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Modification of Humic Acid by Ether Functional Group As Biosorbent to Au(III) Adsorption in The Presence of Sn(II) and Ni(II)

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Abstract. Modification of humic acid on the phenolic functional group with dimethylsulfate (DMS) for adsorption Au(III) in the presence of Sn(II) and Ni(II) have been conducted. Ash content was analyzed and characterized by Fourier-Transform Infrared (FTIR). Determination of Au(III) adsorption in the presence of Sn(II) and Ni(II) was conducted by Atomic Adsorption Spectroscopy (AAS). The isolated humic acid has 19.8% ash content and after purification has 0.6% ash content, etherified humic acid (EHAs) has 1.4% ash content. Adsorption percentage of Au(III) in the presence of Sn(II) and Ni(II) by EHAs decreased until 4.936% and 41.782% respectively. The addition of Sn(II) and Ni(II) as competitors of Au(III) in the Au(III) adsorption by using EHAs, were affect the percentage of Au(III) adsorption.

INTRODUCTION

Electronic waste in the environment is an important concern because if not managed properly can contaminate the surrounding environment. Electronic waste contains a variety of metal such as Au 0.1%, Ag 0.2%, Pd 0.005%, Cu 20%, Ni 2%, Sn 4%, and Pb 2% [1]. Gold metal has a high economic value than the other metals because the benefits are quite extensive as jewelry, electronic components and in the health sector. Recovery of metal ion in solution is usually done with an extraction process, precipitation and adsorption [2,3,4]. Adsorption method has been used for the recovery of heavy metal ions in water [3]. Selection of the adsorbent in the adsorption process of metal ion is very important. The adsorbent used must have a high adsorption capacity, low cost so that the adsorption process can take place effectively [5]. Therefore the adsorption method is usually synonymous with an easy, green process and has a high adsorption capacity so this has been selected [4]. Utilization of humic acids (HAs) as metal ion adsorbent has been done by the authors before such recovery of Pb, Cu, Zn, Cd and Ni [3,6]. Gold metal ion adsorption using HAs and modified HAs has been done by previous researchers.

Research has taken advantage of HAs as a metal ion biosorbent talked a lot about the adsorption capacity and modification of functional groups of HAs, but some researchers have yet to discuss the influence of the presence of other metal ions on the interaction of metal ions with HAs especially gold ions adsorption. Previous research more emphasis on the adsorption capacity and kinetics of metal ion adsorption.

The study of the influence of other metal ions on the process of recovery of gold ions in solution becomes important to investigate. This study was conducted to determine the effect of the presence of tin and nickel ions in the solution to the adsorption of gold ion used etherified humic acid (EHAs). The determination of these effects do with determine the adsorption capacity of Au(III) By EHAs without and with lead and gold ions.

EXPERIMENT METHOD

General

The peat soil was obtained from Rawa Pening, Central Java, Indonesia. HCl, HF, HNO₃, NaOH, CH₃OH, DMS, SnCl₂·2H₂O, NiCl₂·6H₂O were purchased from Merck and were used without purification. The solution of Au(III) was prepared by dissolving of gold metal from ANTAM in acid solution (HCl and HNO₃). All the water used was deionized water free CO₂.

Experimental

Extraction of HA

Peat soil has dried crushed and sieved to 42 mesh size. Humic acid (HAs) was isolated from 100 grams of peat with 0.1 M NaOH 500 mL for 24 hours under nitrogen conditions. Solids and the filtrate were separated by means of filtered and centrifuged 2000 rpm for 20 minutes. The filtrate was precipitated with 0.1 M HCl to pH ≈ 1. The precipitate was separated from the filtrate centrifuged 2000 rpm for 20 minutes and dried 40°C. The solid was characterized by a Fourier Transform Infra-Red (FTIR) (Simadzu Prestige-21) and the ash content was measured by using a furnace at 750°C until 4 hours, weight of the HA before and after heating was measured.

Purification of HAs

Humic acid (HAs) was purified with 0.1 M HCl: HF 0.3 M = (1:1) in a plastic container. The washing was repeated up to 4 times. Washery then washed with distilled water. The precipitate was purified and then roasted at a temperature of 40°C. The pure HAs was characterized by FTIR spectrophotometer.

