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Research Article

Humic substance extraction from leonardite, lignite Mae Mho Mine by base-acid treatment process

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Abstract

Humic substance (HS) is very important for soil agriculture that affects physical and chemical properties and improves soil fertility. Humic substances are complex mixtures of polydispersed materials formed by biochemical and chemical reactions during the decay and transformation of plant and microbial remains. Humic substances were extracted from leonardite of lignite Mae Mho Mine in Lampang province by using base-acid treatment and centrifugation. This research studied the effect of time and temperature in base treatment process and the effect of soils particle size. The humic substance which contain humin, humic acid (HAs) and fulvic acid (FAs) were extracted by base-acid treatment. Firstly, soil sample were stirred in base solution and precipitated by centrifugation. The humin precipitate that the fraction is not soluble in water at any pH value was dried at 90 ^{o}C. Then, the soluble(HAs and FAs) were pH adjusted to 2 by using 3M HCl and stirred in room temperature The humic fraction precipitate were separated by centrifugation and was dried at 90 ^{o}C. The soluble was pH adjusted to 4-5 and settled for 24 hr. The fulvic acid precipitate was dried at 90 ^{o}C. Humic substances were studied for element analysis and chemical structure by FT-IR and CHNO. The yields of humic acid were increased at the increase of soils particle size and base reaction time.

Keywords: Humic substance, Humic acid, Fulvic acid, leonardite, soil extraction

Introduction

Leonardite is a natural oxidation product of lignite with brown and coal-like appearance, associated with near surface mining (Qian et al., 2015). It is a rich source of humic acid (up to 90%) (Tothirakun et al., 2009) Leonardite is used to condition soils either by applying it directly to the soil as soil fertilizer, as a stabilizer for ion-exchange resins in water treatment (Clasen et al., 1998)

Mae moh lignite mine from Lampang province in Northern of Thailand is the largest open-pit lignite mine in Southeast Asia. It produces 16 million tons of lignite per year for requirements of Mae Moh's mine-mouth thermal power plants. The mine causes both direct and indirect environmental impacts on land use, quality of life, forests and wildlife; it has also

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caused pollution in such forms as dust, noise, and water contamination, odors from the spontaneous combustion of lignite and vibration from blasting (Teparut et al., 2011).

Humic substance (HSs) is very important for soil agriculture that affects physical and chemical properties and improves soil fertility.(Bartschat et al., 1992) HSs are known to significantly affect the behavior of pollutants in natural environments, such as trace metal speciation and toxicity (Nederlof et al.,1993; Shin et al.,1996), mineral growth and dissolution and redox behavior in soils, improving nutrient uptake, especially phosphorous, sulfur and nitrogen, improving water holding capacity for better drought resistance and reduction in water usage. Recent studies that it may be dynamically in volved in carbon and electron flow in anaerobic. (Scott et al., 1998; Lovley et al., 1996)

Humic substance (HSs) can be divided into three main fractions by solubility in varios pH: Humin, Humic acid (HA or HAs) and Fulvic acid (FA or FAs). Humin is an organic matter that is insoluble in water at all pH. These dark brown solids are inhomogenous and their structures are often vaguely described. HA and FA solution are extracted from soil and other solid phase using a strong base at high pH. Humic acids are insoluble at low pH, that they can precipitated by adding strong acid or adjust the solution to pH 1. Fulvic acid is the materials that dissolved at all pH and precipitated by adjusting pH to 4-5.(John & Russell, 2007) Humic substances can extract from leonardite, soil and sediment by base-acid treatment process that using strong base and strong acid solution for precipitation of Humin, Humic acid and fulvic acid fraction. (Garcia & Abad, 1996) Humic substance can be extracted by two conventional methods that are NAGOYA method and IHSS method. NAGOYA method, in base extraction process must be standed in N_2 atmosphere for 48 hours and HA solutions was diluted with 50 times of the volume of 3% NaCl solution and were repeated until the acid supernatant became almost colorless. FA fraction was passed through the cation exchange resin to be transformed to the H+-form and freeze-dried to get a powder of FA sample. In IHSS method, soil sample must be acidified to pH 1-2 before extracted. The extraction process must be standed in N_2 atmosphere and used column of Amberlite XAD-8 and ultrafiltation to separate the FA fraction. (Kuwatsuka & Arai, 1992)

This present work is to study the extraction of humic substance from leonardite of lignite Mae Mho Mine from Lampang province in Northern of Thailand by using base-acid treatment and centrifugation. This research studied the effect of time and temperature in base treatment process and the effect of soils particle size.The objective of this work is to find the obtimize condition for extraction humic acid from Thailand's leonardite soil with easy, safty and low energy process.

