

## Investigation of Surface Acidity of Coal by Aqueous Potentiometric Titration

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**Summary:** Surface acidic functional groups in virgin and variously extracted coal samples were determined by aqueous potentiometric acid-base titration employing KOH as a titrant. The various extractants used in this study were H<sub>2</sub>O<sub>2</sub>, HCl, KOH and distilled water. The obtained titration curve of virgin coal showed inflections at pH 4-5, 6-7 and 8-11, which indicate that the coal surface may contain carboxylic, carbonyl, phenolic and other weak acidic groups like enols and C-H. The titration curves of treated coal samples showed a normal break at pH 4-10 range and small inflections at pH 10-11, which did not show a similarity to the inflection of carboxylic acid groups but may be due to the existence of acid groups such as CO<sub>2</sub>, Phenols, enols and C-H. The aforementioned extractants oxidized (by increasing the peak intensity at 1310-1250 cm<sup>-1</sup> regions due to stretching vibrations of C-O-C in ether and ester) the coal sample and were verified by FT-IR spectral analysis.

### Introduction

Coal, petroleum as well as their industrial derivatives, such as road bitumens and cokes, may undergo major degradation when exposed to oxidation and can cause acidic functionalities such as carboxylic (–COOH), carbonyl (C=O), phenolic (–OH) and keto-enol. These acidic functional groups have been determined by various researchers. Redlich *et al.*, [1] determined acidities of model compounds, coal and coal derived products by non-aqueous potentiometry. Singh *et al.*, [2] studied models for the prediction of total and carboxyl acidity of low rank coal. Allardice *et al.*, [3] determined the acid distribution and total acidity of low rank coal and coal-derived materials by an improved barium exchange technique. Chang *et al.*, [4] studied the effect of air-oxidation on the coal liquefaction. Ahmed *et al.*, [5] characterized an Egyptian coal by Mossbauer and FTIR spectroscopy. D'Alessio *et al.*, [6] studied the structural changes of Sardinian and South African coal under progressive heating in vacuum by FT-IR. Murata *et al.*, [7] studied the distribution of oxygen groups such as alcohols, phenols, carboxyl, carbonyl and ethers in four brown coals (Australian Yallourn, Indonesian South Banko and Adaro and US Beulah Zap) by chemical analysis and <sup>13</sup>C NMR measurement. Blaine *et al.*, [8] found hydroperoxide, carboxylic acid, aldehydes, ketenes, esters and alcohols during autoxidation of lubrication oil. They used iodometric and potentiometric acid-

base titration along with <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. Tamarkina *et al.*, [9] studied reactivity and structural modification of coal in nitric acid-acetic anhydride mixture. Khan *et al.*, [10] carbonized walnut shells and then determined the surface acidity of charcoal by selective neutralization technique. Merce *et al.*, [11] studied model compounds of humic acid and oxovanadium cation by potentiometric titration and EPR spectroscopy. Saeed *et al.*, [12] determined the surface acidity of coal by non-aqueous potentiometric titration.

The present study deals with the investigation of acidic functional groups on the surface of virgin and variously extracted coal samples using potentiometric titration method in aqueous medium.

### Results and Discussion

Table 1 shows the approximate analysis, total sulfur and chlorine of virgin coal sample. The results indicated that the moisture contents and fixed carbon are low, while the volatile matter, ash, sulfur and chlorine are high, which indicate that the coal is of low rank and may be considered between peat and lignite. Determination of ash, sulfur and chlorine is very important because they not only cause deleterious effects on coal utilization processes like liquefaction, gasification and deactivate catalyst, but

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Table-1: Determination of Proximate and elemental analysis of virgin coal [12].

