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# Production of Humic And Fulvic Acid From Low Grade Coals By Catalytic Oxidation Method With High Purity, High Extraction Efficiency

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**ABSTRACT**

It has been investigated that humic acid and fulvic acid, which have been used rapidly in recent years, are obtained from low quality coals by oxidative method with the help of phase transfer catalysis. The coal sample was oxidized at 60°C with sulfuric acid, nitric acid and hydrogen peroxide in the presence of catalyst. Impurities such as calcium and magnesium were removed with hydrogen fluoride. From oxidized coal samples, humic and fulvic acids were extracted with sodium hydroxide in high purity and high yieldResults: High humic acid extraction rate was obtained in low quality coals using Tetraethylenepentamine as catalyst. Oxidation at low temperature in the presence of catalyst increased the oxidation capacity and oxidation stability of hydrogen peroxide, thus maintaining the biological activity of humic acid and fulvic acid. Hydrogen fluoride was added to the crude humic acid solution and ions such as calcium or magnesium, which could pass into the humic acid solution, were removed by forming compounds such as $CaF_2$ and $MgF_2$. Thus, the purity of humic acid obtained was increased. The solid precipitate obtained at the end of the study may contain a high proportion of humic acid and fulvic acid. The solid precipitate can be mixed with N, P, K and trace elements to obtain organic fertilizers. Thus, all coal raw materials used in the study can be used.

## 1. INTRODUCTION

Maintaining food production for a growing world population without compromising natural resources for future generations represents one of the greatest challenges for agricultural science, even compared with the green revolution in the 20th century. The intensification of agriculture has now reached a critical point whereby the negative impacts derived from this activity are now resulting in irreversible global climate change and loss in many ecosystem services. New approaches to help promote sustainable intensification are therefore required. One potential solution to help in this transition is the use of plant biostimulants based on humic substances. Current evidence suggests that the biostimulant effects of humic substances are characterized by both structural and physiological changes in roots and shoots related to nutrient uptake, assimilation and distribution (nutrient use efficiency traits (Canellas et al. 2015).

Young lignites with low carbonization and high moisture and ash values have an important reserve in our country. Therefore, nowadays, these types of coal are burned in thermal power plants and used for energy production. However, low quality lignites and some peats are also used for the purpose of obtaining fertilizer in the agricultural industry in recent years due to the high percentage of nitrogen and humic acid they contain (Ozdemir, 2011; Ozkan, 2007). Turkey's known coal reserves, coal 1.33 billion tons, is 12.4 billion tons of lignite, a total of 13.73 billion tons. Almost all of the hard coal reserve is in the Zonguldak Basin. Although our lignite reserves are of different quality and type in various regions of our country, our biggest lignite reserve

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is Afsin-Elbistan region of Kahramanmaras in Turkey with low thermal value and quality but high humic acid content (Ozdemir, 2011; Ozkan, 2007).

Gong et al (Gong et al. 2020) was studied coal-based FA which was separated by microwave-assisted oxygenation from lignite originating from Inner Mongolia in China. They were determined the representative microscopic molecular structure of FA through elemental analysis, infrared spectroscopy, nuclear magnetic resonance spectroscopy, classical quantitative titration experiments, and quantum chemistry combined with software analysis. They were found that coal-based FA mainly contains three kinds of benzene ring substituents, ether bonds, hydrogen bonds, carbonyl groups, hydroxyl groups, carboxyl groups, phenolic hydroxyl groups, and semiquinonyl groups. The two-dimensional planar molecular structure of FA was established; the chemical formula is $C_{38}H_{32}NO_{24}$, and the relative molecular mass is 886.

In work of Gong et al, FA was extracted from shallow low-rank lignite by hydrogen peroxide ($H_2O_2$) in a microwave field, and the functional groups of FA were characterized. The optimal extraction process was determined, with the $H_2O_2$ concentration being the key factor affecting the yield of FA (Zhang et al. 2020).

As stated in Ozdemir (2011) master's thesis, humic substances in soil consist of three basic components: humic acid, fulvic acid and humic acid (Hiradate et al. 2007). These substances differ according to their solubility in acidic and alkaline environments. Fulvic acid and humic acids are highly soluble in water when converted to alkali metal salts. Molecular weights of humus are much larger than fulvic acid and humic acids and do not dissolve at any pH (Allard & Derenne, 2007; Baglieri et al. 2006). Humic acids have a large molecular weight and their color is between dark brown and black. In contrast, fulvic acids are the simplest of humic substances. It has a low molecular weight and its molecular structure is simpler than that of humic acids. Their color is yellow to yellow brown. Humic acids are converted to their salts, which are expressed as alkali metal humates in alkali environments such as NaOH, $Na_2CO_3$ or KOH. These humates are highly soluble substances in water (Andrews & McDaniels, 1970).

