Characterization and Comparative Study of Pakistani Coals by Liquid Adsorption Methods

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(Received 16th August, 2005, revised 5th October, 2005)

Summary: Coal samples were collected from the four major coal fields i,e Sore Range, Sharigh, Degari and Makerwal Proximate and ultimate analysis were performed by standard chemical methods. Specific surface area was determined by adsorbing methylene blue dye, iodine and water vapors. Methylene blue adsorption was studied by spectrophotometric techniques. Iodine adsorption was estimated by standard volumetric methods and water vapors adsorption by standard gravimetric procedure Most of the adsorption isotherms obtained from dye (at room temperature) belong to type L of Gilies classification for solution which indicate mesoporous and macro porous nature of these coals. The reasonable long plateau shows saturation of the monolayer. The specific surface area from the dye adsorption ranges from 264 $m^2 g^{-1}$ to 587 m^{2-1}. Iodine (from water) gives 111-203 $m^2 g^{-1}$ and from carbon tetra chloride solution gives 130-211 $m^2 g^{-1}$. Total pore volume (10.46-11.58 cc g^{-1}) and % porosities (86-95 $m^2 g^{-1}$) are reported. High ash content (3.75 - 8.19 %) and the presence of sulphur (1.54-2.97 %) and chlorine (0.05-0.13 %) place these coals in the lower class.

Introduction

Coal has traditionally been used as a source of heat, a feed stock for the chemicals or synfuel industries, and a raw material for the production of coke. It is used for an electric Power generation in chemical plants, as a process heat in various industries including brick kilns (which in Pakistan use 95 % of the coal production) and for domestic home heat. Increase in the oil prices since 1973 and fear for short fall in supplies, focused attention on the replacement of the oil with cheaper fuels such as coals.

The utilization of coals requires technological, economical and environmental evaluation of data e,g coal type, rank, grade, coal texture and elemental constituents which are potential environmental contaminants to both atmosphere and water. Some end use require coals/chars with definite physical parameters such as specific surface area, porosity etc. The major environmental concerns are contamination of air by sulfur and chlorine which are present in coal [1].

During combustion sulfuous emissions may cause air pollution. The economic evaluation depends on the end use of the coals but generally requires data from the determination of calorific value, ash yield, moisture and constituents that cause slagging, erosion and corrosion. Characterization of coals before combustion is essential [2-6]. Therefore, an effort has been made to investigate some physical and chemical aspects of the coals from the major coal fields of Pakistan to get valuable information.

Results and Discussion

Proximate and ultimate analysis (Table-1 and 2) show high ash content with the presence of sufficient amount of sulfur and chlorine, which cause slagging problems, acid precipitation and contaminate surface and ground water. During utilization of coal, sulfur and chlorine pollute the air which may endanger the human health, plant and animal life and cause corrosion problems in various industrial units.

Table-1: Proximate Analysis of Coal Samples Under Study

S #	Property	Makarwal	Sore Range	Khost Sharigh	Degari
1.	Total Moisture %	4.15	8.19	3.75	7.35
2.	Volatile Matter %	41.80	31.01	55.65	63.85
3.	Ash Content %	2.53	6.75	8.76	26.27
4.	Fixed Carbon %	51.52	54.04	31.84	2.53

Table-2: Ultimate Analysis of Different Coal Samples

S#	Property	Makarwal	Sore Range	Khost Sharigh	Degari
1.	Sulphur %	2.97	1.71	1.54	1.79
2.	Chlorine %	0.08	0.10	0.05	0.12

Surface area is one of the most important physical parameter which determine the role of the substance (especially porous structure) during its use

such as adsorption, and combustion processes etc. For sorption on coals, pores are essential [7-8]. Results of surface area (Table-3) indicate that the active surface per unit weight is comparatively low in most of the cases. It means the surface is mostly external i,e the pores are wide enough. Surface area was calculated by well known eq ıtion as below:

$$S = \frac{X_m \times N \times Am}{M}$$

Where

S = specific surface area

Xm = monolayer amount

N = Avogadro number

Am = cross sectional area of adsorbate in A^{o2}

M = molecular weight of the adsorbate

In case of iodine adsorption, the amount adsorbed per gram was calculated and inserted in the above formula to get specific surface area (Table-4)

Water vapor adsorption gives type lll isotherms for all samples (Fig 5-8). These cannot be used for surface area estimation because point B is not clear. However, the shape of the isotherms indicates that most of the surface area is external. Heat of adsorption is equal to or slightly less than heat of liquefaction. These isotherms show mono and multiplayer adsorption followed by capillary condensation.

