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# A study of weathered coal spectroscopic properties

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**Abstract**

Current coal industry causes significant environmental pollution and the most air pollution deaths in the world, making the development of new eco-friendly applications one of the top priorities. Coal contains up to 50 % humic substances (HS), the majority of which is humic acid (HA). HA is well known for its beneficial properties and thus compounds extracted from coal can be used to develop new applications. To address this issue, we assessed structural composition of coal HS by measuring their spectroscopic properties. As the result, obtained spectra can be used to identify information about the molecules and thus allowing describing the composition of HS. The purpose of this study was to identify HS properties of weathered coal in regards to finding new uses for this otherwise neglected natural resource. The results show that weathered coal contains relatively high oxygen content and indicate transformations of O-containing functional groups. Weathered coal has high amount of bioactive molecules as well as condensed aromatics. The major coal forming compounds are acridine, anthracene, perylene, tetracene and naphthalene and it does not depend upon where the study site is located.


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## 1. Introduction

Coal has a variety of important uses worldwide, but the most significant uses are in the generation of electricity,

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steal production, cement manufacturing and as a liquid fuel [1, 2]. However, the current coal industry and mining itself has a significant downside, which is a high pollution [3, 4]. The coal production causes emissions of carbon dioxide and monoxide, sulphur dioxide, nitrogen oxide, hydrocarbons, many toxic heavy metals etc. Accordingly, the coal industry leads to Climate Change; causes air pollution and smog [5–7]. The use of coal also causes serious health issues and increases the mortality rate [8]. Placing limits on coal use can reduce the effects of Climate Change and human healthcare. Moreover, EU energy roadmap 2050 defines mid-term transformation of carbon intensive sectors (coal) with gas [9–11].

Coal is formed in coalification when peat is altered physically and chemically due to the impact of pressure, heat, compaction and bacterial decay. The pressure compacts the peat layer and squeezes out the remaining water. Continuous pressure with the addition of heat and time causes the breakdown and alteration of hydrocarbon compounds in peat. The alteration products such as methane are typically expelled from the deposit, and deposit becomes more and more carbon-rich as the other elements disperse. The stages of transformation proceed from plant debris through peat, lignite, sub-bituminous coal, bituminous coal, anthracite coal, to graphite [12].

Coal contains up to 50 % humic substances (HS), the most of which is humic acid (HA), smaller amount of HS consist of fulvic acid (FA). HS are alkali-soluble fraction and are significant part of natural organic matter independent of its source. Thus HS, extracted from coal, can be used to develop new applications. HS do not belong to any specific chemical category and they cannot be defined in unambiguous structural or functional terms [13].

In naturally oxidized coal HA content usually is high because of high amount of oxygenated functional groups such as –COOH, –CO, –CO-O-C-, –OH and others in HS composition. To address this issue, we assessed structural composition of weathered coal HS by measuring their spectroscopic properties, because each molecule of HS provides unique spectra. As the result, these spectra can be used to identify and quantify a variety of HS forming compounds [14].

Weathering substantially alters coal properties, such as calorific value, beneficiation, coking, liquefaction, and gasification characteristics. Coal weathering also changes experimental results, in regards to a non-weathered coal, thus has significant implications with respect to fundamental research on the structure and properties of coal [15, 16]. The major contributor to weathering is the exposure of coal to the oxygen in air and their subsequent reaction. The reaction of the coal with oxygen results in oxidation of coal organic constituents and leads to an increase in the oxygen content and a decrease in the atomic hydrogen/carbon (H/C) ratio of the coal [17]. In the early stages of coal oxidation, as transient intermediates, are forming peroxides [18, 19], the decomposition of these compounds leads to the formation of oxygen-containing functional groups [20]. The weathering of coal inorganic constituents, apart from the iron bearing pyrite that is readily air-oxidized, does not have any apparent effect on the change of coal properties [21]. Pyrite is oxidized to iron sulphates that are transformed into iron oxyhydroxide [22]. Although oxidation of organic and inorganic constituents takes place simultaneously, they must be addressed as separate processes [15, 19].

The present study aims to describe HS of weathered coal samples that were taken from 5 common coal production areas in China to compare their characteristics using a variety of spectroscopic methods. The aim of this research was to characterize properties of HS of weathered coal by means of spectroscopic measurements to find potentially new uses for this otherwise neglected natural resource.

## 2. Experimental

### *2.1. Source and extraction of weathered coal humic substances*

Weathered coal samples from mostly northern Chinese region were used as a source for HS material. 9 different weathered coal samples were collected in 5 of the most common coal production areas of China: 1) Inner Mongolia (Wuhai); 2) Shanxi (Shanyin, Jiaokou, Huozhou, Lingshi, Zuoquan); 3) Heilongjiang (Hegang); 4) Xinjiang (Hami); 5) Yunnan (Zhaotong). The HS solution was prepared by alkali extraction procedure of original weathered coal samples: 100 g of original weathered coal was mixed with 2000 mL of alkaline solution (1 M KOH) and shaken for 24 h. Any lignin residues were removed by triple filtering of the solution. The HA was collected by acidic extraction procedure of HS solution. The HS containing supernatant was acidified with concentrated HCl (36 %, w/w, 11.6 M) to pH around 2 in order to precipitate HA. The precipitated HA was rinsed with distilled water to pH around 7. Spectroscopic features of FA were measured using the acidic supernatant left after HA removal.