Etherification of HAs

Etherification of HAs was done by mixture 1.0 g of HAs, 5.0 mL of DMS, 24 mL of H₂O free CO₂ and 40 mL of methanol. The mixture was refluxed for 24 hours at a temperature of 65°C. Results of etherification was removed the solvent by evaporated and then the results was filtered. Etherified humic acid (EHAs) was dried and then was measured ash content and characterized by FTIR spectrophotometer.

Isothermal Study

Isothermal studies of adsorbent performed by adsorption Au(III) in the presence of Sn(II) using EHAs adsorbent with variation in concentration of Au(III) and Sn(II) (20:1; 5:1; 1:1; 1:5; 1:10; 1:20; 1:30 and 1:40) at pH 2. After contacted between Au(III), Sn(II) and EHA adsorbent in the 10 mL of solution, filtration process used Whatman paper and adsorbent dried at 40°C for 24 hours. Measuring the residue of Au(III) in the filtrate used Atomic Absorption Spectroscopy (AAS) (Perkin Elmer 3110). Characterization of solid materials used a FTIR spectrophotometer. Isothermal studies of adsorbent performed by adsorption Au(III) in the presence of Ni(II) using EHAs adsorbent was done the same method of adsorption Au(III) in the presence of Sn(II) using EHAs adsorbent.

RESULT AND DISCUSSION

Humic acid (HAs) isolation results showed some characteristic absorption peaks at wave numbers 1200, 1400, 1600, 1700, 2900, and 3400 cm⁻¹. Fig.1 shows the difference between the spectra of HAs before and after purification. The process of washing with a mixture of HCl and HF (1:1) led to the emergence of several new peaks and some peaks are missing as well as several other peaks shift.

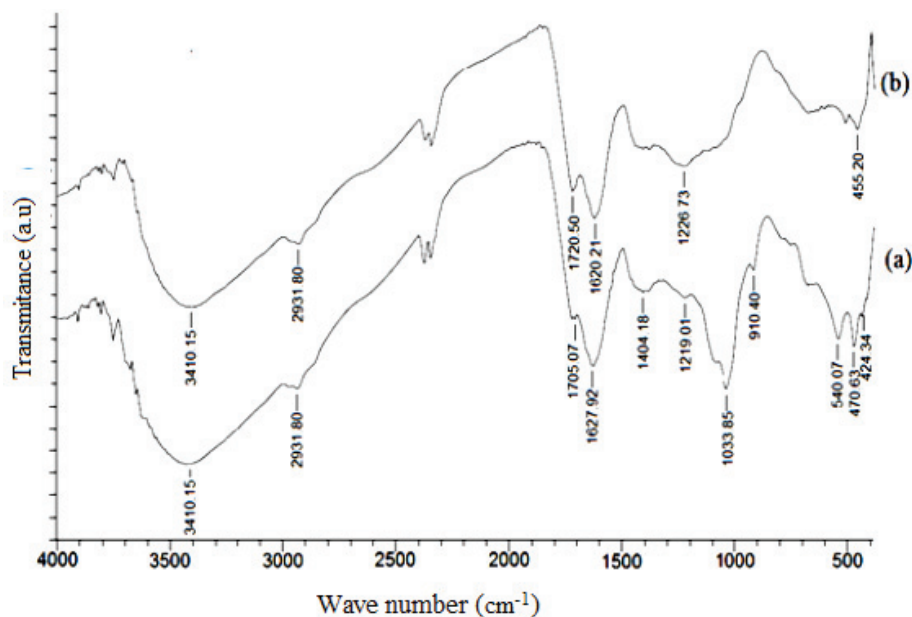


FIGURE 1. FTIR spectra of HAs (a) before and (b) after purification



The loss of Si-O absorption peak at wave number 1033 cm^{-1} after the washing process using a solution of HCl and HF (1:1) indicates a reduction of silica in HAs. The loss absorption peaks at wave number 910, 540, 470 and 424 cm^{-1} indicates that the reduced inorganic impurities especially silica bound to HAs. Silica attached to the structure of HAs soluble in the presence of washing using HF solution which then reacts with the Si-O form SiF_4 and H_2O according to Eq. 1. The reaction occurs under acidic conditions in which HCl is added which aims to prevent the solubility of HAs on the other hand so that impurities such as Na, K, Ca and Mg contained in the HAs can be dissolved with HCl.

