Effect of Mechanochemical Activation on Peat Humic Acid

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Abstract. Mechanosynthesis method is an efficient processing method that uses mechanical means to change the structure and physical and chemical properties of objects. This article takes peat from Erlintu Town, Yuyang District, Yulin City, Shaanxi Province as an example. It is activated by mechanochemical method, and then humic acid and fulvic acid are extracted by alkali-soluble acid purification technology. The results show that mechanochemical method can improve the extraction rate of humic acid and fulvic acid in peat. Among them, the mechanochemical method with percarbonamide as the oxidant and sodium hexametaphosphate as the grinding aid has the best effect of activating peat. Mechanochemical methods can increase the molecular condensation degree and molecular relative mass of humic acid, but reduce the molecular condensation degree and molecular relative mass of fulvic acid.

1. Introduction
Peat belongs to a kind of organic mineral resources rich in humic acid, with huge reserves and widely distributed in nature, and belongs to the first stage of coal formation. Due to the difference of the genetic environment, the content of peat is also quite different [1-3]. Generally speaking, the organic matter of peat accounts for about 30~98%, humic acid is about 20~65%, and the major mineral elements are Ca, P, K, Mg, Na. My country's peat resources are mainly distributed in the northeast mountainous and hilly areas, the Sanjiang Plain, the Qinghai-Tibet Plateau, the eastern coastal plain, the middle and lower reaches of the Yangtze River and the Yunnan-Guizhou Plateau. Peat in Shaanxi is mainly distributed in northern Shaanxi and the southern slope of the Qinling Mountains in southern Shaanxi.

Peat belongs to the initial stage of coal formation, so the humic acid in peat can be called the original ecological humic acid. Humic acid is a natural polymer mixture with similar structural characteristics, and its molecular weight distribution ranges from a few hundred to several million. Due to its different molecular weights and hydrophilic functional groups, the properties of humic acid are different, which can be divided into fulvic acid, brown humic acid, black humic acid, and humin according to the water solubility of humic acid. Humic acid has the ability to retain water and fertilizer, regulate acid-base, improve soil physical and chemical properties, and promote soil microbial activities, which has an important impact on the exchange process of the earth's biosphere [4-6].
In the agricultural field, only soluble low molecular weight humic acid can be directly absorbed by crops. Therefore, humic acid needs to be activated to improve the biological activity of humic acid. The main purpose of the so-called "activation" of humic acid is to increase the reactivity of humic acid, reduce the molecular weight, and increase the solubility of humic acid. The process mainly includes three methods of physical, chemical and biological activation.

The Erlintu area, Yuyang District, Yulin City, Shaanxi Province, China is rich in peat resources, but few are currently being developed and utilized. This project uses a pollution-free mechanochemical method to activate and extract peat in the Erlintu area of Yulin, which has practical significance for the development and application of peat in this area.

2. Materials and methods

2.1. Raw material collection
Peat was collected from Erlintu Village, Yuyang District, Yulin City, Shaanxi Province.

2.2. Experimental steps

2.2.1. Mechanical activation step. After removing impurities, crushing and drying the peat, it is passed through a 0.15mm sieve to obtain peat powder. According to the ratio of ball-to-battery ratio of 6:1, weigh 30g of peat powder into a grinding tank, and add 2.5g of activator (solid oxidant) and grinding aid at the same time. Grind for 20min at 250 rpm to obtain Activated peat powder.

2.2.2. Humic acid and fulvic acid extraction. Weigh 10g of peat powder into a three-necked flask, add 5% potassium hydroxide solution with a mass fraction of 1:10, adjust the pH to 12.0 with 30% potassium hydroxide solution, and stir for 2h at 80 degrees Celsius Then put the slurry in a beaker and let it stand overnight. Pour out the supernatant. After centrifuging the remaining slurry for 10 minutes at 10000rpm, collect the clear liquid. Adjust the pH to 1.0 with 15% sulfuric acid. After standing overnight, centrifuge at 10000rpm after separation, the clear liquid is fulvic acid, which is collected, concentrated and weighed; the remaining centrifugal sediment is humic acid. After washing the sediment repeatedly with deionized water, the humic acid is dried under reduced pressure at 60°C.

