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CHEMICAL LEACHING OF AN INDIAN BITUMINOUS COAL AND CHARACTERIZATION OF THE PRODUCTS BY SPECTROSCOPIC TECHNIQUES

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ABSTRACT

Fourier transform infrared (FTIR) spectra of high volatile bituminous coal as well as their insoluble organic matter, obtained by chemical leaching with HF, EDTA and acid mixture (HF + HCl and HF + HNO_3) were recorded between 500 and 4000 cm^{-1}. UV-Visible-NIR spectroscopy was used to study the sample and its leached products in the 200-800 nm wavelength region. Oxygen containing structures were observed in the 1800-1000 cm^{-1} zone, aliphatic hydrogen in the 2920-2800 cm^{-1} zone, aromatic out-of-plane structure in the 900-670 cm^{-1} zone. A great abundance of C=C structure was noticed at 1600 cm^{-1} region, while clay and silicate minerals were identified in the 540 cm^{-1} and 1030 cm^{-1} region. With chemical leaching silicate bands showed a decrease in intensity and were least for EDTA and HF leached samples. The UV-Visible -NIR spectrum showed absorption maximum at 235-270 nm and was shown a red shift with leaching. The Π-Π^* electronic transitions of the poly-nuclear aromatic hydrocarbons was responsible for the absorption at 680 nm. The weak bands observed in the visible region (400-500 nm) were due to the presence of SO_2 in the sample and decreased with chemical leaching. It was evident from the results that amongst the leachants used, hydrofluoric acid and acid mixture had significant effect in removing the mineral matter and oxygenated functional groups.

Key words: Chemical leaching, FTIR, Sub bituminous coal, Inorganic minerals.

INTRODUCTION

Coal is chemically and physically a complex and heterogeneous material, consisting of organic and inorganic constituents. The acceptance of coal for a particular process in industry depends critically on both components. The organic structure of coal consists of heterogeneous aromatic structures, with aromaticity increasing from low rank to high rank coals. The organic part also contains sulphur, oxygen and nitrogen functional groups. Minerals to a certain degree are required to bring a catalytic effect in gasification and liquefaction. Presence of minerals in excess will pollute water, air and soil. Concerted efforts

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are needed to reduce 'ash forming' inorganic elements and to develop clean methods of using coal. Demineralization prior to utilization is an effective way to ensure an environmental friendly fuel[1-3]. Fossil fuels, particularly derived from coal have been investigated from different angles. Coal minerals are objectionable due to the process involved as well as due to the gamut of environmental problems. There are many techniques for demineralization of coal[1-8]. Of this, many are tedious, obnoxious and costly. New techniques are being viewed for removal of ash from inorganic elements from coal with EDTA[1] and acid mixtures[2,8].

Various analytical procedures have been used for mineral identification[1-6]. Fourier Transform Infrared (FTIR) spectroscopy is a widely used analytical technique for determining the different functional groups of a coal structure. This method helps to reveal carbo-hydrogenated structure (aromatic & aliphatic) and hetero atomic functions (mainly oxygenated) as well as to detect the presence of minerals is one of the powerful technique for coal characterization[1,2,6]. The present paper demonstrates the use of Fourier transform infrared spectroscopy and chemical analysis to evaluate the ability of some leachants in demineralizing the coal under study.

EXPERIMENTAL

Materials and methods

Preparation of coal sample

High volatile bituminous coal samples were randomly handpicked from Korba coal fields, crushed and ground in a pestle and mortar. The definite sized coal sample was dried in an oven at 80°C for an hour and cooled in a dessicator. 10 g of well powdered sample under study was treated separately with EDTA (0.1N), HF (40%), and Acid mixture (35% HCl + 40% HF). The coal sample was treated for a two stage leaching of nitric acid and hydrofluoric acid (40%). The specified amount of sample was slurried in 50 mL of extracting solution in a beaker and stirred continuously for 1 hour at a temperature of 30°C. The precipitate was removed and the slurry was filtered using filter paper. The residual coal was washed exhaustively with copious amount of distilled water and dried in an oven at 80°C and allowed to cool slowly in a dessicator.

