Characterization of Ludwa Soil

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Summary: The characterization of a soil sample collected from Ludwa near Khewra has been carried out using X-ray spectrometric techniques and nitrogen adsorption. X-ray diffraction investigations show the presence of quartz and muscovite minerals. The X-ray fluorescence study reveal that major constituents of the soil are SiO_2 and Al_2O_3 while the oxides of calcium, copper, iron, cobalt and manganese are minor constituents. The pore size distribution curve obtained through nitrogen adsorption indicates the mesoporous nature of the clay with a surface area of 20.80 m^2/g and having a pore volume of 0.494 cm^3/g.

Introduction

Soil is made up of a number of different minerals in various proportions. It has small particle size thus the term soil is usually used in reference to fine grained, earthy material. The soil essentially constitute hydrous aluminum silicate [1]. Due to good adsorptive properties and being abundantly available at low cost, the soil has been used for the fixation of radioactive waste solution containing radionuclides [2-7]. The adsorption properties of the soil depend upon the chemical composition, surface area, pore volume and pore size distribution. The present work reports the characterization of soil sample collected from Ludwa near Khewra, Punjab (Pakistan) (Lat. 32.38°, long 73.01°) [8]. The characterization of the soil sample was carried out by employing X-ray diffraction (XRD), X-ray fluorescence (XRF) spectrometry and nitrogen adsorption.

Results and Discussion

The soil sample collected from Ludwa near Khewra had a light brown color with course texture. The light color of the sample points towards its richness in water, silicon, aluminum, sodium and potassium content alongwith lower concentration of iron, magnesium and calcium [1]. The nature of the soil can be investigated by employing different X-ray techniques [9]. The chemical composition of the soil given in Table-2, determined by X-ray fluorescence spectrometer reveal the presence of the oxides of aluminum and silicon as the main components alongwith smaller quantities of the oxides of calcium, iron, and copper thus pointing towards the sandstone nature of the soil [1].

The X-ray diffractogram presented in Figure 1, has strong set of lines at 4.27, 3.35 and 1.80 Å alongwith smaller lines at 4.77, 3.26, 2.78, 2.59 Å. The former set of lines point towards the presence of quartz (SiO_2) as the major mineral in the soil. The later set of lines confirm the small concentration of muscovite [KAl_2 (Al Si_3O_{10}) $(OH)_2$]. The presence of quartz and muscovite [10] in the clay sample fall in accordance with the Bowen's reaction principle developed to explain the formation of different minerals in a rock magma [11]. In addition, the presence of iron (11.43, 2.00 Å) and sodium (2.13, 3.02 Å) in minor proportions is observed from X-ray diffraction pattern.

The nitrogen adsorption and desorption isotherms are shown in Figure 2 where volumes of nitrogen adsorbed and desorbed are plotted against the relative pressure P/P^o. These isotherms are classified as Type II according to the Brunauer, Deming, Deming and Teller (BDDT) classification

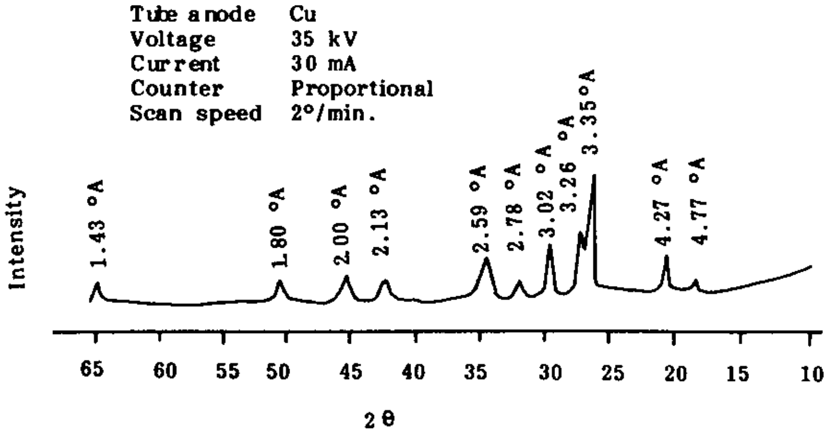

Fig. 1: X-ray diffraction pattern of Ludwa soil.

