Effective Chemical Leaching and Ash Depletion of Low Rank Coal with EDTA and Citric acid

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Summery: Both physical and chemical methods are in practice to clean the coal and reduce its ash content. Mineral acids are used as chemical leachants, but because of their strong oxidizing power, they might have some disadvantages. In the present research work, demineralization of low grade coal with mild chemical leachents like EDTA and citric acid were studied. They were found as effective as mineral acids like HCl, HNO_3 HF, etc. They may be considered as preferred alternatives of the acids because Energy Dispersive X-ray Spectrophotometry (EDX) study has revealed that EDTA and citric acid leaching do not harm the carbon content of the coal as the acids did. Moreover, the environmental hazards due to use of acids may be avoided. In the current research, the coal samples were leached with HCl, HNO_3, CH_3COONH_4, acid mixture (H_2O, HCl, HNO_3, and HF), EDTA, buffered EDTA and citric acid. The treated coals were investigated for elemental analysis with EDX. The digestates of the ashes of treated coals were studied for metal contents with the help of Atomic Absorption Spectrophotometer (AAS). The coal under study was found to be high volatile lignite based on its Proximate and Ultimate analyses effectuated. The mild leachants investigated in the current research will be helpful to utilize low rank coals in an environment friendly way without deleterious effects associated with their combustion.

Introduction

There are huge deposits of low rank coals in countries like Pakistan, USA, Canada, Australia, Russia, India, China and many others. Worldwide, as supplies of energy have dwindled, therefore, other alternative sources are being sought. The possible candidate amongst these is coal. Low rank coals generally contain minerals and other undesirable constituents like sulfur, chlorine and nitrogen. Therefore, their combustion accompanied clinker formation and release of fly ash and compounds of sulfur, nitrogen, chlorine etc. The ash produced during coal combustion is directly related to the mineral matter content of coal. There is a need to control ash fouling and environmental impacts associated with coal utilization. Demineralization prior to utilization is an effective way to reduce ash content of coal and ensure environment friendly combustion of coal

Many techniques are employed for coal beneficiation in order to demineralize and desulfurise the coal [1-5]. Among these methods, leaching of coal with different leachants is presently carried out worldwide [6-11]. Mineral acids are generally used to demineralize the coals but due to their strong oxidizing power, they modify the coal surface morphology, harm the carbon, reduce the calorific value and create environmental problems. Therefore, it is preferred to investigate some mild leachants for ash depletion of coal, to avoid mentioned disadvantages.

In the present research work, coal sample was collected from Degari coal field of Pakistan, characterized and then subjected to leaching with a variety of leachants like EDTA, citric acid, HCl, HNO_3, ammonium acetate, acid mixtures, etc. The objective was to reduce mineral content and sulfur to overcome deleterious effects associated with combustion of low rank coal, without harming the carbon content of coal and to compare the leachibility of EDTA and citric acid with the conventional leachants like HCl, HNO_3, ammonium acetate, acid mixtures, etc.

Results and Discussion

The proximate and ultimate analysis of original coal sample is provided in Table-1. The levels of parameters like moisture, volatile matter, fixed carbon, total sulfur, pyretic sulfur, sulfate sulfur, organic sulfur, and chlorine were determined. The levels of fixed carbon, volatile matter, and ash are 42 ± 3%, 32 ± 3% and 11 ± 2% respectively, which are near to those of other Pakistani coals like Makerwal, Sharigh, Sor-range etc [12]. The coal seems to be high volatile lignite. The contents of ash and sulfur are not too high and by prior suitable beneficiation, the coal may merit for steam and power generation and can play a vital role in over-coming the energy crisis of the country. The analysis shows that the sulfur is mainly present in the sulfate form (1.0 %) and the organic form (1.50 %) and the most

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Table-1: Proximate and Elemental Analysis of Degari Coal