When the structure of the soil is examined, it is seen that the organic compound consists of two main structures. These are the humic part and the non-humic part. Sugar, lipids, carbohydrates, amino acids, resins and the like. substances form the non-humic part of the soil. The humic part consists of three components:

1. Fulvic acid
2. Humic acid
3. Humin

The chemical structure of humic acid (Stevenson, 1982) and fulvic acid (Buffle and Leppard, 1995) is given in Fig. 1 and Fig. 2. As can be seen from the figure, the carbon content of fulvic acid is higher than humic acid and its oxygen content is lower. The physical and chemical properties of humic acid, fulvic acid and humine in coal are given in Table 1.

**Table 1.** Physical and chemical properties of humic substances (10)

| HUMIC MATERIALS | | |
|---|---|---|
| FULVIC ACID | HUMIC ACID | HUMIN |
| Yellowish Colors | Brownish Colors | Blackish Colors |
| Light color | Color darkens | Dark color |
| 2000 | Molecular weight increases | 300000 |
| %45 | Increases carbon content | 62% |
| %48 | Oxygen content decreases | 30% |
| 1400 | Reduces acidity | 500 |
| High resolution | Resolution decreases | Low resolution |

Humic acids can be found in the soil as well as in peat and lignite layers and in the Leonardite mine (Srivastava & Walia, 1997). Lignite, a humic acid source, emerges in the second stage of the carbonization process of carbon. Humic acid is present in the lignite structure at rates ranging from 10% to 80% (Allard & Derenne, 2007; Allard, 2005). Leonardite is a completely natural organic substance which contains highly humic acids and macro and micronutrients and is highly oxidized form of lignite layers near the surface (Olivella et al. 2002; Lao et al. 2005). Leonardite contains 25-90% humic acid and fulvic acid (16).

Shinozuka et al (Rasmussen & Allen, 2001), using coal in the Xinjiang region of China to obtain humic acid in NaOH environment. They then oxidized this humic acid using hydrogen peroxide and ozone and acidified the liquid mixture to pH 1 with 6 M HCl. Investigators separating humic acid from the bottom have passed the liquid residue through XAD resin to form fulvic acid as well as formic acid and oxalic acid. They found that fulvic acid obtained as a result of oxidation contains more oxygen and carboxyl groups than fulvic acid in the original coal.

Lehtonen et al (2001), the peat charcoal was dried in air and ground through a 2 mm sieve. The peat was sequentially dissolved with chloroformed water for 24 hours, 10 grams of the dissolved sample was stored in 10 separate containers of 100 ml with 0.1 M NaOH. The resulting products were combined and centrifuged at 14000 rpm for 2 hours. The solution was acidified to pH 2 with 6 M HCl and humic acid precipitated. As a result of the experiment, humic acid yield was 44% on dry basis. In the obtained humic acid again 56.5% C, 2.0% N, 1.2% ash were determined on dry basis. In addition, total hydroxyl group was determined to be more than carboxyl group.

Humic substances generally affect the physical, chemical and biological properties of soil and contribute to plant development and ecosystem balance. The benefits of humic substances increase the amount of organic matter in the soil, the water retention capacity of the soil, the stability of the soil, the root growth of the plant, increase the fruit yield and hence, the absorption of mineral substances and other micro elements in the soil by the plant to facilitate the resistance to harmful substances and pollution and so on. (Ozdemir, 2011; Ozkan, 2007).

