Humic Acid Isolations from Lignite by Ion Exchange Method

E Kurniati, S Muljani*, D G Virgani, B P Neno
Chemical Engineering, Engineering Faculty, University of Pembangunan Nasional Veteran East Java
*sriemuljani.th@upnjatim.ac.id

Abstract The humic liquid is produced from lignite extraction using alkali solution. Conventional humic acid is obtained by acidifying a humic solution using HCl. The purpose of this research is the formation of solid humic acid from lignite by ion exchange method using cation resin. The results showed that the addition of cation resin was able to reduce the pH from 14 to pH 2 as well as the addition of acid (HCl), indicating the exchange of Na+ ions with H+ ions. The reduction of pH in the humic solution is influenced by the concentration of sodium ions in the humic solution, the weight of the cation resin, and the ion exchange time. The IR spectra results are in good agreement for humic acid from lignite characterization.

1. Introduction
The conventional method for obtaining humic acid is by extracting the humic acid source with an alkaline solution. Humic acid are uniform chemically substances, humic acid are hydrophilic, reversible colloids with molecular weights varying from 300 to as high as 10,000 units (carboxyl and phenolic hydroxyl groups make up a good part by weight of the molecule) [1]. Humates are dissolved in the extracting solution and separated from insoluble tailings. The extract is then acidified and the humic acid is precipitated. The material is considered as an acid and is called humic acid are generally classified into three categories: humic acids, fulvic acids, and humin. These three humic fractions are structurally similar, but their properties differ, especially with respect to their molecular weight and the numbers of functional groups present [2]. Humic acid is a weak organic acid, which has both principal factors (phenol and benzoic carboxylic groups) and some secondary functional groups such as methoxi, amine, sulphonic and alcoholic [3]. Humic acid isolated from lignite when used as an adsorbent for metal ions, its effectiveness and sorption capacity increases substantially. In comparison with humic acids isolated from various soil types, lignitic humic acids exhibit a very high sorption capacity and a low degree of desorption [4].

The humic acid was extracted from the lignite by combining the method of nitric acid preoxidation and the method of alkali solution and acid eduction [5]. The extracted solution, rich in humic substance, can find direct uses, however, it can also be used in solid form as humate salts (sodium, potassium etc.) obtained after precipitation, filtration, vaporization, and crystallization stages [6]. The humic substances also prepared by alkaline extraction from peat using potassium [7]. Process of extracting HA values from a source thereof which comprises, using as the extracting solution an aqueous solution of a sulfite salt selected from the group consisting of sodium sulfite, potassium sulfite and ammonium sulfite, said solution having a pH of at least about 6, and separating the extracting solution containing humic acid values from the insoluble residues [8]. The isolation (extraction, fractionation and purification) of humic acids from soils is time consuming and expensive. The extraction, fractionation and purification periods of these substances vary from 12 h-7 days. Rosliza et al [9] was reported the used of distilled water for...
purifying humic acid of the peats within 1h without altering the true chemical nature of humic acid as it significantly reduced the mineral content of humic acid. By combining the method of nitric acid preoxidation and the method of alkali solution and acid eduction, the humic acid was extracted from the lignite [10].

Extraction of humic acid from lignite with sodium hydroxide solvent produced an extract solution containing sodium element with a high enough alkalinity (pH14). This study developed the utility of cation resin to reduce the element of sodium in order to obtain a humate solution with a low pH (pH 2). The extract were characterized with respect to the organic matter content, the total organic carbon (Ciavatta method) and the humic substance content (humic and fulvic acids separately) using the method suggested by the IHSS, International Humic Substances Society [11,12].

2. Materials and Method
Isolation of humic acid from lignite in this work using cation resin and alkali extraction methods as recommended by IHSS, International Humic Substance Society. Lignite obtain from Pekalongan, Indonesia. Humic acid was extracted from lignite with alkaline solution as solvent. Lignite crushed and sieved using 80 mesh size. 10 grams of lignite was extracted with 200 cc of 0.5 M NaOH solution for 60 min with a rotation speed of 150 rpm. The extracted solution was filtered using a whatchman paper and the solution was then divided into 2 parts by volume. One portion of the volume is then treated using acid while the other volumes in the treatments use a resin cation in order to obtain a humic acid solid. Humic acid obtained dark brown then identified by infrared spectroscopy.