Parameter	Level (%) (Mean value ± SD)
Moisture	8.5 ± 1.5
Volatile Matter	32 ± 3
Fixed Carbon	42 ± 3
Ash	14 ± 2
Total Sulfur	3 ± 1
Sulfate Sulfur	1.0 ± 0.1
Pyretic Sulfur	0.5 ± 0.05
Organic Sulfur	1.5 ± 0.1
Chlorine	0.5 ± 0.05

Table-2: Levels of Ash in Virgin and Variously Leached Coal Samples

Sample	Ash (%) (Mean value ± SD)	%ash depletion
Virgin Coal	14 ± 2	
Leached With HCl	4 ± 1	64
Leached With HNO_3	3 ± 1	71
Leached With C H_3COONH_4	9 ± 1	35
Leached With Acid Mixture (H_2O:HCl:HNO_3:HF)	4 ± 1	64
Leached with EDTA	11 ± 2	21
Buffered EDTA(pH-4)	6 ± 1	57
Citric Acid	5 ± 1	64

Leachant concentration =1N,
Leaching time =1h.

dangerous pyretic sulfur (0.5 %) is low in amount. To combat and control the problem of slagging, ash fouling and agglomeration associated with coal combustion, variety of physical as well as chemical processes are taken into account. A lot of research work has been reported on acid leaching of coal to reduce the ash content. These corrosive reagents attack the coal surface and cause swelling and other changes in the surface morphology. Further, the use of acid is also not environment friendly and imbibed acids may cause release of acidic fumes to the atmosphere. Therefore, the real motivation of the present research work was to investigate effective mild leachants other than acids. For this purpose, comparison of the effectiveness of leachants like EDTA, buffered EDTA, citric acid, HCl, HNO_3 and acid mixture(made of H_2O,HNO_3, HCl and HF in molar ratio 10:5:1:1) was performed. The time of leaching and concentration of leachants were also varied. Table-2 provides the % of ash in the virgin and residual coal after leaching with 1N aqueous solution of the different leachants. It is clear from the table that HCl, HNO_3, and acid mixture have reduced the ash in the virgin coal by 64-71 %. The buffered EDTA (pH-4) and the citric acid have also reduced the ash in the virgin coal by 64 % and these mild leachants may be considered as effective as acids in case of low rank lignite coal (Degari coal). Therefore, by deminralizing the coal understudy with these mild leachants, the problems associated with the use of acids like corrosion, pickling and other environmental hazards may be avoided.

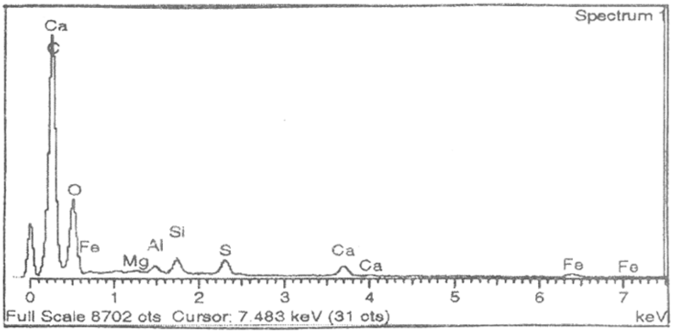
Table-3: % ages of Ash in Residual Coals after Leaching with Different Concentration of Leachants for Different Time Intervals. (% age of ash in virgin coal =14 ± 2%)