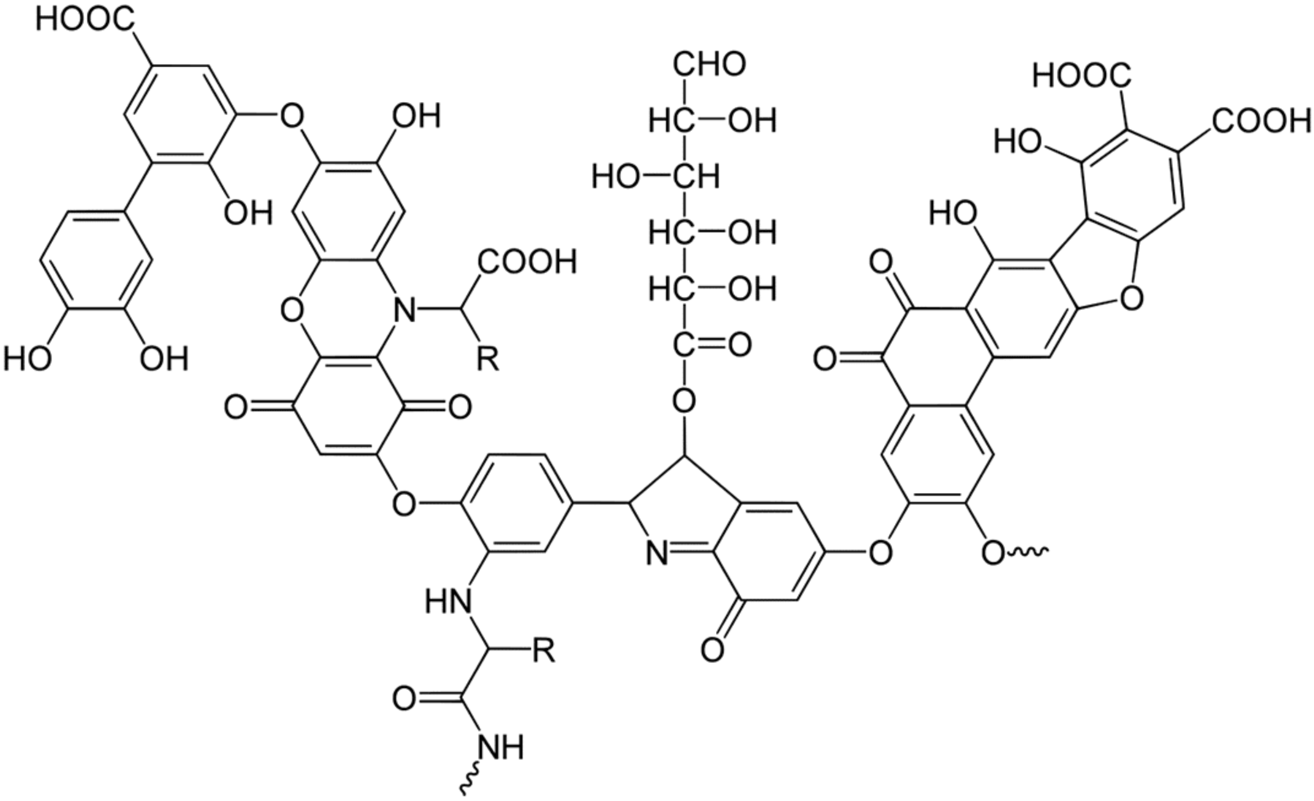


**Figure 1.** Molecular structure of humic acid (Stevenson, 1982)

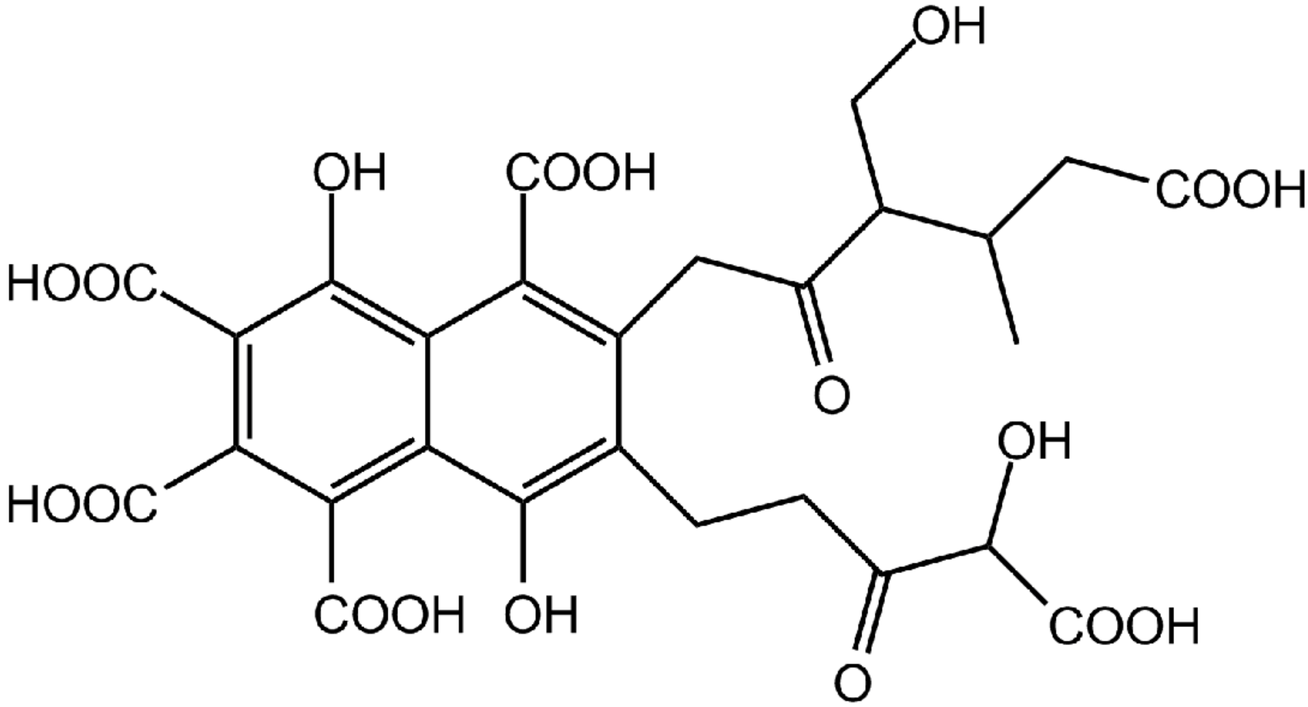


**Figure 2.** Molecular structure of fulvic acid (Buffle, 1995)

Ahmad et al. (Ozdemir, 2011; Ozkan, 2007) have aplied to wheat a mixture of DAP fertilizer and organic-mineral liquid fertilizer containing humic acid, fulvic acid (were obtained by alkaline extraction of lignite coal), nitrogen (N), phosphorus (P), potassium (K), zinc (Zn), sulfur (S), manganese (Mn). They have found that application of the fertilizer composition along with 50 kg of urea per acre showed the best biological yield (grain plus straw yield).

Mulberry powdery mildew often leads to a severe loss in cocoon production during the late autumn silkworm season. Zhang et al. (2019) have investigated reduce losses of cocoonn production with fulvic acid sodium salt (FANa) were obtained from brown coal. They have examined the effects of FANa on 9 types of bacteria isolated from diseased silkworms, it its effects on starvation resistance, and high-temperature survival of silkworms. Zhang et al. (2019) have determined that FANa had no noticeable influence on bacteria, but it significantly increased survival of silkworms during fasting and in high-temperature conditions (increased 12.21 and 24.16%, respectively. They have found that

FANa improve resistance to malnutrition in silkworms and reduced the loss caused by mulberry powdery mildew (Zhang et al. 2019).

Sadiq and coworkers have studied the different concentration of coal-derived HA on growth of sunflower. It was concluded that the application of coal-derived HA with low concentration under calcareous soil can help in improving soil quality and increasing yield on sustainable basis (Sadiq et al. 2014).