Materials and methods

Materials

Leonardite soil sample was collected from lignite mine at Mae moh, Lamphang province, Northern Thailand since August 2016. The sample was dried at 90ºC for 24 hour to remove water and moisture contents. After that, the soil piece was milled into powder by mortar and sieved for selection of particle size to three sections that are over 180 μm, between 125-180 μm and less than 125 μm, respectively.

Humic substance extraction method

The Humic substance extraction from leonardite had been carried out following the method suggested by John & Russell, 2007, using base-acid treatment in figure 1. Soil extraction experimental consists of mixing 40 g of dry leonardite powder with 400 ml of

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0.01M KOH solution during 30 minute, 1, 2 and 3 hour at room temperature, 40ºC and 60ºC. Then, the soluble containing HA+FA were separated from insoluble fraction containing humin by centrifuge at 5000 rpm for 15 minute. The humin fraction was dried at 90ºC for 24 hour. The HA+FA solution were carefully removed and adjust to pH 2.0 by adding concentrate HCl. The precipitates formed at pH 2.0 that conventionally known as humic acid (HA) were separated from solution by centrifuge at 5000 rpm for 15 minute and dried at 90ºC for 24 hour. The solution containing FA was adjusted to pH 4.5 by adding concentrate KOH and the fulvic acid (FA) precipitates was formed. The FA precipitate were separated from solution by centrifuge at 5000 rpm for 15 minute and dried at 90ºC for 24 hour.

Characterization

The humic substances were characterized morphology, element composition and chemical sructure by Scanning electron microscope (SEM), CHN analyzer and Fourier transform infrared spectroscope (FT-IR), respectively. In FT-IR spectroscopy, One milligram of dried humic fraction was mixed, ground with 100 mg of potassium bromide (KBr) and then mechanically pressed to form a pellet.

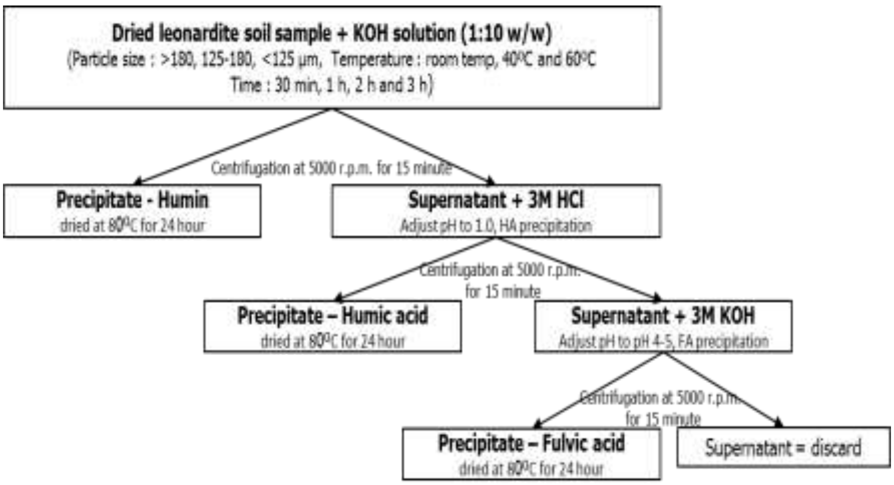

Figure 1. Scheme of humic substances extraction and fractionation

Results and discussion

Scanning electron microscopy (SEM) was conducted to study the morphology of humic substance. The SEM images in figure 2 indicated the three fractions of humic substances with different microstructures morphology. In figure 2 (I), the morphology of humin is shown which is non conductive bulk material with few porous structure. Furthemore, in figure 2 (II) and (III) are showing the microstructure morphology of fulvic acid and humic acid, respectively. The HA and FA fraction morphology are composed of particles with various shapes and sizes distribution; however, HA was more homogeneous than FA due to the agglomeration of small particle.

