Research on transformation characteristics of humic acid based on improved three-dimensional fluorescence regional integral

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Abstract This paper mainly studied transformation characteristics of humic acid in aqueous medium from coal-mining region of Pingdingshan. To achieve the research purpose, we carried out soil columns experiment. In this experiment, humic acid solution is used as water sample, meanwhile, marl rock are used as testing rock sample. Soon after the experiment, three-dimensional fluorescence technology was took to test humic acid. In order to improve precision of three-dimensional fluorescence, we applied the analytic hierarchy process (AHP) to the traditional regional integration method. Then the improved regional integral was utilized to analysis experiment result. The three-dimensional fluorescence regional integral results of marlstone show that from 192h to 600h, proportion of region V let up from 0.456 to 0.065, however, proportion of region IV added from 0.372 to 0.502. Apparently Humic acid has transformed in the marlstone. This kind of transformation is mainly degradation Humic acid was degraded into soluble metabolic products by microorganism. And for that the percentage of region V minished when the percentage of region IV added.

Key words Humic acid, 3DEEM, improved regional integral, marlstone

Introduction

Humic acid is a kind of polymer organic compound with fat and aromatic structure, which is made by carbon, hydrogen, oxygen, nitrogen, sulfur and other elements. Three-dimensional excitation-emission matrix(3DEEM) is a common technical means of humic acid research. At present, we mainly rely on the traditional peak position to identify humic acid qualitatively. With the appearance of the regional integration method, it is quantitative for Three – dimensional fluorescence analysis. However, traditional integration method simply use the reciprocal of the region area as the balance weight, which is not completely consistent with the actual situation, and its accuracy still needs to be improved.

In this paper, the marl rock extracted from Pingdingshan coal field is used as the medium to carry out a simulation experiment. Then, three-dimensional fluorescence spectra of humic acid was detected in leaching solution. We introduced analytic hierarchy process(AHP) to improve Three-dimensional Fluorescence Region Integral Method, analyzing the spectral characteristics of three dimensional fluorescence quantitatively. The degradation characteristics of humic acid were studied, and this will lay the scientific foundation for the study of groundwater recharge, runoff and excretion mechanism in the water filled aquifer of coal mine.

Materials and Methods

Test material

There distributes the Neogene marl aquifer with Non-uniform thickness in superficial layer of the Pingdingshan basin. Deep sandstone and limestone aquifers are supplied through marl rock aquifer indirectly. Consequently, this brings inrush risk to coal mining. Therefore, we choose the marl rock as rock samples. Before use, roots and other impurities were removed, and the samples were air dried and grinded to pass through a 2mm screen. When it comes to infiltration solution, it is determined using analytical purity humic acid. Fig.1 shows you the 3DEEM feature of humic acid.
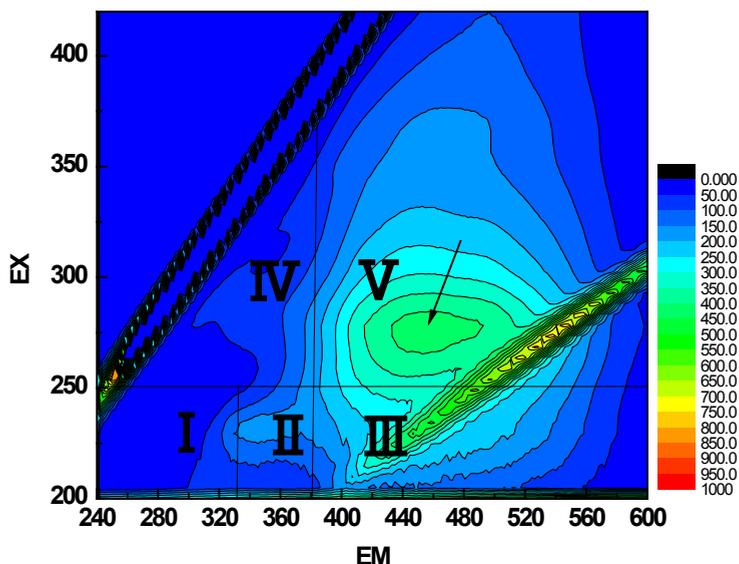