Ebrahimi and Miri have investigate the effect of humic acid on the germination properties of medicinal plants Borago officinalis and Cichorium intybus in a completely randomized design with five replications. The results revealed that effect of humic acid on the germination properties of C. intybus was significant ($p<0.01$) except for the germination percentage and mean germination time ($p<0.01$). In addition, humic acid was effective on the morphological properties of C. intybus except for radical and pedicel dry weight (Ebrahimi & Miri, 2016).

Hatami has done tests to evaluate the effect of zinc and humic acid applications on yield and yield components of sunflower in drought stress condition. Results showed that sunflower yield decreased under increasing drought stress, but zinc application improved yield by showing increased evaluations for diameter and number of seeds per head. Humic acid application also significantly increased grain yield by increasing grain weight, diameter and number of seeds per head under water stress conditions. They were said that the synergistic effect of zinc and humic acid applications improved sunflower yield in drought stress, by increased evaluations of diameter and number of seeds per head and weight of grain (Hatami, 2017).

The most common method for the production of humic acid is the extraction of the raw material containing humic acid with base such as NaOH or KOH. The yield of humic acid obtained from lignites varies between 15-30% and the purity of humic acid obtained is around 30%. The obtained humic acid is derived from the salts formed from metals in lignites as impurity (Stevenson, 1982).

