Spectral study of humic substance extract from pressurized oxidizing slag of Carlin-typed gold deposit

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Abstract: Carbonaceous matters in Carlin-type gold deposit, especially the humic substance, which have a serious preg-robbing effect on the process of cyanidation. In this paper, the humic acid and fulvic acid were extracted from oxidizing slag via pre-activation alkaline-heat method, and using FTIR and UV-Vis spectra to study the molecular structure of humic acid extract and fulvic acid extract. The FTIR spectrum demonstrated that hydroxyl, carboxyl and benzene rings characteristic stretching vibration peaks occurred in spectra of humic acid and fulvic acid, but humic acid extract had a finer molecular structure. The result of UV-Vis spectra analysis showed that the extract contained alkyl-substituted benzene ring structure, and the amount of carboxyl groups and hydroxyl groups in fulvic acid molecule was larger than that of humic acid. The fulvic acid extract contained more chromophores, while humic acid molecules have a higher degree of humification and a higher average molecular weight. Although there were some differences in the molecular structure of the both, they were both complex macromolecular organic compounds with a benzene ring as a basic unit.

1. Introduction
The Carlin-type gold deposit is a double refractory gold ore which contain carbonaceous matter and arsenic [1]. The gold particles are mostly encapsulated in sulfide minerals (pyrite and arsenopyrite) in the form of microscopic gold or submicroscopic gold. Generally, the pretreatment method such as pressurized oxidation is used to oxidize and decompose the sulfide minerals, in order to the gold encapsulated are exposed, which is beneficial to cyanide leaching and gold extraction [2]. However, some studies show that, the presence of carbonaceous materials in the Carlin-type gold deposits may lead to the phenomenon of “preg-robbing” during the cyanidation and gold extraction process, resulting in a serious decline in gold leaching rate [3]. Carbonaceous matters mainly include element carbon, humic substance and high molecular hydrocarbon [4], in particular, humic substance can be classified into humic acid, fulvic acid and humin based on acid-alkali solubility [5]. The researchers found that the humic substance are a complex macromolecular organic acid with carboxyl, hydroxyl or other oxygen-containing functional, meanwhile contain aromatic ring structure and various heterocyclic ring
units, and linked by a group of -CH₂-, -O- and others [4, 6]. At present, the carbonaceous materials are decomposed and deactivated by means of pressure oxidation, roasting oxidation, cover inhibition or other pretreatment methods, while, the carbon removal pretreatment methods are difficult to eliminate humic materials completely.

In this paper, the humic acid and fulvic acid after pressure oxidation were studied. The structure analysis of the two humic substance extracted and separated from oxidizing slag was carried out by means of infrared spectroscopy and ultraviolet spectroscopy. By comparing the structure and properties of different humic extracts, which has a certain theoretical guiding significance for molecular structure of humic materials and reducing the preg-robbing effect in the process of cyanidation.

2. Experimental materials and methods

2.1. Oxidizing slag

The pressurized oxidizing slag was obtained from a Carlin-type gold deposit of Guizhou province, and its XRD diffraction pattern is shown in Figure 1. After acidic pressure oxidation, pyrite and arsenopyrite are decomposed into jarosite, carphosiderite and iron arsenate. In addition, new phase gypsum is formed. Other main minerals are quartz and montmorillonite.

![XRD diagram of oxidizing slag.](image)

**Figure 1.** XRD diagram of oxidizing slag.

The carbon and multi-element analysis data of the pressurized oxidizing slag are shown in Table 1. The analysis results showed that inorganic carbon (including elemental carbon, activated carbon or graphitic carbon) has obvious decompose effect under acid pressure oxidation, while organic carbon (including humic substance and hydrocarbons) has poor oxidative degradation effect. The content of Au in pressurized slag was 23.7 g·t⁻¹, arsenic and sulfur were reduced to 0.611% and 9.07%, respectively.

| element | C_total (%) | C_inorganic (%) | C_organic (%) | Au/（g·t⁻¹） | Fe/% | As/% | S/% | SiO₂/% |
|---------|-------------|-----------------|---------------|--------------|------|------|-----|-------|
| content | 4.08        | 0.01            | 4.07          | 23.7         | 9.29 | 0.611| 9.07| 31.38 |