Fig.1 *3DEEM feature of humic acid*

Experimental Device and method

The plexiglass column was used in the experiment, with a height of 50cm and a inner diameter of 7cm.To achieve the uniformity of lixiviant spreading, medium sand with a grain size of 3cm were places at the top and the bottom of the test column reaching about 3cm high. Soil columns were prepared by hand packing air-dried fine sand and marl rock in acrylic cylinders(7cm and 50cm in diameter and height, respectively).The upper and lower ends of the column are open and connected with a hose as an inlet and an outlet.In the test, the high bucket and the peristaltic pump were used as the water supply device to provide a stable flow field for the soil column, as shown in Fig.2.We used HITACHI F-7000 fluorescence spectrophotometer to detect Three- dimensional fluorescence spectra.

Firstly, distilled water was pumped into test column at a certain flow from the bottom to remove the air in the test column slowly. After that, non-reactive solute humic acid with

mass concentration of 70.9 mg/L respectively was poured into the soil column at a rate of 2.5 mL/h. The temperature was controled 25° C by thermostat. Meanwhile, samples from the end of the soil column at a certain time were detected three- dimensional fluorescence spectra.
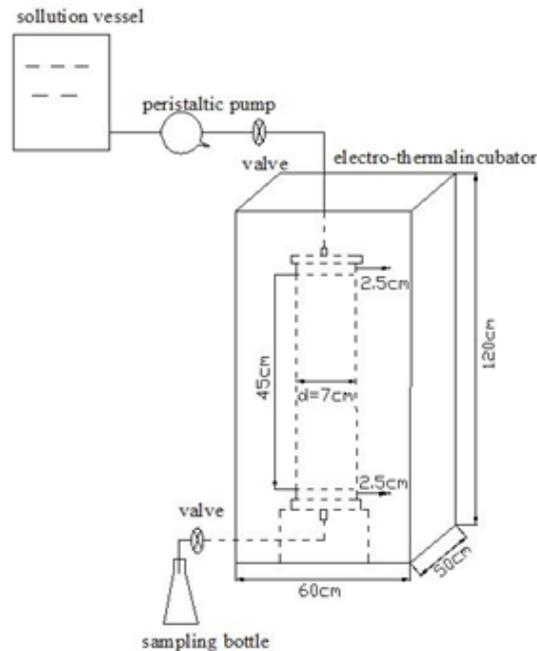

Fig.2 experimental device

Improved three-dimensional fluorescence regional integral

Traditional Fluorescence regional integral method (FRI) divides the three dimensional fluorescence spectrum into different areas. And percent of a given area can be got by Regional integral value multiplying reciprocal value of different areas. This can characterize the change of fluorescent material quantitatively. In this study we combined Analytic Hierarchy Process(AHP) with FRI. Weight calculation calculated by AHP instead of simple reciprocal value of different areas improves makes it more objective to regional integral.

Traditional three-dimensional fluorescence regional integral

Generally, according to the excitation wavelength (EX) and the emission wavelength (EM), Three-dimensional fluorescence spectra of dissolved organic matter(DOM) in groundwater can be roughly divided into five regions (Fig.3). Area I: EX<250, EM<330, tyrosine; area II: EX <250,330 <EM<380, tryptophan; area III: EX<250, EM>380, fulvic acid; area IV: EX> 250, EM <380, soluble microbial metabolites; area V: EX> 250, EM> 380, humic acid. Because of the fluorescent material characteristics of same area are similar, total fluorescence of different regions, $\Phi_{i,n}$ can be calculated as flowing,

$$\Phi_{i,n} = MF_i * \int I(ex/em)d\ (\lambda ex)\ d\ (\lambda em) \qquad (1)$$

Where MF_i represents multiplication factor of each region, equaling to the reciprocal of responding region projection square meter. $I(\lambda ex, \lambda em)$ represents fluorescence intensity of each region, λ_{ex} and λ_{ex} stands excitation wavelength and emission wavelength.
For another, proportion of fluorescent integral, Pi,n, can be calculated as flowing,

$$P_{i,n} = \Phi_{i,n}/\Phi_{T,n} \qquad (2)$$

Among them, $\Phi_{T,n} = \sum_{i=1}^{5} \Phi_{i,n}$ (3)