2.3. Structural characterization and testing

2.3.1. E4/E6. Weigh 20 mg of the humic acid sample to be tested, and dissolve it in 100 mL of a NaHCO3 solution with a concentration of 0.05 mol/L, and adjust the pH value of the solution to be 8-9 with 0.1 mol/L NaOH. The measurement was performed on a UV-1601 ultraviolet-visible spectrometer. The measurement conditions were to measure the absorbance at 465nm and 665nm respectively, and the ratio of the two was the value of humic acid E4/E6.

2.3.2. FTIR. Measured with Fourier transform infrared spectrometer (Spectrum GX type, product of Perkin Emerl). Experimental conditions: scanning range 400 ~ 4 000 cm-1, resolution 4 cm-1, detector: DTGS, scanning cumulatively 16 times.

3. Results and discussion

3.1. Microstructure characteristics of compound soil micro-aggregates
The mechanochemical activation of peat process is shown in Table 1, where R-AWP is humic acid/fulvic acid extraction without mechanical activation process; MAP is humic acid/fulvic acid extraction after mechanical activation process, but in the mechanical activation process Without activator and grinding aid; MAP-1 is humic acid/fulvic acid extraction after mechanical activation process, activator is percarboxamide, without grinding aid; MAP-2 is processed after mechanical activation process Humic acid/fulvic acid extraction, the activator is percarbonamide and sodium hydroxide, the grinding aid is
sodium hexametaphosphate; MAP-3 is the extraction of humic acid/fulvic acid after the mechanical activation process, and the activator is over Carbonamide, the grinding aid is sodium hexametaphosphate.

Under 5 different process conditions, the extraction rate of humic acid and fulvic acid in peat is shown in Table 2. The results show that compared with no mechanochemical activation, peat can be greatly improved after mechanochemical activation. The extraction rate of humic acid and fulvic acid in peat, among which the extraction rate of humic acid can be increased by 47.76%. In the mechanochemical process conditions, the choice of activator and grinding aid has an important influence on the extraction rate of peat humic acid/fulvic acid. Among them, the activator is percarbonamide and sodium hydroxide, and the grinding aid is SHMP. The effect is most obvious under the conditions of this process. Under this process, the extraction rate of humic acid is the highest, but the extraction rate of fulvic acid is the lowest. This is mainly due to the effect of percarbonamide, sodium hydroxide and SHMP. It is oxidized and decomposed into humic acid to fulvic acid, and the original fulvic acid is further oxidized and degraded.

Table 1. The effect of mechanochemical activation on the extraction rate of HA/FA in peat

| project    | Activator            | Grinding aid | HA%  | FA%  |
|------------|----------------------|--------------|------|------|
| R-AWP      | /                    | /            | 20.1 | 18.5 |
| MAP        | /                    | /            | 24.7 | 20.3 |
| MAP-1      | Percarbonamide       | /            | 24.7 | 20.8 |
| MAP-2      | Percarbonamide + Sodium hydroxide | SHMP | 29.7 | 19.2 |
| MAP-3      | Percarbonamide       | SHMP         | 24.6 | 21.6 |

3.2. Humic acid UV spectrum analysis

The Fourier infrared spectrum of peat humic acid is shown in the figure 1. The figure shows that the main absorption of humic acid is with 3420, 2927, 1717, 1650, 1223, and 1032 cm⁻¹, indicating that humic acid is rich in lipids, Volume, active functional groups such as carbonyl and amino groups, have high aromaticity. The ratio parameter (the ratio between the optical density of the absorption band at a specific wavelength) in Fourier infrared spectroscopy can be used to classify and compare the structural characteristics of humic acid. For example, D3400 / D2934 represents the amount of alkyl substitution, D1040 / D1270 represents the relative concentration. It can be seen from Table 2 that after peat is activated by mechanochemical method, the ratio of D3400/D2934 of the extracted humic acid increases, and the number of alkyl substituents in the surface humic acid structure increases, indicating that mechanochemical activation can increase The number of alkyl substituents in humic acid increases its activity; after substitution and mechanochemical activation, the ratio of D1040/D1270 of humic acid has been increasing to varying degrees, which also means that the relative relative concentration is changing.