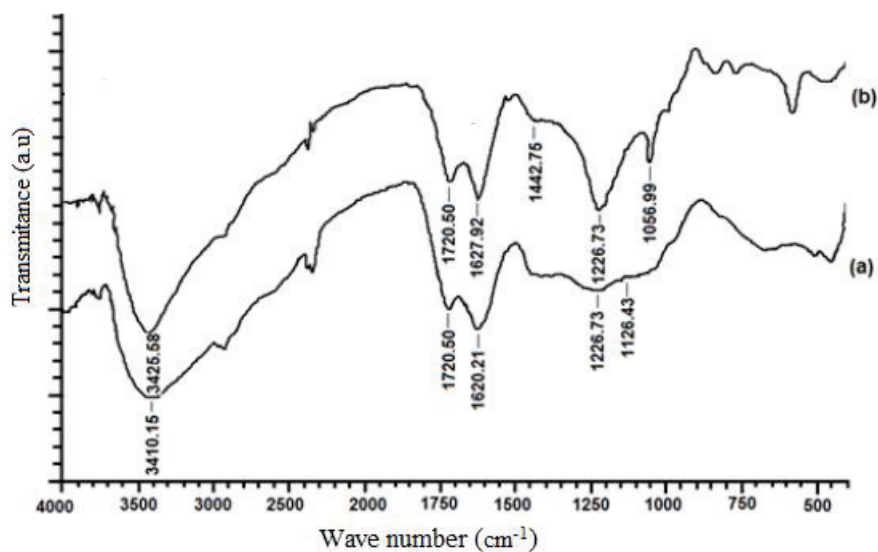


FIGURE 2. FTIR spectra of (a) HAs and (b) EHAs

Fig.2 shows that after etherification in HAs, the absorption peak 3410 cm^{-1} experienced a shift wavenumber towards greater namely to 3425 cm^{-1} and experiencing sharpening peak which indicates reduction in the number of hydrogen bonds after etherification (EHAs). Absorption peaks at wave number 1620 cm^{-1} which shows the vibration buckling O-H overlapping with stretching vibration of $\text{C}=\text{C sp}^2$ on humic acid pure but after etherification do happen peak shift toward the wave number that is larger than 1620 cm^{-1} to 1627 cm^{-1} indicating that it has formed a compound which has a higher stability in this case are ether compounds. Absorption peaks at wave number 1056 cm^{-1} and 1226 cm^{-1} contained in the EHAs an increasingly sharp absorption peaks symmetric and asymmetric stretching vibration of C-O from ether. This indicates the number of C-O ether groups are formed which indicates the success of the process of etherification on humic acid.

The data obtained at the Tab. 1 is known that the ash content of the isolated HAs prior to purification is much higher than the ash content of HAs is pure, it is because the presence of inorganic compounds such as metal and clay minerals mainly in HAs [7]. Purification using a solution of HCl/HF capable of reducing mineral impurities such as metals and especially metals attached to the HAs such as Si, Na, K, Mg and Cd. The ash content of HAs after the process of etherification is 1.4% ash content, it increased compared to the HA before etherification process that the ash content only reached 0.6%. The ash content in the EHAs increased to 1.4% likely due to the influence of the rest of the reagents are still missing at the time of washing and other impurities present in EHA.

TABLE 1. Ash content of humic acids (HAs) and etherified humic acids (EHAs)

No.	Sample	Ash content (%)
1.	HAs before purification	19.8
2.	HAs after purification	0.6
3.	EHAs	1.4

Adsorption capacity of Au(III) by EHAs at pH 2 without any Sn(II) and Ni(II) of 19.7 ppm in the 10 mg of EHAs so that the adsorption capacity of Au(III) by EHAs is 19.241 mg.g^{-1} or 97.675% of nearly 100% in which 10 mL of Au(III) 20 ppm adsorbed by EHAs. Based on these results is actually the initial concentration of Au(III) can be increased so that the possibility of adsorption capacity Au (III) by EHAs can be more accurate.