FTIR Analysis

For analysis, about 10 g of the sample was crushed to fine powder of about 5 µm in size. 2 mg of the powdered sample was then mixed with KBr in the ratio 1:200. The grinding time and the sample to KBr ratio were kept constant for all the samples under study to ensure uniformity. The mixture was then placed in a 13 mm diameter die cavity and pressed under high pressure. The spectra were recorded by using Shimadzu FTIR-8400 spectrometer in the region 4000-400 cm^{-1}. This spectrometer has the resolution of 4 cm^{-1}. To obtain consistent records the FT-IR spectra was recorded in 20 scan mode. The FTIR spectrum of virgin coal and residual coal after chemical leaching was shown in Fig. 1. UV-Visible-NIR spectra of the powdered coal samples were obtained using the standard sampling cup supplied with the Praying Mantis accessory. The Praying Mantis DRA was installed into the Cary 500 spectrophotometer and aligned. The wavelength range was set to scan from 800 to 200 nm and was recorded in Fig. 2.

RESULTS AND DISCUSSION

Spectral analysis of chemical leached sample

The identification of the most prominent bands of FTIR spectrum of bituminous coal and its insoluble material is shown in Table 1. Intense bands are observed at 540 cm^{-1} (Fig. 1), resulting from clay and silicate minerals (1). Bands at 1030-1090 cm^{-1} is also arises due to silicate minerals (2). These bands decrease its intensity with leaching. Spectral graph (Fig. 1) showed that all the samples had more or less similar broad characteristic absorption bands. It was observed that absorption peaks were changed and it was an indication of the effect of chemical treatment on the structure of coal.

Table 1: Band assignment of the most prominent peaks in the FTIR spectra of coal and its leached products

Bands (cm^{-1})	Assignment
540	Clay and silicate minerals
669	-
1032-1090	Silicate minerals
1600	C=C aromatic stretching
2851	Aliphatic symmetric $-CH_2$ stretching
2920	Aliphatic asymmetric $-CH_2$ stretching
3618-3620	Clay minerals
3696-3700	Kaolinite and illite minerals

Fig. 1 showed the FTIR spectrum of samples treated with EDTA (KE), HF (KHF), acid mixture (KM) and two stage leaching (KNF). FTIR spectrum of untreated sample (KX) was included for comparison purpose. The spectrum showed significant changes in the intensity of bands arising from the inorganic matter. The bands at 1031 cm^{-1}, 1010 cm^{-1} and 466 cm^{-1} were attributed to silicates and kaolinite. These bands decreased its intensity when treated with HF and EDTA. This was reported by some of the researchers in the case of high-volatile bituminous coal[3-9].