Total pore volume and % porosities as obtained from the densities are given in Table-3. The magnitude of all these results is enough to convince that these coals are of low rank. Total pore volume and percent porosity were calculated by the following equations:

Total pore volume $= (1/\rho Hg - 1/\rho H_2O)\ ccg^{-1}$ and

Percent porosity $= (Vg-Vs/Vg) \times 100$

Where

ρHg =density in mercury

ρH_2O= density in distilled water

Vg = pore volume in mercury

Vs = pore volume in distilled water

The magnitude of all these results is enough to convince that these coals are of low rank. However, coal is a heterogeneous material and has a very complicated structure. Therefore, it needs comprehensive investigation to establish its physical and chemical structure with certainty. It may differs in different locality and even differ in different seams of the same locality.

Experimental

According to the priority list set up by Geological Survey of Pakistan (G.S.P) and U. States for the coal fields of Pakistan, the coal samples were collected with the help of Pakistan Mineral and Developmental Corporation (P.M.D.C) as below.

Priority-A

1. Sore range 2. Degari coal field (Balochistan)

Priority-B

1. Khost-Sharigh Harnai fields (Balochistan)

Table-3: Densities, Pore Volume and Percent Porosity

S.No.	Property	Makarwal	Sore Range	Khost Sharigh	Degari
		Punjab-N.W.F.P	Baluchistan	Baluchistan	Baluchistan
1.	Density in distilled water gcc-1	0.6871	0.7980	0.7182	0.7286
2.	Density in mercury	0.0825	0.0857	0.0771	0.0845
3.	Total Pore Volume ccg-1	10.66	10.41	11.58	10.46
4.	Percent Porosity	88	86	95	86

Table -4: Specific Surface Area (M^2g^{-1})

S.No.	Locality	Methylene blue Am=(78A0)2	Iodine Contact Time 72 hours	
			Aquous Solution	CCl_4 Solution
1.	Makarwal	264	134	144
2.	Sore Range	366	121	130
3.	Khost Sharigh	352	173	178
4.	Degari	578	203	211

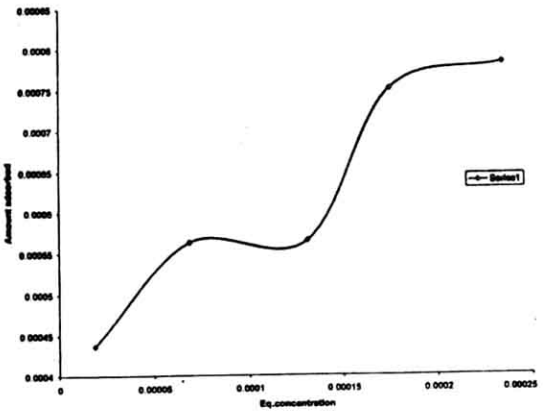

Fig. 1: Methylene Blue Adsorption Isotherm of Makarwal Coal

Priority-C

1. Makarwal coal fields (N.W.F.P/Punjab.)

All these samples were air dried and ground to 60 mesh before investigation.

(1) Chemical constituents

(a) Proximate analysis: All the samples were analysed on moisture free basis by standard chemical methods involving volumetric and gravimetric procedure. The results obtained are the average of at least three readings (Table-1).

(b) Ultimate Analysis: The emphasis was given on the nuciance elements, sulphure and chlo-rine. These elements were determined by ESCHA methods. Results are given in Table-2.

