Acidic Surface Functional Groups and Mineral Elements in Lakra Coal (Sindh, Pakistan)

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Summary: Surface acidity of virgin coal (Lakra Sindh, Pakistan) and variously extracted/leached coal samples leached with HNO_3, NaOH, and $KMnO_4$, were investigated by aqueous potentiometric titration employing KOH as a titrant. The titration curve of virgin coal showed that its surface might contain carboxylic, carbonyl, phenolic and other weak acidic functional groups such as enols and C–H bond. The titration curves of leached coal samples showed inflections at pH 4-11, being not similar the inflections of carboxylic groups. This inflection might be given by functional groups like CO_2, phenolic, enols and C–H. Mineral matter such as Fe, K, Zn, Mn and Ni were determined in the ash of coal by atomic absorption spectrophotometer and was found that Fe (3104 μg/g) in the highest and Ni (36.05 μg/g) in the lowest quantity is present in virgin coal sample.

Introduction

Coal is a natural source of energy *via* coal conversion processes such as combustion, liquefaction and gasification and inturn used in production of electricity. Coal is sensitive to oxygen, therefore in the presence of air, it may degrade resulting in the formation of acidic functionalities. These acidic groups are determined by various techniques such as aqueous and non-aqueous potentiometric titration, barium ions exchange technique, chemical analysis and FT-IR, EPR spectroscopy, iodometric and potentiometric acid base titration along with ^{1}H and ^{13}CNMMR [1-8].

Coal is heterogeneous material composed of organic and inorganic constituents [9]. The organic components define the nature of coal (such as rank and type), and its suitability for different utilization processes. It was reported that the coal benefits are derived effectively from the maceral contents [10]. The inorganic constituents are present in the form of aluminosilicates, carbonates, sulfides and silicates (mainly quartz). These constituents as a part of organic structure of coal [11], an absorbed species on the organic part of coal [12], and discrete mineral matter. These inorganic elements in coal are present to variable extent depending on the plant origin, rank and the coalification process. The mineral matters are beneficial in terms of catalytic effects and used as a catalyst during coal liquefaction and gasification [13].

In the present study, we report our results of analysis of acidic functional groups and mineral elements in Lakra coal and compared with other Pakistani coals [1, 14, 15].

Results and Discussion

Table-1 presents the proximate analysis, total sulfur and chlorine content of the coal samples. The results show that the moisture, ash and volatile matter were high while fixed carbon was low as reported earlier [14].

Table-1: Determination of Proximate and elemental analysis of virgin coal [14].

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

The acidic surface functional groups in virgin and various leached coal samples were determined by direct and indirect aqueous potentiomentric titration (Figs. 1, 2). The titration of curve of virgin coal (Fig. 1) showed inflections at pH

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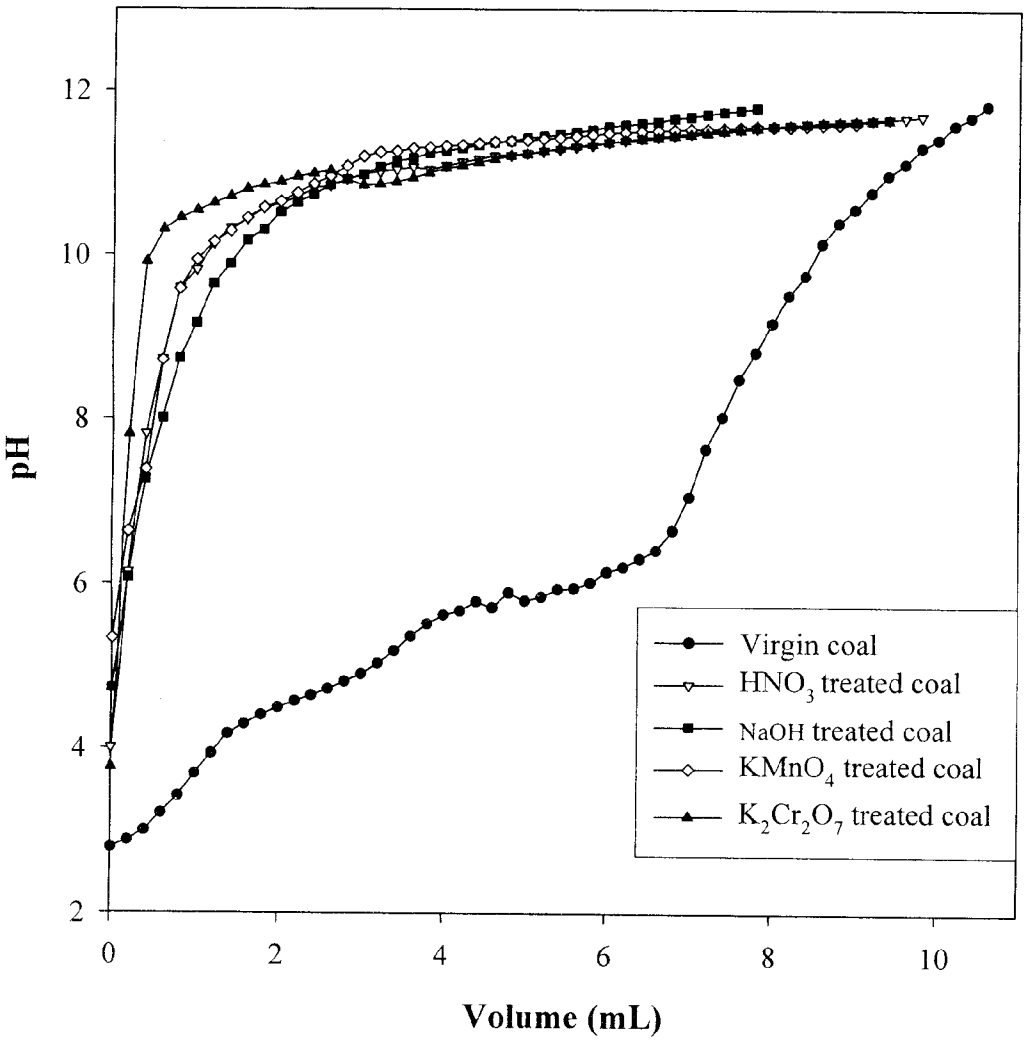