		Ash (%)				
Leachant Concentration		0.02N	0.04N	0.06N	0.08N	0.1N
HNO_3	1h	8.3	6.2	5.5	4.5	3.0
Leaching Intervals	5h	7.0	5.08	5.0	4.0	2.96
HCl	1h	8.9	7.5	6.5	5.2	4.0
Leaching Intervals	5h	7.8	7.0	6.1	4.5	3.82
Acid Mixture	1h	8.2	7.0	6.2	5.2	4.0
Leaching Intervals	3h	8.0	6.5	6.0	5.0	3.9
	5h	7.4	6.0	5.6	4.5	3.9
CH_3COONH_4	1h	12.5	11.9	10.8	10.1	9
Leaching Intervals	3h	10.8	9.6	8.7	7.9	7
	5h	9.5	8.3	7.6	6.8	6
EDTA	1h	13.0	12.0	11.5	11.2	11.00
Leaching Interval	2h	11	10.8	10.6	10.4	10.00
	3h	9	8.7	8.5	8.3	8.1
	4h	8.5	8.2	8.0	7.8	7.5
	5h	8.0	7.8	7.6	7.2	7.0
Buffered EDTA	1h	9.82	8.12	7.94	6.5	6.00
Leaching Intervals	2h	8.68	8.00	7.50	6.2	5.80
	3h	7.39	7.10	6.30	6.0	5.69
	4h	7.00	6.88	6.10	5.8	5.53
	5h	6.98	6.50	6.00	5.5	5.19
Citric acid	1h	8.4	7.3	6.4	5.5	5.0
Leaching Intervals	2h	8.0	6.8	6.0	5.3	5.0
	3h	7.6	6.5	5.8	5.2	4.9
	4h	7.4	6.1	5.4	5.0	4.8
	5h	7.2	6.0	5.4	4.9	4.8

The effect of the concentration of leachants and leaching time was also studied and is shown in Table-3. It may be observed that the enhancement in the concentration of EDTA and its leaching period has positive effect and the ash of virgin coal was reduced by 50 % for 5h leaching with 0.1N EDTA. In case of buffered EDTA, concentration has more positive effect but the time of leaching has not shown significant effect. One hour leaching with buffered EDTA has leached the amount of minerals nearly to the extent of 5h leaching. Citric acid like buffered EDTA is more effective and about 64 % of the minerals have been removed by 1h leaching with 0.1 N aqueous solutions.

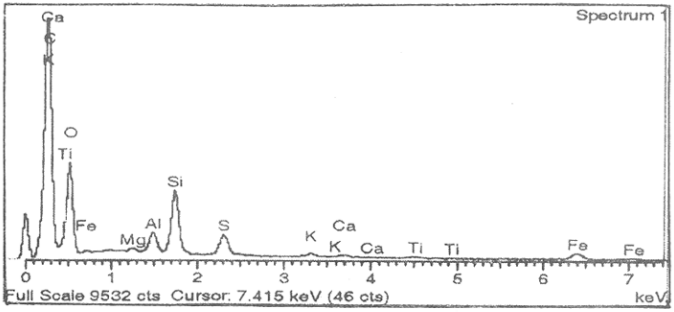
Energy dispersive X-ray spectrophotometric (EDX) study of the leached coal was also carried out in order to compare the carbon harming by the leachants used. The Figs.1-7 show the EDX spectra of virgin Degari coal and treated coals. It may be observed from the Fig.1 that the coal understudy has carbon (59.23 %), oxygen (36.27 %), Mg (0.16 %) Al (0.43 %), Si (0.95 %), S (1.07 %), Ca (1.00 %) and Fe (0.89 %). It may be noted from EDX study that % of carbon in the virgin coal is reduced to 54.38 % by 1h leaching with 0.1N HNO_3 and 47 % by 1h leaching with 0.1N CH_3COONH_4, while it hike up to 63-67 % by 1h leaching with citric acid or buffered EDTA. The carbonization of coal at 900 ^{0}C under nitrogen was carried out to enhance the % age of carbon and up to 65 % enrichment in carbon was achieved in the carbonization process effectuated. Therefore, it may concluded from the EDX study that leaching with mild leachants like EDTA and citric acid did not harm the carbon structure of the coal surface and therefore, may be preferred over acids which otherwise have caused much harm to the carbon and hence, the calorific value.