In this study, catalytic oxidation of low quality lignites and subsequent extraction of high yield and high purity humic acid from oxidized lignite samples were performed. Catalytic oxidation and obtaining humic acid according to the standard method are described below as shown in Figures 3 and 4.

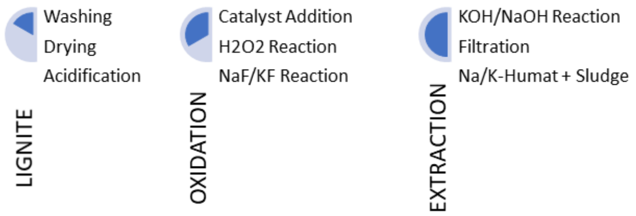


**Figure 3.** Hunic acid axtraction by Catalytic oxidation method

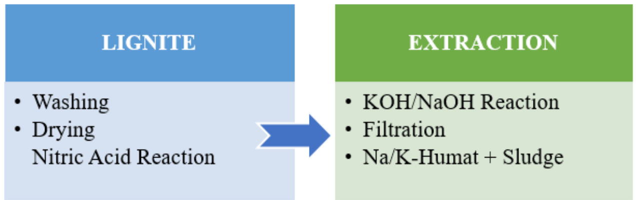


**Figure 4.** Humic acid extraction by standart method

## 2. METHOD

The lignite coal used in the experiment was obtained from Afşin-Elbistan thermal power plant. The chemical composition of coal is given in Table 2 below. The chemicals used in the experiments are of technical quality. Further purification was not required. Thermomac TM45 heated magnetic stirrer is used for heating and mixing. For weighing, Aczet brand CY 224 C model precision balance is used. The drying process was carried out in a Thermomac oven. Humic acid and fluvic acid ratios were determined by titrimetric and gravimetric methods.

HA Extraction with Catalytic Oxidative Method: 100 g of low-quality charcoal is washed with deionized water and dried in an oven at 110°C. Laboratory type ball mill is micronized to 40 mesh and placed in a beaker and dilute sulfuric acid is added on it. Hydrogen peroxide, water and catalyst (Tetraethylenepentamine, TEPA) were added to the acid-treated charcoal, which was kept overnight, and stirred at a constant temperature of 60°C. The solid-liquid phase is separated by filtration. The resulting solid phase is mixed with sulfuric acid /nitric acid mixture and water. Hydrogen fluoride is then added and stirred for a further half hour. NaOH was added to the residue and stirred for a further 40 min. The mixture is filtered to separate the humic acid phase and the solid phase.

**Table 2.** Composition of Afşin/Elbistan lignite sample used in the experiments

| Parameters | Original | Air Dry | Dry | Dehydrated ashless |
|---|---|---|---|---|
| Moisture | 46,54 | 5,26 | - | - |
| Ash | 17,91 | 33,32 | 36,53 | - |
| Volatile Substances | 23,57 | 39,66 | 39,83 | 60,79 |
| Carbon | 11,08 | 21,86 | 23,74 | 39,51 |

Table 3 summarizes the substances used in the experiments and the processing times. Table 3 shows the amount of chemical used in each process step, processing time and temperature for 100 g of washed and dried coal samples each.

HA Extraction with Oxidative Method, Comparison: 5% Nitric acid was added to the lignite solution, followed by stirring at 60°C for 2 hours. 8% KOH was added to the precipitate and stirred for 2 hours. The solid phase and humate phase were separated by filtration.