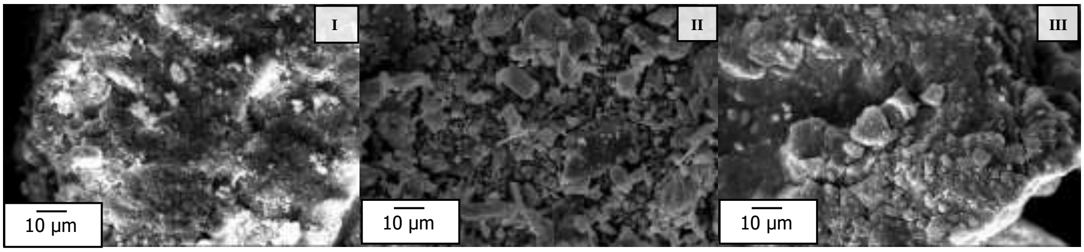

Figure 2. SEM image of (I) Humin, (II) Fulvic acid and (III) humic acid that extracted from leonardite soil with 0.01M KOH and particle size at 180 μm for 3h at room temperature

The solid yield result of humin and humic acid are displayed on figure 3. In figure 3(I), several of particle size conditions are shown. The result indicate that the solid yield of humic acid increase with increasing of the particle size. This is because of the hard mashing property of lignite composition in raw material can make lignite and leonardite in large particle however soil particle is normally in small particle. Leonardite was composed in large size (>180 μm) higher than small particle leading to higher extraction of humic acid. However, in figure 3(II) show decreasing of humic acid solid yield with increasing of the reaction temperature and highest at room temperature reaction condition. Humic acid extracted with higher temperature (40-110 ºC) result in cyclic and structure change that affect soluble and chemical properties. (Kolokassidou et al., 2007) In different reaction time in base extraction as shown in figure 3(III), the humic acid yield is increase with increasing reaction time.

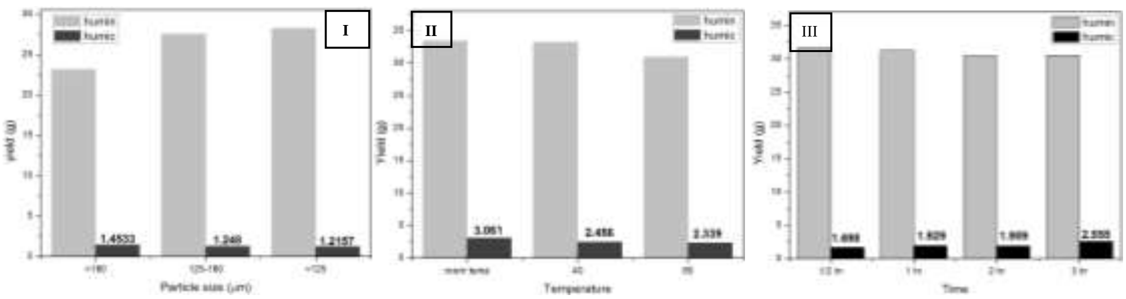

Figure 3. Yield of humin and humic acid derived from leonardite with different conditions: (I) varying the soil particle size with 0.01M KOH for 3h at room temperature, (II) varying base treatment temperature with 0.01M KOH and particle size at 180 μm for 3h and (III) varying reaction time in base treatment concentration with 0.01M KOH at room temperature and particle size at 180 μm

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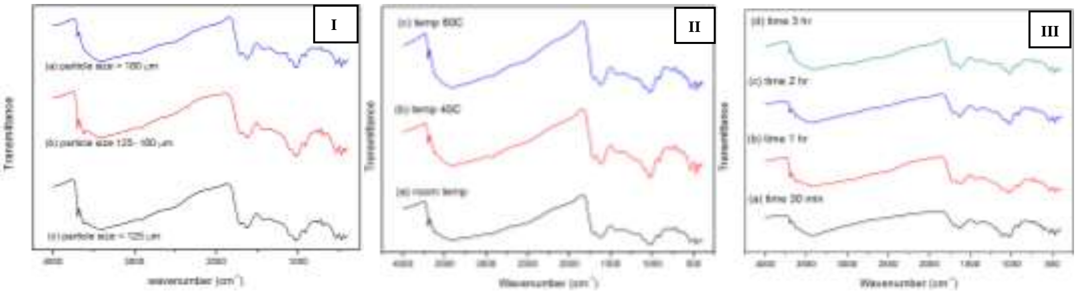

Figure 4. FTIR spectra of humic acid derived from leonardite with different conditions: (I) varying the soil particle size with 0.01M KOH for 3h at room temperature, (II) varying base treatment temperature with 0.01M KOH and particle size at 180 µm for 3h and (III) varying reaction time in base treatment concentration with 0.01M KOH at room temperature and particle size at 180 µm.