Where $\Phi_{i,n}$ stands total fluorescence of each area, $\Phi_{T,n}$ stands total fluorescence of five areas.
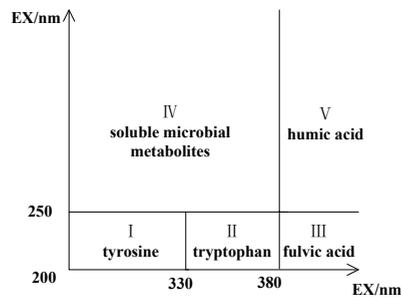

Fig.3 *regional division of three-dimensional fluorescence spectrum*

Traditional regional integral calculation is simple and easy to realize, however, the accuracy is not high. This paper introduces the analytic hierarchy process (AHP) to the regional integration, calculating the five regions corresponding weight value replacing of MFi.

Now, this paper states detailed steps using improved regional integral, with 3DEEM of 70.9mg/L humic acid as an example.

We formed a decision matrix named "A" according to the degree of importance about factors in target evaluation area:

$$A = \begin{bmatrix} 0 & -1 & -1 & -1 & -1 \\ 1 & 0 & 1 & 1 & -1 \\ 1 & -1 & 0 & 1 & -1 \\ 1 & -1 & -1 & 0 & -1 \\ 1 & 1 & 1 & 1 & 0 \end{bmatrix}$$

Where a_{ij}=1 that "i" is more import than "j";a_{ij}=0 that "i" is as import as "j"; a_{ij}=-1 that "i" is less import than "j".

Where, $r_{ij} = \dfrac{1}{n}\sum_{k=1}^{n} (a_{ik} - a_{jk}) = \dfrac{1}{n}\sum_{k=1}^{n} (a_{ik} + a_{kj})$ (4)

R is the optimal transfer matrix of A:

D is the judgment matrix of R:

$$D = \begin{bmatrix} 1.00 & 0.30 & 0.45 & 0.67 & 0.20 \\ 3.32 & 1.00 & 1.49 & 2.23 & 0.67 \\ 2.23 & 0.67 & 1.00 & 1.49 & 0.45 \\ 1.49 & 0.45 & 0.67 & 1.00 & 0.30 \\ 4.95 & 1.49 & 2.23 & 3.32 & 1.00 \end{bmatrix}$$

Where $d_{ij} = \exp(r_{ij})$ (5)

The theoretical weight can be expressed as W=[$W_1,W_2,W_3,W_4...W_n$]^T, we calculate the "w_i" of five areas: W=[0.08,0.26,0.17,0.11,0.38]

We integrated aiming to 3DEEM of humic acid(fig.1) . Finally, we got the regional integral proportion of all areas, and they are shown in table 1.

Table 1 3DEEM regional integrals of Humic acid concentrate of 70.9 mg/L

Stoste of humic acid	Integral value	Theoretical weight	Actual integral value	Proportion
I	0.18	0.08	0.0144	0.002
II	0.77	0.26	0.2002	0.014
III	9.17	0.17	1.5589	0.107
IV	1.82	0.11	0.2002	0.014
V	33.25	0.38	12.635	0.863