(2) Physical parameters

(a) Densities: Density of all four coal samples were determined in mercury and distilled water by mercury pycnometer and specific gravity bottles respectively (Table-3).

(b) Surface area is the most important physical property which plays prominant role in adsorption and chemical reactions occurring on the coal surface. For this purpose, it was extensively studied through liquid adsorption methods using different adsorbates such as methylene blue, iodine (from aquous and organic media) and water vapours.

(i) Dye adsorption

Methylene blue was supplied by E. Merk. It was of analytical grade and was not treated further. Adsorption was carried out from a series of standard solution and the concentration was determined before and after adsorption by spectrophotometer, Model, Unico 1100 RS (U.S.A.) for each sample. Adsorption isotherms were constructed between the amount adsorbed and equilibrium concentration which give monolayer capacity at the point B (Fig. 1-4).

(ii) Iodine adsorption

0.4 N standard iodine solutions were prepared both in water and carbon tetra chloride. Definite

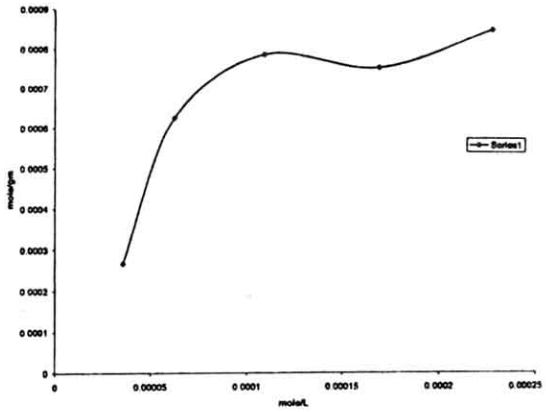

Fig. 2: Methylene Blue Adsorption Isotherm of Sor-Range Coal

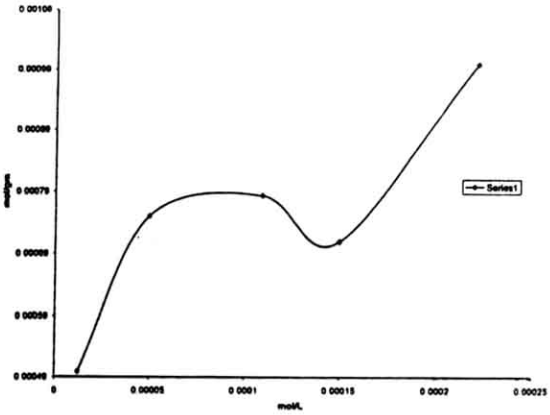

Fig. 3: Methylene Blue Adsorption Isotherm of Sharigh Coal

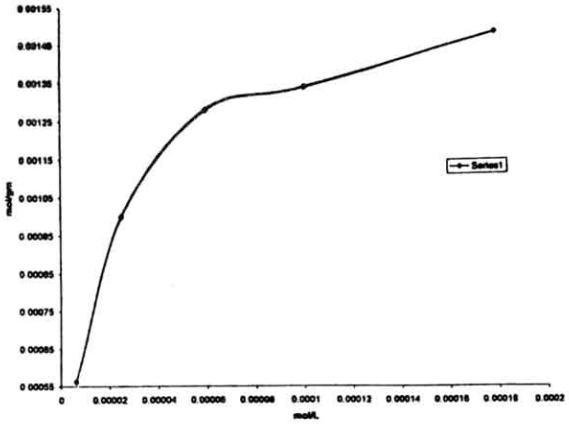

Fig. 4: Methylene Blue Adsorption Isotherm of Degari Coal