Sample contents	Percentage (%)
Moisture	5.13
Volatile * Matter	33.98
Ash *	22.67
Fixed carbon	30.22
Total sulfur	5.60
Chlorine	0.19

\*dmf basis

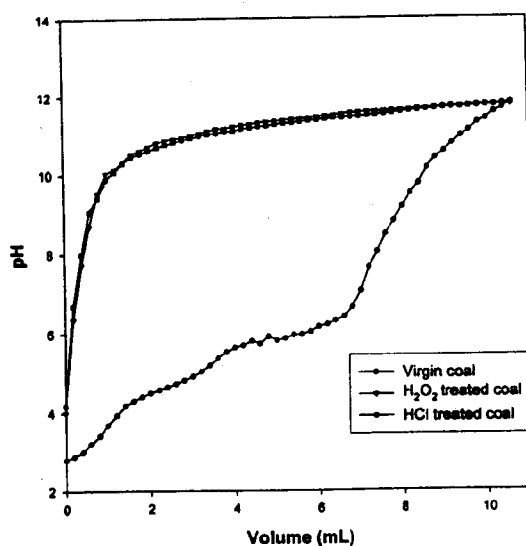
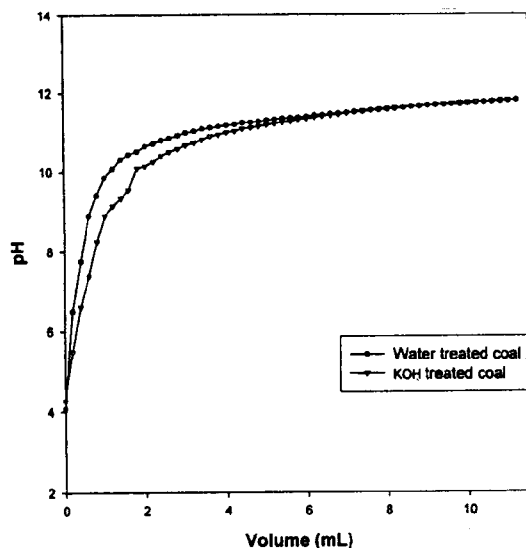
Fig. 1: Titration curves of virgin, H<sub>2</sub>O<sub>2</sub> and HCl treated coal samples.

Fig. 2: Titration curves of KOH and distilled water treated coal samples.

also causes corrosion of the metallic parts of the combustion appliances and reduces the heating value. Moreover, they are converted into oxides of carbon, sulfur, and chlorine, which cause global warming, acid rain, smog formation and also contaminate water [13].

The titration curves of virgin and variously treated coal samples in aqueous medium by direct method are presented in Figs. 1-2. The titration curve of virgin coal sample (Fig. 1) indicated a slight inflection in the region between pH 4-5 and pH 6-7, which was due to the existence of carboxyl group [14, 15]. The inflections between pH 8-10 and pH 10-11 were not stronger to indicate the carboxyl groups, which may be due to the existence of acid groups such as CO<sub>2</sub>, phenols, enols and C-H [15, 16].

Figs. 1-2 also show the titration curve of H<sub>2</sub>O<sub>2</sub>, HCl, distilled water, KOH and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> treated coal samples. The titration curve showed a normal break at pH 4-10 range and small inflection in pH 10-11, which did not show a resemblance to the one in carboxylic acid groups; it may however be due to the removal of carboxylic acid groups from the coal surface by these leachants. However, the titration curve showed some weak inflections, which may be due to CO<sub>2</sub>, phenols, enols or C-H bond. The sudden increase in the pH was due to the acidic groups dissociation. It could be attributed to sudden neutralization of the acid groups (present on coal surfaces) with an addition of potassium hydroxide solution. Because H<sup>+</sup> from acid (coal) and OH<sup>-</sup> from base are equal at this stage, their combination may eventually cause acid base reaction [14].

In the second set of experiments, indirect potentiometric titration was undertaken for virgin and variously treated coal samples. Figs. 3 and 4 show the titration curves obtained by the indirect method, which indicate similarities with the curves obtained by the direct method. It presented that the coal samples may contain carboxylic, carbonyl, phenolic, enolic and C-H groups. It is also reported that the aforementioned extractants oxidized the polynuclear aromatics and hydroaromatics systems of the coal that cause various functional groups like carboxyl, carbonyl, phenols, enols groups and C-H [17].