In further study, virgin coal and coal leached for 1hour separately with different leachants were ashed and then digested with acid mixture. The digestates were analyzed by atomic adsorption spectrophotometer for metal contents. The results are shown in Table-4. The presence of metals like Ca, Mg, Fe, Mn, Ni, Pb, Cu, and Cr were noted in the ashes. It may be inferred from the data that the mild leachants like citric acid and buffered EDTA have leached the lithophilic elements (Ca, Mg, Fe) effectively nearly like that of acids. Further, the chalcophilic elements



Ele...	Weight%	Atomic%
C K	59.23	67.29
O K	36.27	30.93
Mg K	0.16	0.09
Al K	0.43	0.22
Si K	0.95	0.46
S K	1.07	0.45
Ca K	1.00	0.34
Fe K	0.89	0.22
Totals	100.00	

Fig. 1: EDX Spectrum of Virgin Degari Lignite Coal



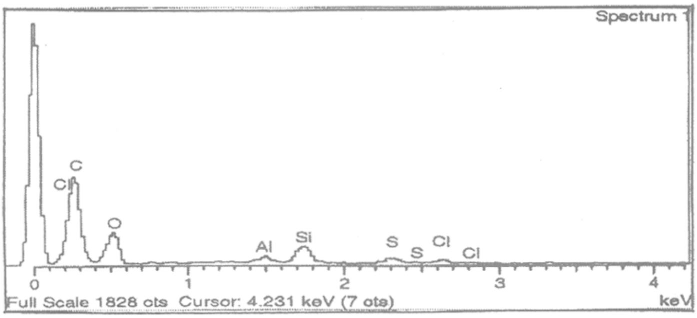
Ele...	Weight%	Atomic%
C K	54.38	63.61
O K	37.24	32.70
Mg K	0.20	0.11
Al K	1.13	0.59
Si K	3.64	1.82
S K	1.36	0.60
K K	0.26	0.09
Ca K	0.17	0.06
Ti K	0.14	0.04
Fe K	1.48	0.37
Totals	100.00	

Fig. 2: EDX Spectrum of Residual Coal Leached with 0.1N HNO_3 for 1hour

Table-4: Levels of Metals in Ashes of Virgin Coal and Residual Coal Leached with Different Leachants (μg/g)

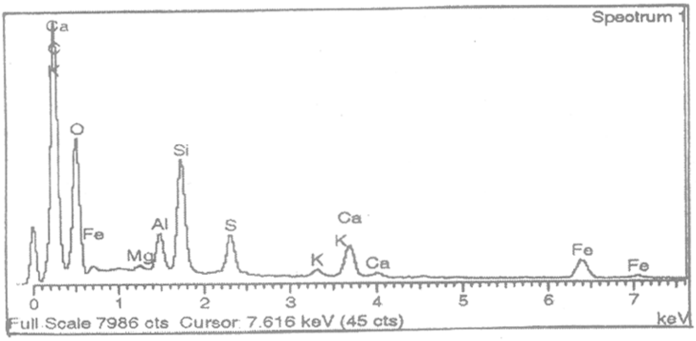
Samples	Cu	Fe	Mn	Ni	Pb	Ca	Mg	Cr
Virgin Coal	106	3300	108	86	106	21200	1650	117
Coal leached with HCl	26	1314	58	55	52	3300	612	97
Coal Leached with HNO_3	19	1166	41	31	66	1950	337	25
Coal Leached with Acid Mixture	20	1171	51	29	49	1800	350	26
Coal Leached with 0.1N EDTA	51	1634	67	53	96	8400	1112	95
Coal Leached with 0.1N Buffered EDTA	72	1470	60	40	70	4100	875	102
Coal Leached with Citric acid	31	1300	48	65	95	3290	603	86

Leachant Concentration =1N,
Leaching Time =1h.