Fig. 1: Potentiometirc titration curves obtained by direct method.

2-7, which was due to the presence of carboxyl group [1, 16]. The inflections at pH 8-11 were not clear enough to be assigned to the carboxylic acidic groups, but might be due to the presence of acidic groups such as CO_2, phenols, enols and C–H [17, 18]. The titration curves of HNO_3, NaOH, $KMnO_4$ and $K_2Cr_2O_7$ (Fig. 1) showed normal breaks at pH 4-11. These infections did not show similarities with the inflection of carboxylic acid groups but these inflections might be due to other functional groups such as CO_2, phenols, enols or C–H.

The indirect potentiometric curves are shown in Fig. 2, which presented similarities with the titration curves obtained by direct potentiometric method. The curves indicated that the coal samples might contain carboxyl, carbonyl, phenols, enols or C–H. It has also been reported that when coal is expose to air or the oxidizing agents are mentioned above, the polynuclear aromatics and hydroaromatics systems of the coal are oxidized resulting into various functional groups such as carboxyl, carbonyl, phenols, enols or C–H on coal [19].

The mineral elements in the ash of virgin and variously leached treated coal (leached with nitric acid, sodium hydroxide, potassium permanganate and potassium dichromate) samples are

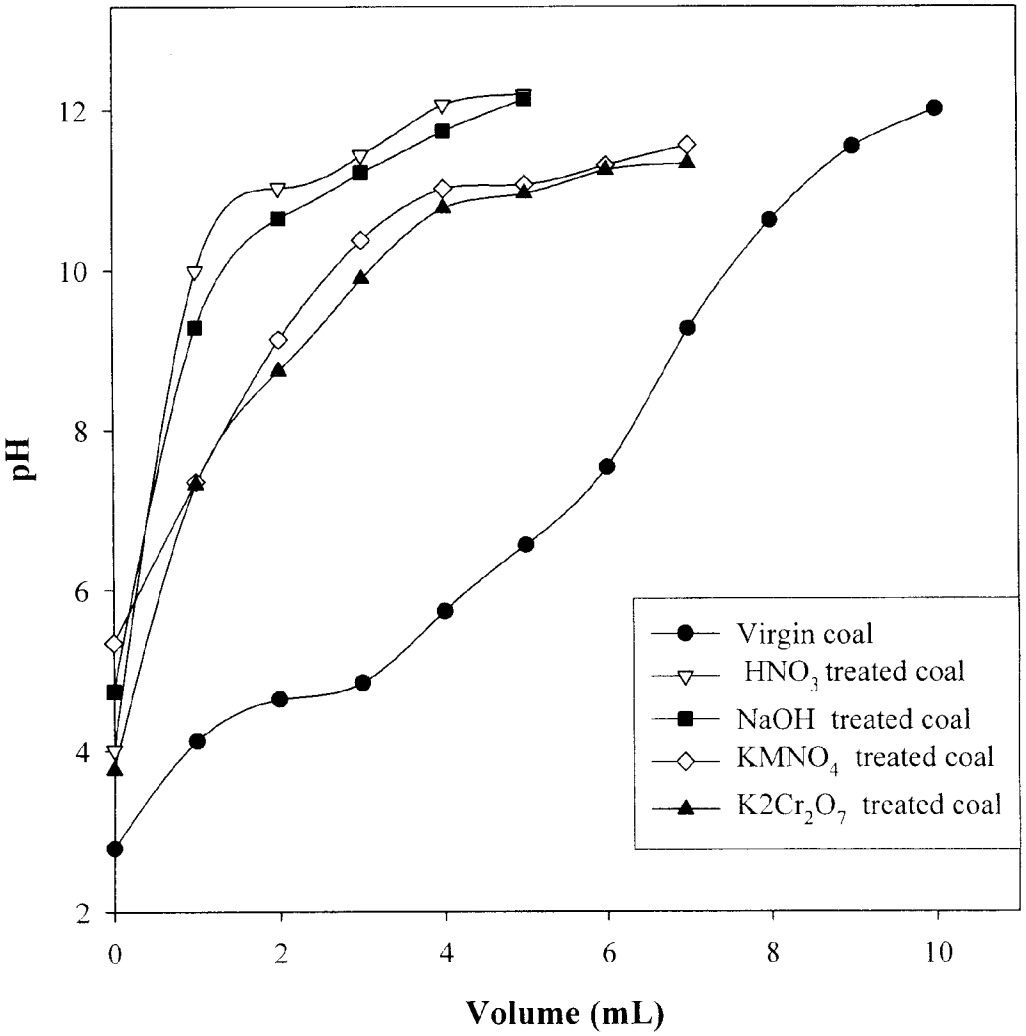

Fig. 2: Potentiometirc titration curves obtained by direct method.

shown in Table-2. The results show that the amount of iron (3104 μg/g) was high while nickel (57.75 μg/g) was low in virgin coal. It might be due to the presence of pyrite, which is generally important iron bearing mineral in coals [20]. The data also indicated that iron (3104 μg/g) and potassium (2295 μg/g) were high while zinc (289.4 μg/g), manganese (57.75 μg/g) and nickel (36 μg/g) present in small quantities, which showed that coal contain abundantly lithophilic than chalcophilic minerals. It was also observed (Table-2) that the demineralized coal samples had small amounts of inorganic elements compared to virgin coal sample, except potassium (virgin coal, 2295 μg/g), which was high in the coal sample leached with KOH (3285 μg/g). The high quantity of potassium in KOH treated coal might be due to the extractant that contain potassium itself, which might be reabsorbed on the coal. The data also