3. Result and Discussion
Figure 1 shows the IR spectra of the two humic fractions a) liquids extract from lignite extraction at pH 14 and b) liquids remaining after precipitation at a pH of about 2 indicating significant differences in both. They have a diversity of bands more or less typical to those distinguishing the humic materials [4]. The infrared spectra for liquid after precipitation process tends to shows as the fulvic acid. This indicates that most of the humic acid in the liquid extract has become a precipitated solid humic acid.

![Figure 1: IR Spectra](image)

The spectra evidently show predominance of OH, C=C and COO⁻ groups which are the most characteristic features of lignite materials. The fulvic acid is characterized by stronger absorption around 1720 cm⁻¹ which implies the high carboxylate capacity. The spectrum of fulvic acid is also characterized by the carbonyl vibrations at 2200–2000 (aldehyde and ketons).
Figure 2 FTIR spectra for solid humic acid prepared by precipitation at various HCl concentrations: a) 0.5 b) 1 c) 1.5 d) 2 e) 2.5 M.

Figure 2 showed the IR spectra for solid humic acid obtained from the precipitation process at various HCl concentrations: a) 0.5 b) 1 c) 1.5 d) 2 e) 2.5 M. It seems that the greater the acid concentration for the precipitation process, the lower the vibration. The vibrations due to the stretching of O-H alcohols or phenols in polymeric association observed around 3200–3600 cm⁻¹. The bending vibrations in the O-H plane of alcohols and phenols are at around 1400 cm⁻¹. The bond-stretching bands of C=N were observed between 2000 and 2600 cm⁻¹ in secondary amides. Absorption bands were observed between 1500 and 1600 cm⁻¹, which is associated with the C=C vibrations typically observed in aromatic hydrocarbons and carboxylic groups. The vibration of the C=C bonds conjugated with C=O and COO⁻ was observed around 1650-1725 cm⁻¹, this band is related to the presence of unsaturated ketones, carboxyl groups or aryl esters as well as primary amides.

Figure 3 FTIR spectra solid humic acid prepared by ion exchange method

Peak nearest to 1700 cm⁻¹ indicates higher protonated carboxyl group. Around 1100 cm⁻¹ in the spectra of the HA obtained through bacterial activity, a band was observed which is typically present in aromatic
rings with para- and ortho-substitutions. Between 890 and 700 cm\(^{-1}\), bands were observed which are typically found when there is stretching in the C-O-C bonds of carbohydrates.

Asing et al [13] reported that the FTIR spectra of HA from coal, Leonardite and chrysanthemum compost were largely similar but differing in intensity. The positions of the absorption bands of the four spectra fell within typical major absorption bands of HA which were at frequencies 3400–3300, 2940–2900, 1725–1700, 1630–1600, 1460–1440, 1400–1375 and 1260–1200 cm\(^{-1}\). FTIR analyses of extracted humic acid from lignite coal samples have shown the presence of carboxylic, phenols, alcoholic, and amines functional groups [14]. Figure 3 showed the IR spectra pattern for solid humic acid obtained from ion exchange method using cation resin in humic solution. When the ion exchange process takes place in the stirred tank, the humic acid solids begin appeared after the pH reached 4, and increased in number after reached pH 2. Figure 4 showed the IR spectra for two humic acid isolation treatments at pH 2 ie a) prepared by HCl b) prepared by cation resin.

![FTIR spectra solid humic acid prepared by a) HCl and b) ion exchange method](image)

**Figure 4** FTIR spectra solid humic acid prepared by a) HCl and b) ion exchange method

### 4. Conclusion

Yields of oxidation products were considerably lower for the HA-precipitated acid than for the HA-precipitated resin. It is obvious that the IR results are in good agreement for humic acid from lignite characterization.

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