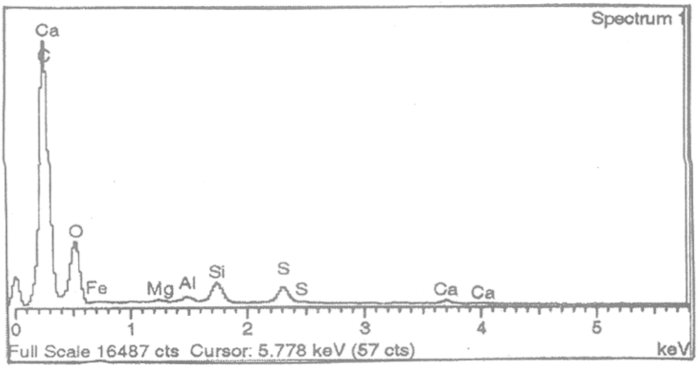
Ele...	Weight%	Atomic%
C K	59.74	67.57
O K	35.70	30.31
Al K	0.75	0.38
Si K	2.46	1.19
S K	0.77	0.33
Cl K	0.57	0.22
Totals	100.00	

Fig. 3: EDX Spectrum of Coal Leached with Acid Mixture.



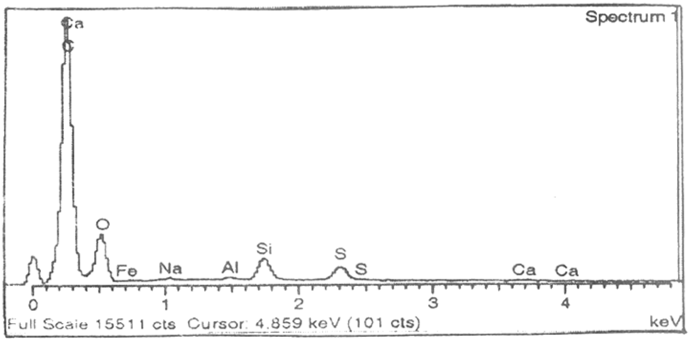
Ele...	Weight%	Atomic%
C K	47.83	58.70
O K	38.37	35.35
Mg K	0.22	0.14
Al K	1.51	0.82
Si K	4.60	2.42
S K	1.81	0.83
K K	0.40	0.15
Ca K	2.01	0.74
Fe K	3.25	0.86
Totals	100.00	

Fig. 4: EDX Spectrum of Coal Leached with 0.1 N CH_3COONH_4



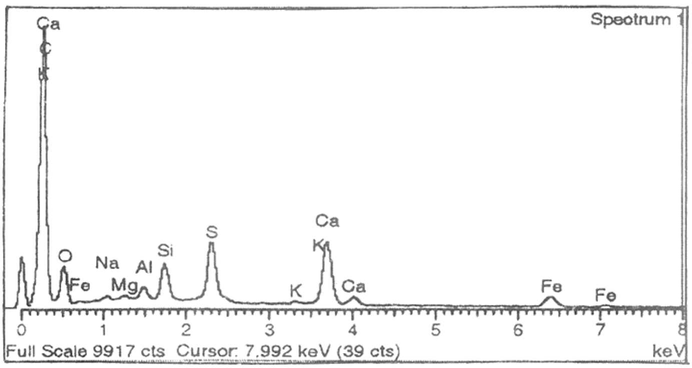
Ele...	Weight%	Atomic%
C K	64.17	71.51
O K	32.31	27.03
Mg K	0.13	0.07
Al K	0.28	0.14
Si K	1.17	0.56
S K	1.07	0.45
Ca K	0.31	0.10
Fe K	0.57	0.14
Totals	100.00	

Fig. 5: EDX Spectrum of Coal Leached with 0.1 N Citric Acid



Ele...	Weight%	Atomic%
C K	67.83	74.71
O K	28.87	23.87
Na K	0.17	0.10
Al K	0.14	0.07
Si K	1.48	0.70
S K	1.05	0.43
Ca K	0.10	0.03
Fe K	0.36	0.08
Totals	100.00	

Fig. 6: EDX Spectrum of Coal Leached with Buffered EDTA



Ele...	Weight%	Atomic%
C K	65.01	76.31
O K	20.38	17.95
Na K	0.35	0.22
Mg K	0.23	0.13
Al K	0.67	0.35
Si K	1.85	0.93
S K	3.51	1.54
K K	0.15	0.05
Ca K	5.40	1.90
Fe K	2.46	0.62
Totals	100.00	

Fig. 7: EDX Spectrum of Carbonized Coal Sample.