Table-2: Inorganic elements (µg/g) determined in the ashes of virgin and variously treated coal samples.

Coal Sample	Iron	Potassium	Zinc	Manganese	Nickel
Virgin coal	3104	2295	289.4	57.75	36.05
HNO_3 treated coal	2032	1890	235.6	7.2	18.9
HCl treated coal	2088	1950	242.7	19.85	22.35
KOH treated coal	3009.5	3285	266.75	20.85	29.55
H_2O treated coal	2319.3	1920	243.2	10.5	24.2
NaOH treated coal	3015.5	1975	252.8	26.85	31.4

indicated that iron, manganese and nickel are appreciably extracted with acids treatment compared to base treatment, it might be that these metals are soluble in acid while with bases they might form insoluble hydroxides. The extractability of zinc was low in all leachants, which might be due to its slow dissolution in acids where as in bases it may form insoluble hydroxide [21]. It was also observed that the acid treatment extract most of inorganic elements in high concentration from the coal samples compared to other leachants, which indicated that the coal samples contain lithophilic minerals because acid treatment removed lithophilic minerals in high quantity [22].

The results of proximate analysis, total sulfur and chlorine of Lakra coal was also compared with other Pakistani coal [14, 23-25], as shown in Table-3. The moisture and volatile matter was found to be higher in Lakra coal as compared to Khushab, S.Waziristan and Hangu but lower than Thur coal. The Lakra coal showed high quantity of ash than Khushab, Hangu and Thur while lower than S. Waziristan. The less amount of fixed carbon was found in Lakra coal compared to Khushab and Hangu but higher than S.Waziristan and Thur coals. The high quantity of total sulfur and chlorine was observed in Lakra coal compared to the other areas reported coal samples.

Table-3: Comparison of Lakra coal proximate and elemental analysis (%) with other Pakistani coals [14, 22, 24, 25].