Figure 1. Effect of mechanochemical activation on infrared spectra of humic acid groups in peat
Table 2. The effect of mechanochemical activation on the infrared spectrum ratio of humic acid groups in peat

| project  | D3400/D2926 | D1720/D1610 | D1040/D1270 |
|---------|-------------|-------------|-------------|
| R-AWP   | 2.26        | 0.932       | 0.933       |
| MAP     | 2.02        | 0.88        | 1.012       |
| MAP-1   | 2.00        | 0.95        | 1.085       |
| MAP-2   | 1.86        | 0.946       | 0.963       |

3.3. Humic acid UV spectrum analysis

The E4/E6 of humic acid represents the ratio of the optical density of the tested solution at wavelengths of 465nm and 665nm, which is an important indicator for the characterization of the composition and structure of humic acid. The E4/E6 value is a characteristic constant for each humic acid. It reflects the relative molecular mass or aromatic condensation degree of humic acid. The ratio is negatively correlated with the molecular mass or condensation degree, that is, the E4/E6 value. The larger the value, the smaller the degree of molecular condensation and relative molecular mass, and the smaller the degree of humification; the smaller the value of E4/E6, the larger the degree of molecular condensation and molecular mass, and the greater the degree of humification [7-9]. The E4/E6 data of humic acid/fulvic acid extracted by mechanochemical activation of peat are shown in Table 3.

The results show that after mechanochemical activation of peat, the humic acid and fulvic acid extracted by alkali-soluble acid extraction have different changes. The mechanochemical activation reduces the E4/E6 of humic acid in peat, but increases The introduction of soluble fulvic acid E4/E6, solid oxidizer and alkali reagents has different effects on the decrease of humic acid E4/E6 in peat and the increase of fulvic acid E4/E6. Among them, the solid oxidant is percarbon. When the amide and the grinding aid are sodium hexametaphosphate, the E4/E6 of humic acid is the smallest and the E4/E6 of fulvic acid is the largest. It shows that the mechanochemical method with percarbonamide as the oxidant and sodium hexametaphosphate as the grinding aid has the best effect of peat activation. It shows that mechanical activation can increase the molecular condensation degree and molecular relative mass of humic acid that can be extracted from peat, but reduce the molecular condensation degree and molecular relative mass of fulvic acid. The main reason is that mechanochemistry can oxidatively degrade part of the humic acid and fulvic acid in peat.

Table 3. E4/E6 of humic acid and fulvic acid

|        | HA      | E4/E6 | FA      | E4/E6 |
|--------|---------|-------|---------|-------|
| RAWP-HA| 6.22    | RAWP-F  | 4.17    |
| MAP-HA | 5.18    | MAP-F  | 4.27    |
| MAP-1-HA| 5.22 | MAP-1-F  | 5.31    |
| MAP-2-HA| 5.18 | MAP-2-F  | 4.10    |
| MAP-3-HA| 4.74 | MAP-3-F  | 6.27    |

4. Conclusion

Taking the peat from Erlintu Town, Yuyang District, Yulin City, Shaanxi Province as an example, it was activated by mechanochemical method, and then humic acid and fulvic acid were extracted by alkali-soluble acid purification technology. The results of the mechanochemical method were investigated. It shows that the mechanochemical method can improve the extraction rate of humic acid and fulvic acid in peat, but different activators and grinding aids need to be selected according to the extraction purpose. Among them, percarbonamide is used as oxidant and sodium hexametaphosphate is used as grinding aid. The mechanochemical method of the agent has the best effect in activating peat. The mechanochemical methods can increase the molecular condensation degree and molecular relative mass of humic acid, but reduce the molecular condensation degree and molecular relative mass of fulvic acid. [1-9]
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