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DIFFUSE REFLECTANCE SPECTRA OF COALS IN THE UV-VISIBLE AND NEAR- IR REGIONS

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ABSTRACT

Chemical leaching of sub-bituminous coal with inorganic and organic leachants has been monitored by the UV-Visible and Near-IR spectra with the diffuse reflectance method. The shape and intensity of the observed absorption bands changed with leaching, reflecting the solubilization of the aromatic molecules and the degree of the intermolecular interaction between organic and inorganic phases. The absorption maximum of benzene-oxygen system was found between 235-270 nm and is showing a red shift with leaching. The characteristic naphthalene ring systems (220 & 280 nm) are masked by the absorption regions of monoaromatic rings; indicating the content of naphthalenoid hydrocarbon is very low. The bands observed in the visible region (450nm) is attributed to SO_2 in the sample and with leaching this band is showing a red shift. The weak band at the 680 nm is attributed to the $\Pi-\Pi^*$ electronic transitions of the polynuclear aromatic hydrocarbons which shows red shift with leaching.

Keywords: diffuse reflectance spectrum; leaching; solubilization.

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1. Introduction

Over the past 15 years, diffuse reflectance spectrometry has been applied to the mid-IR spectra of coal and carbons; this method gives very sharp and reliable IR bands. Osamu Ito et al (1992, 1993) reported that the broad absorption bands observed in the region between 4000- 6000 cm^{-1} by this technique are attributable to electronic transitions and not to the effect of scattering. For the UV-visible and near -IR regions above 6000 cm^{-1} , however, diffuse reflectance spectrometry characterization of coal samples are scarce, even though this method has widely applied to solid organic and inorganic compounds. The UV-VIS-NIR spectra give valuable information about the structure of the molecule because the absorption of UV and visible light involves promotion of electron in σ and Π orbitals from ground state to higher energy state. In this paper, it is reported that the absorption spectra in the UV-Visible and near regions, as measured by diffuse reflectance, change with coal rank and the chemical leaching, and time of leaching.

2. Materials and methods

Sub-bituminous coal sample from Godavari coal fields are brought to the lab as it is and kept in open for 3 months. The sample is well powdered and treated with EDTA for 24 hrs at 27°C. The precipitate is removed and residue is washed with water and filtered. The sample is treated with acetic acid for period of 1 day, 2days and 3 days(GEA1 -GEA3). After the specified contact time sample is washed with distilled water, filtered and dried at a temperature of 80°C and allowed to cool slowly in a dessicator. Virgin sample is treated with dilute nitric acid for 24 hrs and followed by concentrated HF of concentration 40%, 30%, 20% and 10% for an hour (GNF1 -GNF4). The residue is separated and dried as discussed above.

Diffuse reflectance a spectrum of coals in the UV-Visible and near-IR regions is carried out using a Cary 500 spectrometer equipped with a Praying Mantis diffuse reflectance accessory DRA.

3. Result and Discussion

The electronic absorption spectra of sub-bituminous and bituminous coal are measured by the diffuse reflectance spectrometry in the UV-Visible and near IR regions (200-800 nm). In the measured spectra (Figure 1 and Figure 2) the σ band (260-270 nm) has defined structure. This absorption increases with leaching with strong absorption for HF leached samples. The general shape of the spectrum is characteristic for hydrocarbons with a single benzene ring. The presence of

naphthalenoid hydrocarbons will show up in the spectrum and can be judged qualitatively only in the 320 nm regions, where benzoid hydrocarbon give practically no absorption of UV radiation. The two principal bands that are characteristic for the naphthalene system (220 & 280 nm) are masked by the absorption regions of monoaromatic rings; this indicates that the content of naphthalenoid hydrocarbon is very low (Siryuk et al 1979, Satoshi Hashimoto 1989). The absorption maximum of benzene-oxygen (1/1) system was found between 235-270 nm. This is due to the benzene-oxygen charge transfer band and is showing a red shift with leaching, which is more prominent with HF leaching (20% and 40%) and pretreated acetic acid sample (GEA3).