Fig. 5 presents the FT-IR spectra of virgin and variously treated coal samples. Fig. 5a show FT-IR spectrum of virgin coal sample, which presents various bands. The bands, which appeared at 480-410

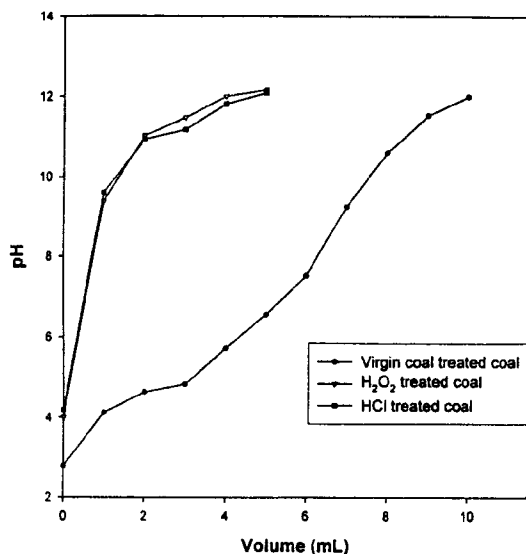


Fig. 3: Titration curves of virgin,  $\text{H}_2\text{O}_2$  and HCl treated coal samples.

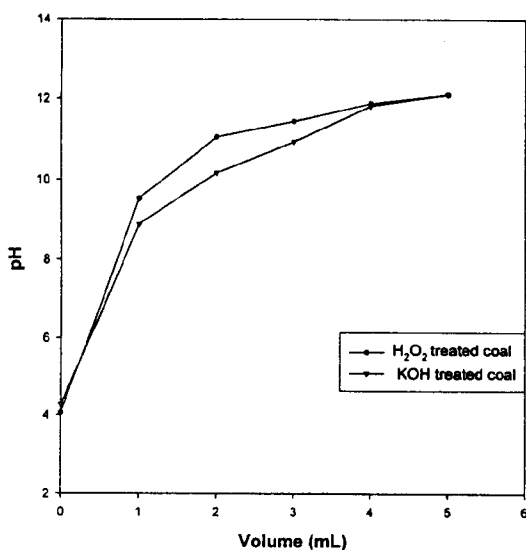


Fig. 4: Titration curves of KOH and distilled water treated coal samples.

$\text{cm}^{-1}$ , were due to mineral clay and iron sulfide because pyrite is generally considered an important iron bearing mineral in coals. The peaks appear at  $600\text{-}500\text{ cm}^{-1}$  and  $800\text{-}600\text{ cm}^{-1}$  were assigned to stretching vibrations of C-Br and C-Cl [18,19] while peaks at  $912\text{ cm}^{-1}$  and  $1100\text{-}1000\text{ cm}^{-1}$  were due to kaolinite. In kaolinite, a sheet of hydroxyl groups replaced one of the silicate anions and the various layers were linked with each other by H-bonding. The peak at  $1554\text{ cm}^{-1}$  was due to the stretching

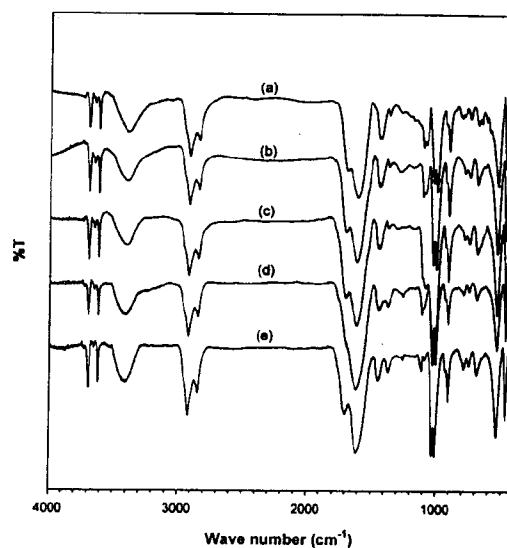


Fig. 5: FT-IR spectra of (a) virgin coal, (b)  $\text{H}_2\text{O}_2$  treated coal, (c) HCl treated coal and (d) KOH treated coal and (e) Distilled water treated coal.

vibration of nitrogen dioxide present in the aromatic compounds, but the contribution may have originated from aromatic C=C bonds in benzene, which is clearly established in lignite and sub-bituminous coal while not appearing in bituminous coal [20]. The peaks appearing at the region of  $1600\text{ cm}^{-1}$  and  $3100\text{-}2920\text{ cm}^{-1}$  were due to stretching vibration of C=O in carboxylic acid and C-H in cycloalkanes, respectively. The peaks appearing at the region  $3400\text{ cm}^{-1}$  and  $3700\text{-}3500\text{ cm}^{-1}$  were due to stretching of N-H and hydroxyl group, respectively [19, 21].