Parameters	Lakra	Khushab	S. Waziristan	Hangu	Thur
Moisture	5.13	4.75	4	2.78	5.94
Volatile matter	33.98	33.75	27	28.76	45.92
Ash	22.67	20.4	48	18.2	15.5
Fixed carbon	30.22	41.13	16	50.26	27.19
Total sulfur	5.60	2.98	5.3	-------	3.28
Chlorine	0.19	-------	0.17	-------	1.06

Table-4 shows comparison of mineral elements of Lakra coal sample with the reported results of other Pakistani coals [14, 24, 25]. It was found that Lakra coal contain less amount of iron (3104 μg/g) compared to Makarwal (3530 μg/g), Degari (5850 μg/g), and Shahrigh (15200 μg/g) coals but higher than Sor-range (2970 μg/g), S. Waziristan (1632 μg/g) and Thur coal (2216 μg/g). The quantity of zinc was high in Lakra coal (289.4 μg/g) compared to other reported coal (as shown in Table-4) except

Table-4: Comparison of Lakra virgin coal mineral elements (μg/g) with other Pakistani virgin coals [14, 22, 25].

Coal samples	Iron	Zinc	Nickel	Manganese	Potassium
Lakra	3104	289.4	36.05	5 7.8	2295
Makarwal	3530	185	------	32	191
Degari	5850	27	------	91	1946
Shahrigh	15200	1022	------	1268	------
Sor-range	2970	45	------	39	518.5
S. Waziristan	1632	13	8	12	1378
Thur	2216.3	416.4	188.4	------	------

Shahrigh (1022 μg/g) and Thur (416.4 μg/g) coal samples. The quantity of nickel in Lakra coal (36.05 μg/g) was lower than Thur (188.4) coal while higher than S. Waziristan (8). The less manganese concentration was observed in Lakra coal (57.75 μg/g) compared to Degari (91) and Shahrigh (1268 μg/g) but higher than Makarwal (32 μg/g), Sor-range (39 μg/g) and S. Waziristan (12 μg/g) coal. The quantity of potassium in Lakra coal was higher than other reported Pakistani coal samples (Table-4).

Experimental

Materials

Nitric acid, potassium hydroxide, potassium permanganate, potassium dichromate, were purchased from Aldrich and used as received.

Sample Collection and Preparation

The coal sample was collected through PMDC (Pakistan mineral development corporation) according to the standard methods of sample collection [1, 14] from Lakra (Sindh, Pakistan) coal mine. The coal sample was crushed, ground and sieved through screen mesh size below 212 μm and used for further study.

The virgin coal sample was characterized according to the standard ASTM methods [26].

Extraction/Treatment of Coal

The sample was treated with the same method as reported in our previous article [1, 30], in which 50 g coal sample was slurried in 100mL of 1 M leachant (HNO_3, NaOH, $KMnO_4$ and $K_2Cr_2O_7$) and stirred for 2 h at room temperature. The coal

slurry was filtered and washed with hot distilled water till free from acid and then dried in oven at 105 °C and stored for further study.

Functional Groups Determination by Potentiometry

1 g virgin coal was slurried with 80 mL distilled water in titration vessel and stirred for 8-10 h. In a case of direct method, the sample was titrated with 0.25 M KOH solution (base) while in indirect method; 1-8 mL base was added to flasks 1-8 in the increasing order, respectively, and stirrer for 1 h with constant stirring on magnetic stirrer.

A pH meter (Hanna, model HI 8314) with combined glass calomel electrode was used. In a direct method, the pH was noted after 10 min, while in the case of indirect method, after 1 h.

Determination of Mineral Elements

1 g of virgin and variously treated coal samples were taken separately in eight different crucibles and heated in an electric muffle furnace at 750 ± 10 °C until carbon particles completely disappeared. The ash contents were cooled and digested in 50 mL acid solution (H_2O + HNO_3 + HCl + HF) in the ratio of 10:5:1:1 by volume, respectively at 100 °C for time duration of 2 h with occasional stirring, cooled and then filtered. The filtrates were collected, make up to its known volume and then stored in polyethylene bottle for the analysis of mineral elements by using atomic absorption spectrophotometer (Perkin Elmer 2380 U.S.A.) [14].

Conclusion

The extent of mineral matter removal from the coal materials depend upon the type of leachants and the method of leaching. Mineral elements from the coal sample were highly removed by acid treatment as compared to other extractants, which indicated that the coal contains lithophilic than chalcophilic minerals. Among the various investigated mineral elements, high concentration of iron had had highest while nickel had lowest concentration. The Lakra coal is low rank (between peat and lignite) because it had high amount of moisture, volatile matter, total sulfur and chlorine. The aqueous potentiometric titration curve indicated that the coal samples might posses the carboxylic, carbonyl, phenolic and other weak acidic functional groups like enols and C–H.

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