**Table 3.** HA extraction from 100 g, 40 mesh washed, dried Afşin / Elbistan Lignite

| Extraction Steps | Experiment-1 | Experiment-2 | Experiment-3 |
|---|---|---|---|
| | 1. Acid Reaction | | |
| Dilute. H2SO3 | %5 | %1 | - |
| Dilute.H3PO4 | - | - | %3,5 |
| Dilute.HNO3 | - | - | - |
| Tima | 12 h | 12 h | 12 h |
| | Catalytic Peroxide Oxidation (Precipitate) | | |
| H2O2 | 10 mL | 10 mL | 10 mL |
| Catalyst | 5 g | 7 g | 5 g |
| Water | 500 mL | 300 mL | 400 mL |
| Temperature | 60 C | 60 C | 60 C |
| Time | 2 h | 1,5 h | 2 h |
| | 2. Acid reaction (Precipitate) | | |
| H2SO4 | %15 | %20 | %30 |
| HNO3 | %15 | %20 | %30 |
| Water | 300 mL | 400 mL | 300 mL |
| Time | 2 h | 1,5 h | 2,5 h |
| | Metal Extraction (Mixture) | | |
| HF | 8 g | 8 g | 5 g |
| Time | 0,5 h | 0,5 h | 1 h |
| | Basic Reaction / (HA + FA) Extraction (Precipitate) | | |
| NaOH | 8 g | 8 g | 7 g |
| Time | 40 min.. | 30 min | 15 min |

## 3. RESULTS

In conventional methods to convert water-insoluble humic acid into a water-soluble humate, humic acids are neutralized with a base. The conventional method of obtaining humic acid from low grade coal using sodium hydroxide has the advantages of simple operation and low input cost, but the alkali humates obtained in conventional methods are of low purity and have long production times. High content of heavy metals.

Humic acid and fulvic acid yields can be increased by the two-step interaction of nitric acid and/or hydrogen peroxide and coal in the production method of humic acid. It is inevitable. Therefore, the yield of humic acid obtained will be high, but the quality will be low. It will also be of low purity since it contains salts of metal components such as calcium and magnesium.

In this study, although the processes seem to be complex, high efficiency, high purity humic acid was extracted from low quality coals with short term processes. Humic acid ratios and impurities obtained as a result of the experiments are given in Table 4 and Table 5.

**Table 4.** Catalytic oxidative method and obtained by oxidative method and impurity rates of humic acid

| Parameter | Experiment-1 | Experiment-2 | Experiment-3 | Experiment-4 |
|---|---|---|---|---|
| %HA | 76,75 | 73,41 | 75,35 | 43,29 |
| %FA | 14,56 | 17,32 | 13,62 | 7,16 |
| % Impurities | 90,16 | 91,93 | 92,89 | 55,68 |

**Table 5.** Catalytic oxidative method as a result of the residual humic acid and fulvic acid ratios

| Parameter | Experiment-1 | Experiment-2 | Experiment-3 |
|---|---|---|---|
| %HA | 44,28 | 50,23 | 45,15 |
| %FA | 5,65 | 4,91 | 6,14 |

## 4. DISCUSSION

The advantages of the present study compared to the known oxidation methods are:

-High humic acid extraction rate was obtained in low quality coals using Tetraethylenepentamine as catalyst. Oxidation at low temperature in the presence of catalyst increased the oxidation capacity and oxidation stability of hydrogen peroxide, thus maintaining the biological activity of humic acid and fulvic acid. By the second stage acid mixture reaction, low quality coal containing solids-rich organic material was further converted into humic acid and fulvic acid. In the second stage, the reaction of nitric acid and the oxidation rate which could disrupt humic / fluvic acid were reduced by using acid mixture.

-Hydrogen fluoride was added to the crude humic acid solution and ions such as calcium or magnesium, which could pass into the humic acid solution, were removed by forming compounds such as CaF2 and MgF2. Thus, the purity of humic acid obtained was increased. The extraction rate of humic acid was more than 75% and the purity of humic acid was more than 90%. The active ingredient, fulvic acid content, was obtained at levels of 16%. The method used in this study will meet the demands of industrial applications with low input cost, simple and easily procured raw materials, easy working conditions, high active components and safer working advantages.

-The solid precipitate obtained at the end of the study may contain a high proportion of humic acid and fulvic acid. The solid precipitate can be mixed with N, P, K and trace elements to obtain organic fertilizers. Thus, all coal raw materials used in the study can be used.

## 5. CONCLUSION

The method studied for the extraction of humic acid is at least 15-20% higher yield and purity, at least 20-25% higher than that of the conventional oxidative humic acid production method; The fulvic acid content in the humic acid component has been significantly improved. Fulvic acid content was increased by 13-17% compared to the initial content of low-grade coal in the dry state. The initial fulvic acid content in coals is about 1-7%. The content of active fulvic acid component reached 15-20% in the study. In addition, the humic acid content in the dried solid residue in the process is still 40-50%, and the fulvic acid content is 5-6%. In this case, it has high economic value and can be made by mixing with N, P, K and trace elements. Thus, low-quality coal resources can be fully integrated into the agricultural economy.

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