The FTIR spectra of treated coal samples showed similarities with the spectrum of virgin coal sample. However, the treated coal samples showed some difference in the regions  $1500\text{-}1100\text{ cm}^{-1}$ . The peak intensity of treated coal samples at about  $1540\text{ cm}^{-1}$  decreased as compared to virgin coal sample. It may be due to NaOH or KOH treatment, which converts the carboxylic acid groups of the coal sample into carboxylic acid salt. The carboxylic salts showed the characteristic bands in the region between  $1695\text{-}1540\text{ cm}^{-1}$  and medium intensity generally two or three peaks in the region  $1440\text{-}1335\text{ cm}^{-1}$  due to the asymmetric and symmetric stretching vibrations  $\text{CO}_2^-$ , respectively. The decrease in symmetric  $\text{CO}_2^-$  stretching frequency was due to the resonance structure and increase in the mass of the  $\text{CO}_2^-$  [22, 23]. The FT-IR spectra of treated coal samples also

indicated that the extractants increased the peak intensity at 1310-1250  $\text{cm}^{-1}$  region, which is due to stretching vibration of C-O-C in ether and ester, respectively [22]. It indicated that the aforementioned leachants oxidized the coal samples.

## Experimental

### Materials

Hydrochloric acid, hydrogen peroxide and potassium hydroxide were purchased from Aldrich and used as received. The coal samples were kindly supplied by Pakistan Mineral Development Corporation (PMDC).

### Sample Collection and Preparation

The coal sample was collected through PMDC according to the standard methods of sample collection from Lakra coal mine [12]. The coal sample was crushed ground and sieved through screen mesh size below 212  $\mu\text{m}$  and used for further study.

### Proximate Analysis

The proximate analysis, sulfur and chlorine determination in coal sample was performed according to the standard ASTM methods [24].

### Extraction of Coal Sample with Various Oxidants

50 g coal sample was slurried in 100 mL of 1 M extractant and stirred for time duration of 2 h at room temperature in order to extract inorganic elements. The slurry was filtered and the residual coal was washed with hot water till all the acid was removed and was dried in an oven at 105  $^{\circ}\text{C}$  and used for further study.

The same procedure was adopted for extraction of coal samples with 1 M  $\text{H}_2\text{O}_2$ , HCl, KOH and distilled water.

### Direct and Indirect Methods of Functional Groups Determination

1 g virgin coal sample was slurried with 80 mL distilled water in titration vessel and stirred for 8-10 h. In case of a direct method, the sample was titrated with 0.25 N potassium hydroxide (base) solutions while in an indirect method, 1-8 mL base was added to the flasks 1-8 in the increasing order, respectively and stirred for a time duration of 1 h

under nitrogen atmosphere with constant stirring on a magnetic stirrer.

A pH meter (Hana, model HI 8314) with combined glass calomel electrode was used. In a direct method, the pH was noted after 10 min, while in case of indirect method, after 1 h. The pH was then plotted versus volume of titrant for the construction of titration curves. The same procedure was adopted for all the treated coal samples as well.

### FT-IR Study

FT-IR spectroscopic study for the determination of acidic functional groups in virgin and variously treated coal samples, was performed using FT-IR spectrophotometer (Shimadzu FT-IR, Model -8201 PC).

The IR beam was passed through the pellets prepared from the finally ground coal sample (10-15 mg) mixed with 200 mg of potassium bromide (KBr). The appropriate sized pellets were prepared in an evacuated die under 10,000 pound pressure for time duration of 2 min and then placed in a desiccators for 1 h to remove the moisture. The spectra covered a wavelength range 4000-400  $\text{cm}^{-1}$ .

## Conclusion

In this work, an attempt was made to determine the acid functional groups and effect of various extractants on coal sample. The direct and indirect methods showed similarities between inflections in the curves, which indicates that the coal samples may possess carboxyl, carbonyl, phenols, enols and C-H groups. The aforementioned extractants also oxidized the coal samples, which was observed from the FT-IR study.

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