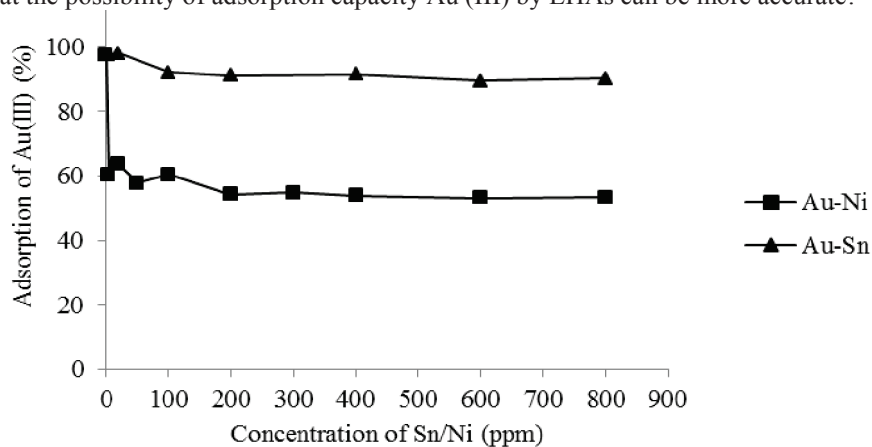


FIGURE 3. Au(III) adsorption by EHAs in the presence of Sn(II) and Ni(II) at pH 2

Fig.3 is known that the adsorption of Au(III) by EHAs in the presence of Sn(II) as a whole did not change significantly even though the concentration of Sn(II) is increased to 800 ppm. A decrease in the adsorption of Au(III), which occurs in the presence of Sn(II) only amounted to 4.936% so that it can be concluded that the presence of Sn(II) does not interfere with the adsorption system Au(III) by EHAs. A decrease in the adsorption of Au(III) by EHAs already occurred in the presence of Ni(II) 4 ppm. Adsorption of Au(III) by EHAs in the presence of Ni(II) decreased until 41.782%.

TABLE 2. Capacity of Au(III) adsorption by EHAs

No.	System	Capacity of adsorption (mg.g ⁻¹)	Percent of adsorption (%)	Decrease of adsorption (%)
1.	Au(III)	19,241	97,675	0
2.	Au(III) and Sn(II)	18,291	92,846	4,936
3.	Au(III) and Ni(II)	11,201	56,860	41,782

The influence of the presence of Sn(II) did not affect the adsorption of Au(III) by EHAs only significantly lowers the adsorption of Au(III) amounted to 4.936% and the presence of Ni (II) instead of decreasing the adsorption of Au(III) most is 41.782%. It cannot be explained by HSAB (Hard Soft Acid-Base) concept. HSAB concept is a Lewis base that are hard will bind strongly with Lewis acids are hard anyway therefore likely -COO⁻ groups in EHA will tend to form strong bonds with Sn(II) which is a Lewis acid medium of the Au(III) which is a soft Lewis acid [8]. This is likely due to the interaction of EHAs surface which at pH 2, the carboxyl group has not undergone deprotonation so most of the carboxylic groups are still in a state of protonated (-COOH). The state of EHAs groups are still protonated that facilitates the interaction of Au(III) with a surface of EHAs compared with Sn(II) and Ni (II) as at pH 2 speciation of Au(III) is in the form of the anion is AuCl₄⁻ while Sn(II) and Ni(II) in the form of a cation which Sn²⁺ and Ni²⁺ [9-11]. That's what causes the adsorption of Au(III) by EHAs still occur even within the system there are Sn(II) and Ni(II) though.

The amount of decrease in the adsorption of Au(III) by EHAs in the presence of Ni(II) compared with the Sn(II), it is likely due to the size of the Sn(II) < Ni(II). Size of Sn(II) which is smaller than the Ni(II) caused effective nuclear charge of Sn(II) > Ni(II). Effective nuclear charge Ni(II) < Sn(II) cause a decrease in positive charge on the surface of EHA, in case of Ni on the surface adsorption of EHAs. Decreasing positive charge on the surface of EHAs in the presence of Ni(II) causes adsorption Au(III) will also decrease drastically because the species Au(III) at pH 2 is an anion (AuCl₄⁻).

CONCLUSIONS

The adsorption capacity of EHAs to the Au(III) is 19.241 mg.g⁻¹ without the presence of Sn(II) or Ni(II), the adsorption of Au(III) in the presence of Sn(II) amounted to 18.291 mg.g⁻¹ and in the presence of Ni(II) amounted to 11.201 mg.g⁻¹. The presence of Sn(II) and Ni(II) in solution can interfere with the process of adsorption of Au (III) by EHAs. The percentage adsorption of Au(III) by EHAs decreased in the presence of Sn(II) of 4.936% and the presence of Ni(II) of 41.782%.

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