2.2. Extract method

Humic substance in pressurized slag were extracted by "acid leaching - ultrasonic pre-activation - alkali heat" extraction method. The oxidized slag was dipped in deionized water for 20 min. The slag sample was immersed in 0.5 M HCl for 20 min, and rinsed with deionized water for 3-5 times until the pH was neutral. The filtrate residue sample was discarded at a solid-liquid ratio of 1:4 with a concentration of 1 M NaOH-Na₃P₂O₇ mixed extractant, ultrasonic pre-activation for 20 min, ultrasonic power of 100 W, and ultrasonic temperature of 30 °C. After pre-activation, it was placed in a constant temperature water bath for 10 h at a temperature of 65 °C and a rotation speed of 300 rpm. The extracting solution was
preserved for 12 h at room temperature, and then separated by acid precipitation. The sediment and supernatant were separated for 15 min by centrifuging at 2500 rpm. The insoluble black small particle precipitate was humic acid, and the brown solution was fulvic acid.

2.3. Analytical methods

FTIR spectra were recorded over the range 4000-400 cm\(^{-1}\) by a Thermo Nicolet-380 spectrometer through pelleting the 20 mg of sample with 200 mg of KBr.

UV-Vis spectra were provided on a TU-1901 UV-vis spectrophotometer by recording adsorption spectra of HA and adsorbed HA over the range 200-900 nm. Meanwhile, \(E_{465}/E_{665}\) (the absorbance at 465 nm divided by at 665 nm), \(E_{270}/E_{400}\), and \(E_{250}/E_{365}\) were calculated according to the spectra.

3. Results and discussion

3.1. FTIR analysis

The infrared spectroscopy analysis of the humic acid particles and the fulvic acid solution extracted from the oxidizing slag were carried out, and the spectrum are shown in Figure 2. From the infrared spectrum, the intensity of vibration stretching peaks of the two extracts in the functional group zone are slightly different, and the main difference of the spectrum is reflected in the fingerprint area of less than 1000 cm\(^{-1}\), which also indicate that the two extracts have relatively similar functional group composition.

After pressure oxidation, the aliphatic structure of humic acid and fulvic acid molecules is destroyed and chemical bonds are broken, and only weaker methyl symmetric bending vibration peak appears near 1380 cm\(^{-1}\)\cite{7}, which also illustrates that the pressure oxidation has a certain decomposition effect on aliphatic structure. The large and blunt absorption vibration peak occurring at 3450 cm\(^{-1}\) can be corresponded to the stretching vibration of -OH in -COOH, phenol and alcohol\cite{8-10}. Further, a strong vibration peak near 1640 cm\(^{-1}\), which is related to the C=C stretching vibration in the benzene ring, and the -C=O stretching vibration in aldehydes and ketones cannot be excluded\cite{7, 11}. However, the peak of the fulvic acid extract is stronger compared with the humic acid, this indicate that the fulvic acid contains more oxygen-containing active groups such as benzene ring structure, alcohol or phenol.

In addition, in the spectra of fulvic acid, a peak of C-O bond appeared at 2080 cm\(^{-1}\) and 1107 cm\(^{-1}\), which shows that the fulvic acid may be contain more esters, ethers alcohol or phenolic structure\cite{9, 12}. The peak occurs at 1135 cm\(^{-1}\) in humic acid is associated with the symmetric stretching vibration of aromatic sulfonic acid groups\cite{13}. And the bending vibration of out-of-plane N-H bond of the amide in two extracts appears at 618 cm\(^{-1}\)\cite{14}, moreover, in the fingerprint region, the three weak infrared vibration peaks of humic acid appearing at 993 cm\(^{-1}\), 800 cm\(^{-1}\) and 472 cm\(^{-1}\) are resulted from the deformation vibration of aliphatic hydrocarbons CH\(_2\), the out-of-plane stretching vibration of two ortho-CH bonds in the benzene ring, the C-C bond of aromatic hydrocarbons and the vibration of the sulfur-

\[\text{Figure 2. FTIR spectra of humic acid (a) and fulvic acid (b).}\]
containing group and Me-OH bond, respectively[11, 14-16]. While the no peak in the fulvic acid, indicating that the humic acid has a finer molecular structure.

