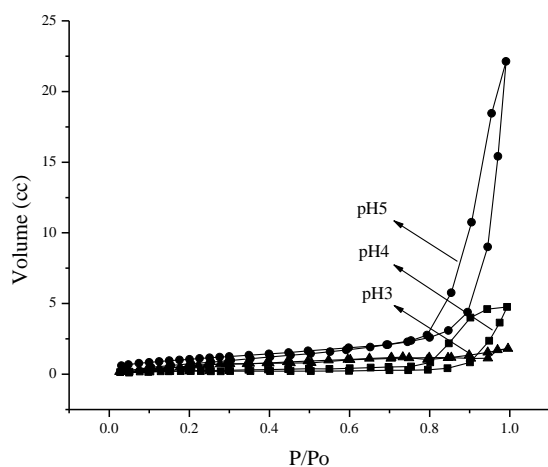

Figure 7. Adsorption–desorption isotherms of Si-K-HAs gels prepared by citric acid.

Figure 7 showed the typical adsorption-desorption isotherms Si-K-HAs matrix gel prepared from geothrmal sludge and peat using citric acid for acidification at adjusted pH 3, 4 and 5. The isotherms were typical type V according to the IUPAC classification which has a convex shape to relative pressure and is characteristic of the weak interaction between adsorbate and adsorbent. This isotherm type indicates indefinite multilayer formation after the completion of the monolayer. Moreover, the hysteresis can be classified as a type H3 hysteresis, in which aggregates (loose assemblages) of plate-like particles forming slit-like pores. This type of isotherm occurs in solids with a pore size of micropore or mesopore.

Tabel 2 showed the BET analysis of SI-K-HAs prepared by ctric acid 2.5 N. The higher surface area at pH 4 of 24.470 m^2g^{-1} followed by pH 3 of 18.22 m^2g^{-1} and pH 5 of 16.494 m^2g^{-1}. The pH affects the polymerization process in which the monomers will form the polymer and the particle size continues to grow until they form a gel. While the pore size may be more influenced by the degree of compaction than the diameter of the primary particles.

Table 2. BET analysis Si-K-HAs gel product

pH	Surface area m^2 g^{-1}	Pore volume cc g^{-1}	Pore diameter nm
3	18.22	0.039	3.372
4	24.47	0.097	10.223
5	16.50	0.098	11.452

Figure 8 showed the pore distribution of Si-K-HAs prepared by citric acid. The distribution curve at pH 4 appears to have a narrow peak in the range of 12.32 - 30.22 nm indicating the pores in the mesopore region. the pore distribution at pH 5 is quite wide where most of it is in the mesopore region (2-50 nm) and partly in the macropore region (> 50 nm) which means less uniform pores. The pore distribution at pH 3 appears to be partially in the micropore region (< 2 nm) and partly mesoporous but the adsorption capacity is very low. It can be explained that at pH 3 the content of humic acid and high silica will make the pore diameter smaller but at pH 5 potassium begin to increase with decreasing silica content.
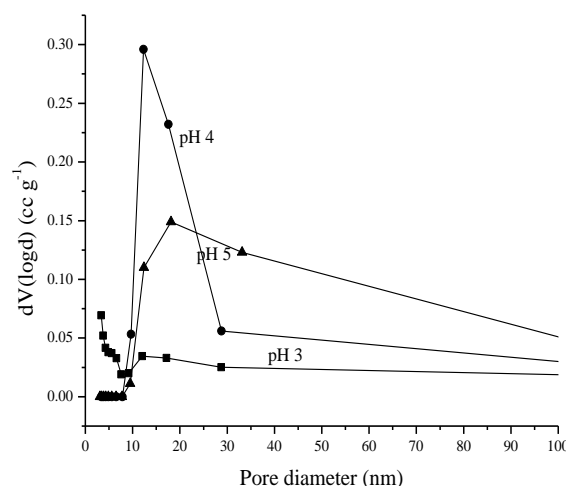

Figure 8. Pore distributions of Si-K-HAs gel prepared by citric acid.

The acid concentration and final pH value in the acidification process as described previously affects the product composition and its characteristics. The results showed that the ratio of silica: potassium was still relatively low (0.3-0.9) when compared to the ratio for commercial fertilizer (1.6-3.2). To be able to get a larger SiO_2:K_2O ratio then it is necessary to increase the concentration of silica.

CONCLUSIONS

Matrix silica potassium humate (Si-K-HAs) gel has been successfully prepared from peat and geothermal sludge by a gradual extraction and acidification method. The Si-K-HAs gel can be formed through polymerization process following the gelation of silica. The presence of humic acid was relative no effected the formation of the gel and also coalesce with the silica. Nevertheless, there is still a need to further study the influence of humic on the polymerization of silica especially on various concentrations of silica.

The results of IR spectra and BET analysis show that the gel formed contains potassium, silica, humic acid and citrate. Gel product composition through XRF analysis obtained $SiO_2:K_2O$ ratio between 0.3-0.9. The gel composition can be altered to increase the $SiO_2:K_2O$ ratio by adjusting the ratio of raw materials and the volume or concentration of potassium hydroxide solvent. In addition, pH value and acid concentration as a controller in the gelation process also become a consideration to obtain the appropriate product characteristics.

The Si-K-HAs gel product has the high oxygen content of the functional group including carboxyl, hydroxyl, phenol, potassium, and silica and is widely recognized as an important natural material.

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