The FTIR spectra of humic acid in different conditions recorded in the 4000–400 cm^{-1} range are presented in Figure 4. The HA spectra bands were similar in various condition. In addition, the spectra bands around 3400–3300 cm^{-1} (O–H and N–H stretch), 1580 cm^{-1} (aromatic C=C, C=O, COO–), 1380 cm^{-1} (O–H deformation, CH_3 bending, C–O stretching of phenolic OH and COO− anti-symmetric stretching), 1110 cm^{-1} (C–OH stretch of aliphatic alcohol) and 618 cm^{-1} (deformation of −COOH). These results accord with those reported by Kang et al., 2002. The results indicate humic acid that was extracted from Thailand's leonardite is purity product with similar spectra with commercial HA (Tahiri et al., 2016).

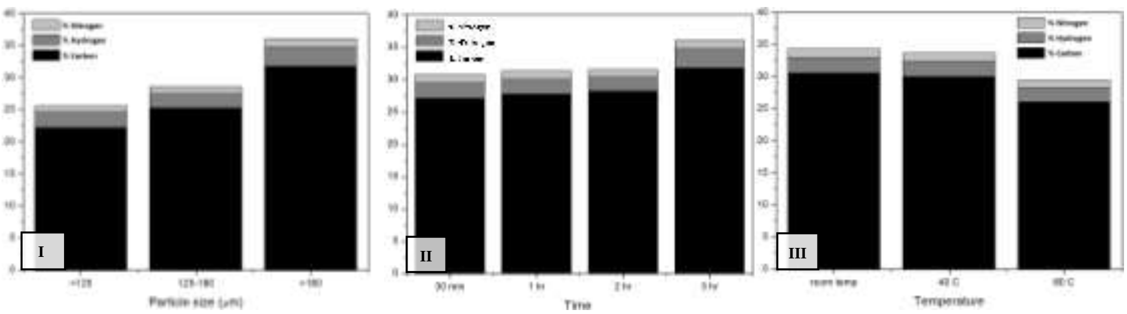

Figure 5. CHN element result of humic acid derived from leonardite with different conditions: (I) varying the soil particle size with 0.01M KOH for 3h at room temperature, (II) varying base treatment temperature with 0.01M KOH and particle size at 180 µm for 3h and (III) varying reaction time in base treatment concentration with 0.01M KOH at room temperature and particle size at 180 µm

CHN element result of HAs extracted is in accordance with solid yield and FTIR results. HAs extracted from leonardite with increasing particle size showed increasing percentages of C. However, in different reaction temperatures, it showed increasing percentages of C when

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decreasing temperatures. Although the solid yield is increasing trend in different time, the percentage of C is increase with increasing reaction time. Also, if increase the reaction time, solid yield and percentage of C will increase but not significant and reach a stable state.

Conclusion

The three fractions of humic substances are humin, humic acid and fulvic acid which can be extracted from Thailand's leonardite soil by base-acid treatment and centrifugation. Humin is major product from the extraction process. The leonardite sample composition has high soil content. The yields of humic acid were increased at the higher particle size but decreased at higher base reaction temperature. According to elemental analysis; the percentage of carbon was increased when increased the particle size and the reaction time. However, in different base reaction temperature, the humic acid yield result was increased with decreased reaction temperature. The optimize condition indicate the highest yield and purity of humic acid which is extraction with 0.01M for 3 hour at room temperature and meshed particle size to 180 μm. The method in this work can be extracted purity HSs fraction from Thailand's leonardite soil with using general scientific equipment and less chemical, less time and normal atmosphere. It is lead to easy, safety and low energy process compare with other method.

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