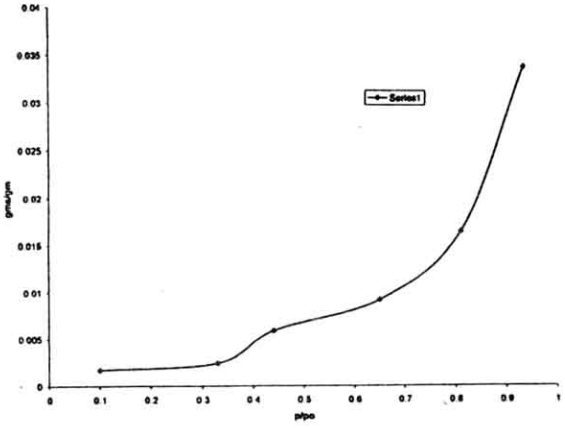

Fig. 5: Water Vapors Adsorption Isotherm of Makarwal Coal

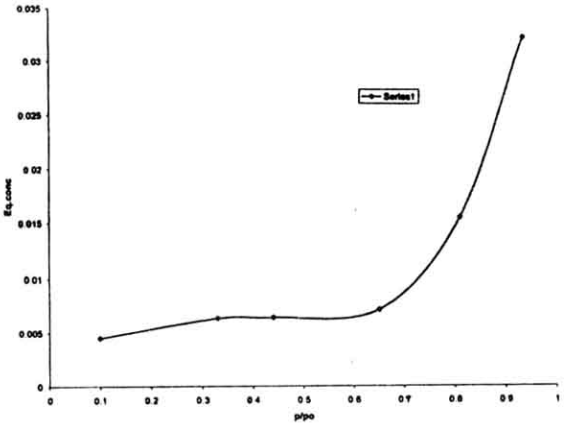

Fig. 6: Water Vapors Adsorption Isotherm of Sor-Range Coal

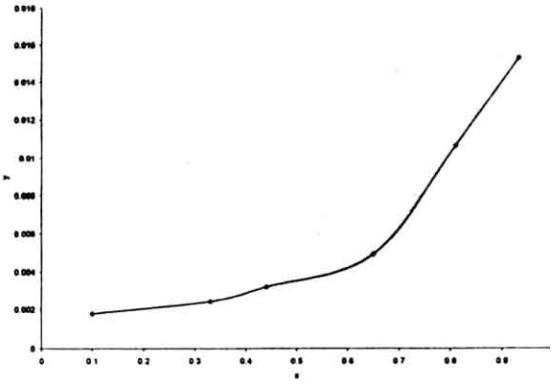

Fig. 7: Water Vapors Adsorption Isotherm of Sharigh Coal

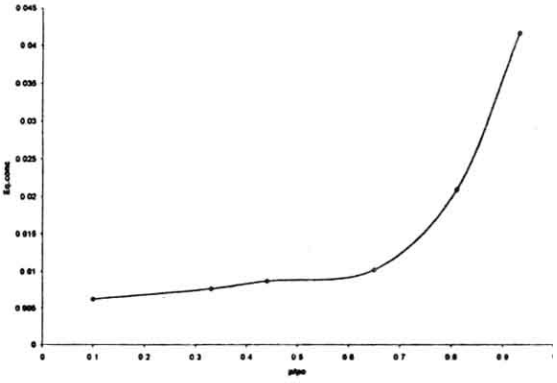

Fig. 8: Water Vapors Adsorption Isotherm of Degari Coal

amount of samples were put in and allowed to stand for seventy two hours with occasional shaking. Then, these solutions were centrifuged and the clear portions were titrated against standard sodium thiosulphate solution. The amount adsorbed was determined as below.

Amount adsorbed = Normality x Volume x Eq. weight of Iodine / 1000.

(iii) Water vapour adsorption

For water vapours adsorption, properly saturated solutions (when no more solute is dissolved) of zinc chloride, magnesium chloride, potassium chloride, magnesium nitrate, ammonium nitrate, ammonium sulphate and potassiumnitrate were prepared from the analytical grade reagents in carfully greased vessels with suitable to provide different constant

relative pressure from 0.1 to 0.93 p/p0 respectively. Then, definite amount of samples was placed in these containers and constant weight for each sample was obtained gravimetrically. In this way, amount of the vapours adsorbed was calculated and isotherms (Fig. 5-8) were contructed.

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