Results and Discussion

Characteristics of Three-dimensional Fluorescence Spectra

Figure 4 shows you the change of the 3DEEM of leaching solution of humic acid in the marl rock. As is shown in Figure 8, there are two peaks at 0h, which stand tryptophan (region II, EM/EX = 342/225) and dissolved microbial metabolites (region IV, EM/EX = 345/280). Concludly, they are organic matters dissolved by marl rock. There are two peaks at 192 h, namely dissolved microbial metabolites (regionIV, EM/EX=342/278) and humic acid (region V, EM/EX=390/321) respectively. At 192h, the concentration of humic acid in the leaching solution reached to the maximum.
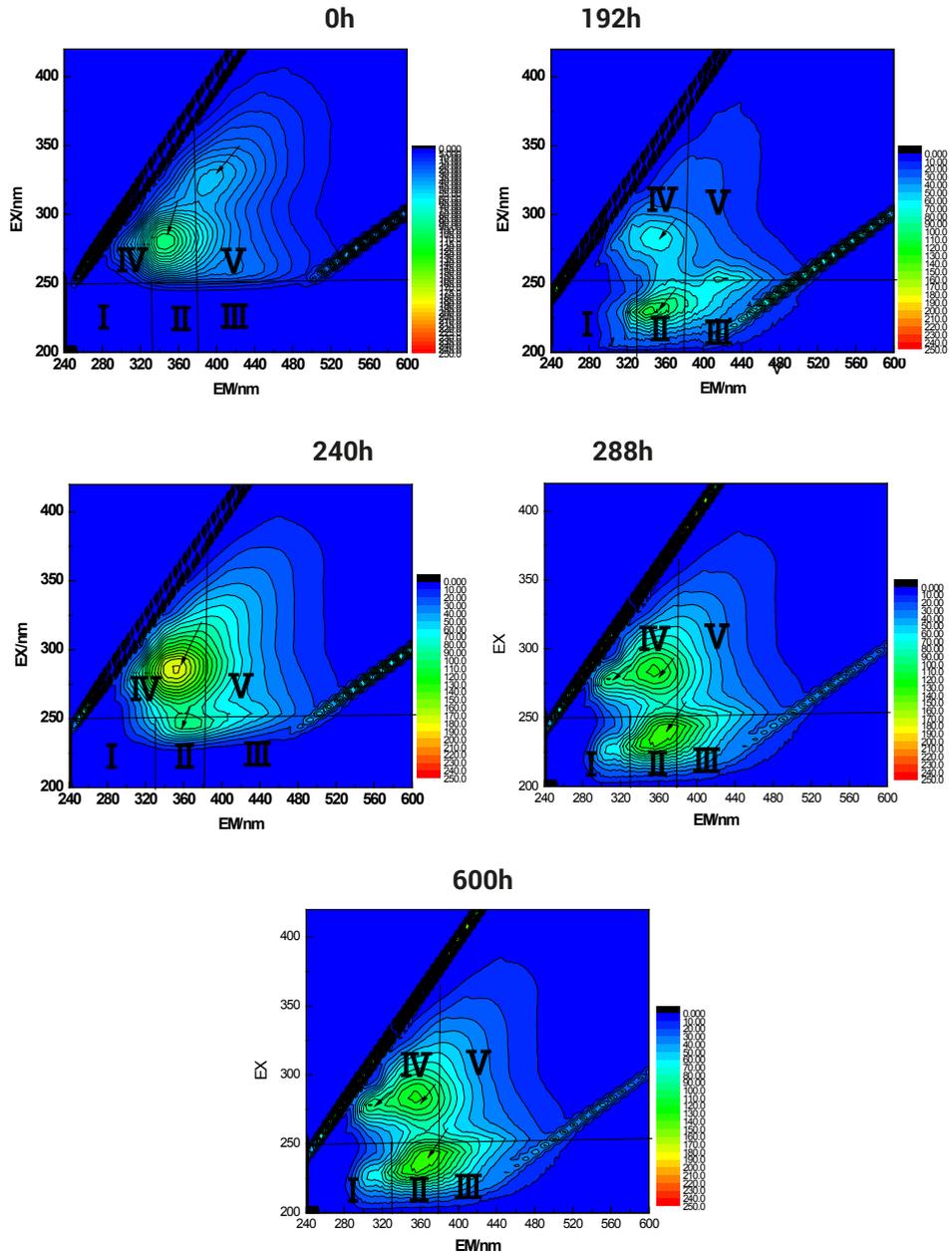
0h