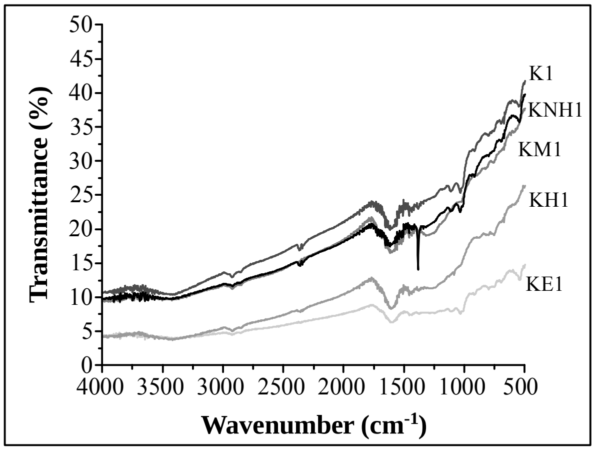

Fig. 1: FTIR analysis of chemical leached coal samples

A similar result was reported by Zhiheng and Karen in the UK bituminous coal[10]. They reported extensive removal of large of kaolinite and bassanite with 3.51 M HF treatment. In the present study, the maximum removal of silicate is taken place with 40% HF and acid mix treatment [40% HF + 35% HCl]. This was evident from the spectral graph (KHF) and (KM) that there was absence of mineral band. The weak band in the region 912 cm^{-1} and 756 cm^{-1} was due to aromatic –CH out of plane structure[1,2]. This bands decreases its intensity when treated with HF and EDTA. The band at 756 cm^{-1} was shifted to lower wave number. From spectral graph it was observed that the EDTA treatment could substantially remove the inorganic mineral phase. The intensity of bands at 1097 cm^{-1}, 1031, 1010 and 466 cm^{-1} was reduced considerably with EDTA treatment. The effectivness of EDTA as a leachant for silcate mineral was reported by Manoj et al.[1] in the case of sub-bituminoucoals. Aliphatic bands (3000-2800 cm^{-1}) and oxygenated functional groups (1800-1000 cm^{-1}) showed lower intensities in the non extractable material compared to raw coal. Very strong peak at 1600 cm^{-1} is attributed either to C=O or C=C aromatic ring stretching. Bituminous coal being moderately ranked coal, this band is attributed to C=C structure.[10] The band at 669 cm^{-1} was due to aromatic out-of-plane C-H deformations. The band due to silicates also might appear in the same range. This band could be attributed to aromatic out of plane C-H deformation rather than due to mineral matter. It was found that the mineral band totally disappeared when treated with HF and acid mixture (HF + HCl). Aliphatic bands (3000-2800 cm^{-1}) and oxygenated functional groups (1800 cm^{-1} -1000 cm^{-1}) show lower intensities in the chemical leached products compared to virgin coal, thus revealing the effectivness of the extraction of these bands with chemcical leaching especially with EDTA (KE) acid mix of HCl and HF (KM) and hydrofluoric acid (KH). The FTIR results were supported by the UV-Visible-NIR study on the sample (Fig. 2).

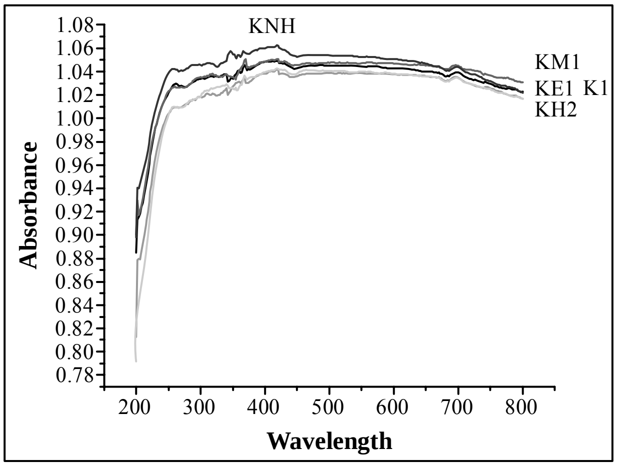

Fig. 2: UV-Vis-NIR analysis of chemical leached coal samples

The electronic absorption spectra of bituminous coal and its chemical leached products are measured by UV-Visible–NIR spectroscopy in the 200-800 nm region. In the spectra, the σ band (260-270 nm) has defined structure. This absorption increases with leaching and is maximum for sample treated with nitric acid and HF (KNF) followed by hydrochloric acid and HF leaching (KM). This is due to the increase of electronic activity with leaching. The presence of napthalenoid hydrocarbons can be judjed qualitatively in the 320-340 nm regions, 220 nm and 280 nm. These principal bands that are characteristic for the napthalene system (220 and 280 nm) are showing small absorption spikes indicating the presence of napthalenoid hydrocarbon in the bituminous coal. This is normally present in mature coals of medium to higher ranks. This particular band is showing a redshift with leaching (7). The absorption maximum of benezene-oxygen (1/1) was found between 240-270 nm. This is due to benzene-oxygen charge transfer band and is also showing redshift with leaching, which is more prominent with nitric acid and HF leached sample. This shows that leaching increased electronic activity in the ring. In the present study, sample shows spikes between 400-500 nm, which increases with leaching and is maximum for sample leached with nitic acid and HF (KNF).