(Mn, Ni, Pb, Cu, Cr) were removed partially by both the classes of the leachants. Thus, the EDTA and citric acid being mild leachants may be used as alternative of the mineral acids for the ash depletion of low rank lignite coal, as their use do not harm the carbon content of the coal as observed by EDX study. The leaching process with EDTA may be rendered cost-effective as from contaminated EDTA; the metals may be removed completely by treatment with Na_2S and Ca $(OH)_2$ as reported by Zeng *et al* [13]. Thus recycling of EDTA solution is possible. Citric acid may be freed from metals. Recovery of citric acid is reported elsewhere [14].

Experimental

Preparation of Coal Sample

The run of mine coal sample was obtained from Degari coal mines through Pakistan Mineral Development Corporation. Degari coal field lies 13 to 25km south-east of Quetta (Balochistan, Pakistan). The coal was crushed and ground in a pestle and mortar, screened through 250-212 μm sieves using a sieve shaker. The definite sized coal sample was dried in a vacuum oven at 70 °C for one hour and cooled in a desiccators. The proximate and ultimate analysis of the coal understudy was carried out according to standard ASTM methods [15-16].

Extraction Procedure

5 g of coal was extracted separately with EDTA, buffered ETDA, citric acid, HCl, HNO_3, acid mixture made of H_2O, HNO_3, HCl and HF (molar ratio of 10:5:1:1) and ammonium acetate. The specified amount of coal was slurried in 50 cm^3 of extracting solution in a beaker. A Teflon coated magnetic stirring bar was also immersed. The beaker was placed on a water bath and the whole assembly was placed on a magnetic stirrer. The contents were stirred for time duration of 5 hours at 50 ^{0}C. The temperature was maintained throughout the extraction process by addition of hot water into the water bath. After being contacted for the specified duration of time, the slurry was filtered using whatman filter paper to remove the capture solution. The residual

coal was washed exhaustively with copious amount of hot distilled water, dried in a vacuum oven at 70 °C till constant mass. Energy dispersive X-ray spectrophotometer (EDX) Model Inea 200, Made UK, company oxford was used for the elemental analysis of treated and virgin coals.

Ashing of coal and extracted coal samples and their treatment with acid mixture:

5 g of virgin and variously extracted coal samples were ignited separately in a muffle furnace at 800 ± 50 °C. 50 cm^3 of acid mixture was added to the ash obtained. The contents were stirred for 2 hours at 25 °C using a magnetic stirrer. The slurry was filtered and the filtrates were collected. The residual coal ash was washed several times with deionized water till free of acid. The washing and the filtrate collected were combined, made to a constant volume of 100 cm^3 and stored in polyethylene bottles for atomic absorption study. The elemental analysis of the digestate of the coal ashed was performed by using Parkin Elmer 3300 Atomic absorption spectrometer equipped with HGA-600 graphite furnace. All the chemicals used were of analytical grade. Each determination was at least carried out in triplicate and the mean value was calculated and presented in the table.

Conclusions

It may be inferred from the present research work that mild leachants like EDTA and citric acid may be employed for the effective demineralization of low rank coal containing high contents of chalcophilic element like Ca, Mg, and Fe. Further, as they do not decrease the carbon content, therefore, may be preferred over acids for environment friendly and cost effective demineralization of low grade coals. The present research will be helpful in overcoming the deleterious effects associated with the combustion of the coal in an environment friendly way, without decreasing the calorific value of coal and changing the coal morphology.

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