192h

240h

288h

600h

Fig.4 3DEEM of leached liquid from marl rock

At 240h, there are two fluorescence peaks. They are dissolved microbial metabolites (region IV, EM/EX=349/283) and tryptophan (region II, EM/EX=362/244).The third stage(192-240 h),with the continuous decreasing of humic acid concentration in leaching

solution (Figure 5), the peak value of region V disappear gradually, most of the humic acid is adsorbed by marl rock. At 288 h, there is only one peak in region II (EM/EX =370/242), at the same time, there appear two fluorescence peaks in area IV including IV_1(EM/EX = 354/281) and IV_2 (EM/EX = 305/275). Peak IV_2 is a new fluorescence peak compared to previous two stages. The reason is that a new peak appears when adsorbed humic acid by marl rock is degraded into dissolved microbial metabolites.

Characteristics of improved regional integral

We calculated the integral of three dimensional fluorescence spectra of leaching liquid from critical time, then we drew the regional integral columnar of three dimensional fluorescence spectra, and the figure6 show you that.
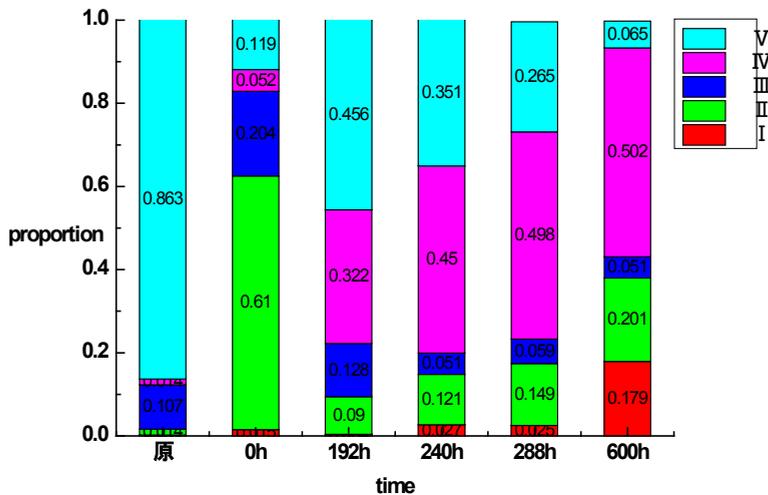

Fig.5 *improved regional integrals of 3DEEM*

From figure 8, we know that material leached from marlstone distribute in region II and region III. At 0h, the proportion of region II is 0.61 and that of III is 0.204.When at 192h, the proportion of region V reaches 0.61 getting to the maximum. With the time going, the proportion of region V decreases. From 192h to 600h, the proportion let up from 0.456 to 0.065. However, the proportion of IV increases from 0.322 to 0.502. we conclude that humic acid has been transformed in the marlstone. And this transform mainly is degradation. Humic acid was degraded into soluble metabolic products by microorganism. Therfore, there appears a new fluorescence peak in IV zone, and the integral proportion increases.

Conclusion

(1) The three-dimensional fluorescence of humic acid from malm show that there appeas a new fluorescence peak IV_2 at 288 h coming along with peak V disappearing at 240h.

(2) The improved three-dimensional fluorescence regional integral show that from 192h to 600h, the proportion of region V decreases from 0.456 to 0.065.At the same time, the proportion of region V increases from 0.372 to 0.502, when there is mainly no change of other regions. It is obvious that humic acid has been degraded into soluble metabolic products by microorganism. Therfore, there appears a new fluorescence peak in IV zone, and the integral proportion increases.