The spectrum is transparent in the region 500-675 nm. Small but distinct absorption spikes are present near ~680 nm and ~750 nm. This band is attributed to the Π-Π* electronic transitions of polynuclear aromatic hydrocarbons, which are observed in medium to higher rank coals. Intensity of this band increases with chemical leaching and is maximum when the sample is leached with HCl and HF (KM).

CONCLUSION

Oxygen containing structures were observed in the 1800-1000 cm^{-1} zone, aliphatic hydrogen in the 2920-2800 cm^{-1} zone, aromatic out-of-plane structure in the 900-670 cm^{-1} zone. A great abundance of C=C structure was noticed at 1600 cm^{-1} region, while clay and silicate minerals were identified in the 540 cm^{-1} and 1030 cm^{-1} region. With chemical leaching, silicate bands showed a decrease in intensity and were least for EDTA and HF leached samples. The UV-Visible-NIR spectrum showed absorption maximum at 235-270 nm and was shown a red shift with leaching. The Π-Π* electronic transitions of the poly-nuclear aromatic hydrocarbons was responsible for the absorption at 680 nm. The weak bands observed in the visible region (400-500 nm) were due to the presence of SO_2 in the sample and decreased with chemical leaching. It was evident from the results that amongst the leachants used, hydrofluoric acid and acid mixture had significant effect in removing the mineral matter and oxygenated functional groups.

REFERENCES

1. B. Manoj, A. G. Kunjomana and K. A. Chandrsekharan, Chemical Leaching of Low Rank Coal and its Characterization using SEM/EDAX and FTIR, J. Minerals & Material Characterization and Engg., **8(10)**, 821-832 (2009).
2. B. Manoj and P. Narayanan, Study of Changes to the Organic Functional Groups of a High Volatile Bituminous Coal During Organic Acid Treatment Process by FTIR Spectroscopy, J. Minerals & Material Characterization and Engg., **8(10)**, 39-43 (2013).
3. F. Rubiera, A. Arenillas and C. Pevida, Coal Structure and Reactivity Changes Induced by Chemical Demineralization, Fuel Processing Technology, **79**, 273-279 (2000).
4. N. A. Őztas and Y. Yürüm, Pyrolysis of Turkish Zonguldak Bituminous Coal, Part 1 Effect of Mineral Matter, Fuel., **79**, 1221-1227 (2000).

5. B. Manoj, A. G. Kunjomana, Chemical Leaching of an Indian Bituminous Coal and Characterization of the Products by Vibrational Spectroscopic Techniques, Int. J. Minerals, Metallurgy and Materials, **19(4)**, 279-283 (2012).

6. B. Manoj and A. G. Kunjomana, Analytical Study of Two Differently Ranked Coals using UV-Vis-NIR Spectroscopy, J. Minerals & Material Characterization and Engg., **10(10)**, 905-911 (2011).

7. B. Manoj, Chemical Demineralization of High Volatile Indian Bituminous Coal by Carboxylic Acid and Characterization of the Products by SEM/EDS, J. Environ. Res. Development, **6(3A)**, 653-659 (2012).

8. F. Rubiera, A. Arenillas and J. J. Arias, Combustion Behaviour of Ultra Clean Coal Obtained by Chemical Demineralization, Fuel, **82**, 2145-2151 (2003).

9. M. Sobkowiak and P. C. Painter, Determination of the Aliphatic and Aromatic CH contents of Coals by FT-i.r.: Studies of Coal Extracts, Fuel., **71**, 1105-1125 (1992).

10. W. Zhiheng and M. Karen, Steel, Demineralization of a UK Bituminous Coal using HF and Ferric Ions, Fuel., **86**, 2194-220 (2007).

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