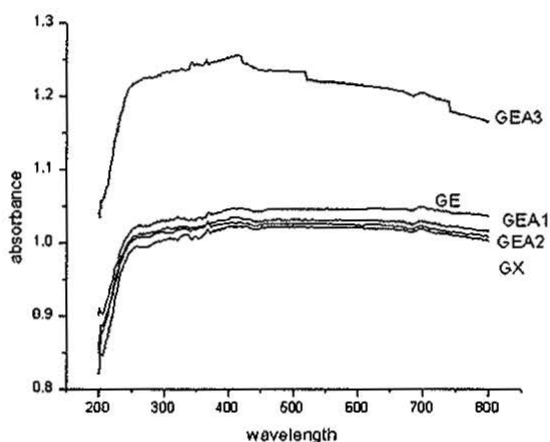


Figure 1 - UV-Visible-NIR spectrum of acetic acid leached sample

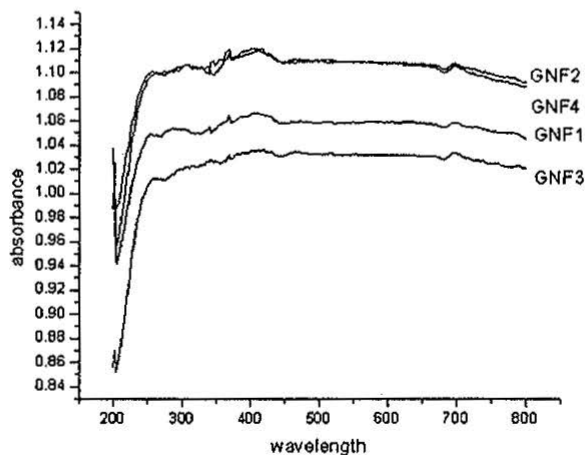


Figure 2 - UV-Visible -NIR spectrum of HF leached sample

Olajire et al (2007) reported prominent peaks at 400 nm (Soret band) and at wavelength ranges of 535-550 nm (β band) and 565-600 nm (α band) for the Nigerian coal minerals. In present study, sample shows peaks at 400 nm which increase with organic acid leaching and is maximum for EDTA and acetic acid leaching. At 409, 450, 503, 518 nm there is a correlation between volatile matter and diffuse reflectivity. Frederick J et al (1983) reported two maxima at 620 and 577 nm in New Mexican coals. They designated the most intense band at 620 nm to the color of vitrinite in transmission. The absorption of the particular maxima increases with Organic acid leaching as well as HF leaching with maximum absorption for sample treated with acetic acid and EDTA for three days (GEA3).

The sample is almost transparent in the region 475 nm to 650 nm and near IR region. There are small distinct absorption peaks in the UV region and 680 nm. The intensity of the broad absorption in the visible (680 nm) and near IR region (759 nm) are attributable to the Π - Π^* electronic transitions of the poly nuclear aromatic hydrocarbons, increases with the rank of coal (Osamu Ito 1992). The intensity of this band increases with chemical leaching is an indication of electronic transitions with leaching.

There are weak bands observed in the visible region (450 nm) is due to the presence of SO_2 in the sample. This band is showing a strong red shift with HF leaching as well as acetic acid leaching. Red shift is observed for pretreated sample leached with acetic acid for 3 days. Leaching increases electron releasing group of the sample which in turn increases both the wavelength and intensity of the secondary absorption band.

4. Conclusion

Chemical leaching processes of sub-bituminous coal have been monitored by the UV-Visible and near IR spectra measured with diffuse reflectance method. The shape and intensity of the observed absorption bands changed with leaching of the sample, reflecting the degree of the intermolecular interaction. In the measured spectra, the δ band (260- 270 nm) has defined structure. This absorption increases with leaching and is highest for GAE sample than GNF sample. This part of the spectrum is characteristic for hydrocarbons with single benzene ring. The characteristic bands of naphthalene ring system (220 and 280 nm) are masked by the absorption regions of the monoaromatic rings; indicating the content of naphthalenoid is very low. The band in the region 680 nm is attributed to the Π - Π^* electronic transitions of the polynuclear aromatic hydrocarbons. Intensity of this band increases with chemical leaching is an indication of increase of electronic transitions with leaching. The weak bands observed in the visible region (450 nm) are due to the presence of

SO₂ in the sample and is showing a red shift with HF and acetic acid leaching. The electron releasing groups increases both the wavelength and intensity of the secondary absorption band.

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