3.2. UV-Vis spectra analysis
10 mg of humic acid extract was dissolved in 0.05 M NaOH and shaken for several minutes. The dissolved humic acid and fulvic acid extractant were analyzed by ultraviolet-visible spectroscopy, and the scanning range was 190-800 nm. The spectra and the second derivative UV-Vis spectra of the two extract are shown in Figure 3 and Figure 4, respectively.

According to Figure 3, both humic acid and fulvic acid have a distinct UV absorption peak, the absorption peak of humic acid appears at 209 nm, while fulvic acid occurs at 217.5 nm, and the peak intensity of fulvic acid is stronger than that of humic acid, which correspond to the presence of an alkyl-substituted benzene ring structure [13]. In addition, UV absorption process of two extract generate the overlapping of functional groups, causing the appearance of an absorption platform due to various chemical groups in humic substance [17, 18]. Therefore, it is necessary to perform the second-order derivation of the spectrum, as shown in figure 4.

There are significant differences in the number of peaks in the second-order UV spectrum of humic acid and fulvic acid extracts. For humic acid extract, the derivation peaks appear at 206 nm and 223.5 nm, respectively, which are caused by alkyl-substituted benzene rings and π-π* electronic transitions in mono- and di-substituted phenylcarboxy and phenolic structures, respectively. [17, 19-20]. While, the peaks of fulvic occurring at 206 nm, 217.5 nm and 230.5 nm also attributed to alkyl-substituted benzene rings and π-π* electronic transitions. However, in the region of 220-240 nm, the peak position of the fulvic shifts toward the long-wave direction compared to the humic acid, wherefore a red shift occurs, indicating that the fulvic extract have more carboxyl, hydroxyl group or others [19], which is consistent with the analysis of the FTIR spectra.

![Figure 3. UV-Vis spectra of humic acid (a) and fulvic acid (b).](image)

![Figure 4. Second derivative UV-Vis spectra of humic acid (a) and fulvic acid (b).](image)
Table 2 shows the absorbance ratios of the specific wavelengths of the two extracts from the oxidizing slag. They are usually used to describe the degree of humification, aromaticity, polymerization and molecular weight [11]. The ratio of $E_{250}/E_{365}$ is inversely proportional to the molecular weight and aromaticity [2]. From the data in Table 2, the value of humic acid is lower than that of fulvic acid, indicating that humic acid has a higher degree of aromaticity and a larger molecular weight. Secondly, the ratio of $E_{270}/E_{400}$, on the one hand, can explain the content of chromophore, and on the other hand, the degree of degradation of the complex functional group to the simple aromatic phenylcarboxyl structure [18, 22]. Therefore, the fulvic acid contains more chromophores and a higher degree of degradation to the aromatic phenyl carboxyl structure according to the result calculated. More importantly, the ratio of $E_{465}/E_{665}$, humic acid is slightly lower than that of fulvic, which implies that humic acid has a higher degree of humification and a larger average molecular weight [23, 24]. The analysis results fully illustrate that there are obvious structural differences between the two extracts, but the basic structure is similar, both of which are complex macromolecular organic acids with benzene rings as the skeleton.

**Table 2.** UV-Vis spectroscopic characteristic parameters of humic acid and fulvic acid.

| humic substance | $E_{250}/E_{365}$ | $E_{270}/E_{400}$ | $E_{465}/E_{665}$ |
|-----------------|-------------------|-------------------|-------------------|
| humic acid      | 2.02              | 2.21              | 1.73              |
| fulvic acid     | 9.19              | 7.93              | 2.13              |

4. Conclusion

The humic acid and fulvic acid extracted from the pressurized oxidizing slag are analyzed by infrared spectroscopy and ultraviolet spectroscopy. Studies have shown that there are significant differences between the humic acid and fulvic acid. According to the FTIR analysis, the characteristic vibration peaks of hydroxyl, carboxyl and benzene rings or other functional groups all appear in the spectrum, but the humic acid extract has a finer molecular structure. In the UV-Vis spectra, the content of carboxyl and hydroxyl groups in the fulvic acid are higher than that of humic acid, and contain more chromophores. While the humic acid molecule has a higher degree of humification and a larger average molecular weight. The difference between humic acid and fulvic acid further explains the complexity of humic substance.

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