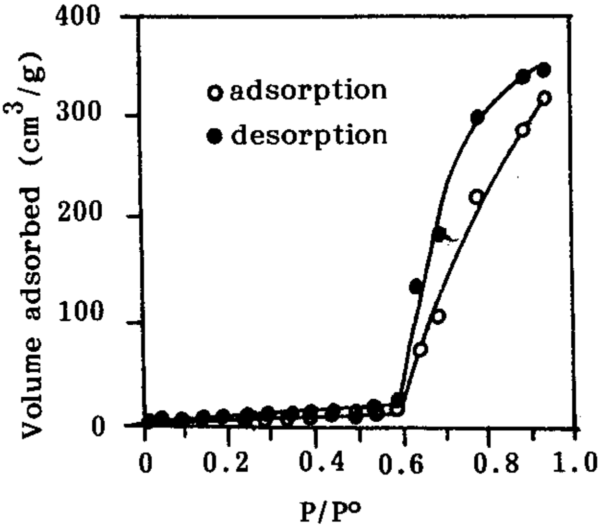

Fig. 2: Nitrogen adsorption - desorption isotherms at 77K on Ludwa soil.

[12]. This type of isotherms are associated with the multilayer adsorption and some reversible capillary condensation phenomena. In the low pressure region, the volume adsorbed rises less steeply and remain, almost linear in slope. At the saturation, the curve is steepening because of interparticle capillary condensation. It is also observed in Figure 2 that the desorption isotherm curve does not coincide with the adsorption isotherm. This behaviour can be explained on the basis of the capillary condensation theory. According to this theory, contact angle on adsorption, when liquid is advancing over a dry surface, is usually greater than the contact angle during desorption, when liquid is receding from a wet surface [13]. The surface area of soil was determined by applying the Brunauer,Emmett and Teller (B.E.T) equation to physical adsorption data of nitrogen at 77K. The most convenient from of B.E.T. equation for the application to experimental data is given below [14].

$$\frac{1}{X[(P^o/P)-1]} = \frac{1}{X_mC} + \frac{C-1}{X_mC}\;\frac{P}{P^o} \qquad (1)$$

where the symbols have their usual meanings. The B.E.T equation gives a linear relationship between $1/X[(P^o/P)-1]$ and P/P^o. The range of linearity is usually restricted to a limited part of the isotherm. The B.E.T. plot for the nitrogen adsorption on soil is shown in Figure 3. From the slope $(C-1/X_mC)$ and intercept $(1/X_mC)$, the values of X_m and C were calculated to 5.97×10^{-3} (g/g) and 52.88 respectively. The value of monolayer capacity, X_m was used to calculate the surface area of the soil using the known molecular cross section of the nitrogen molecule (16.2 Å at 77K) and comes out to be 20.80 m^2/g.

The B.E.T. plot in Figure 3, shows that experimental points deviate from linearity with the increase in the relative pressure. This deviation from linearity is apparent at the relative pressure greater than 0.30. It has been shown by Braunauer [15] that for P/P^o values greater than 0.30, the experimental points do not fall on a straight line. In other words, the B.E.T. equation breaks down for the less active points on the surface. Herman and Emmett [16] indicated that B.E.T. equation give reasonable values of surface area in the range

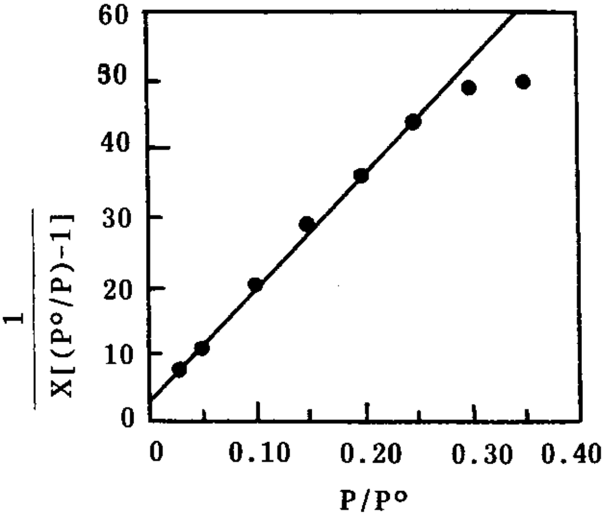

Fig. 3: B.E.T. plot for nitrogen adsorption on Ludwa soil.

of relative pressure from 0.05 to 0.35. They concluded that in this range of relative pressure, monolayer is formed and the C values of B.E.T. equation usually gives heat of adsorption. Thus in the relative pressure range 0.05 to 0.35, the linear B.E.T. range apparently represents a condition in which the high energy sites have been occupied and extensive multilayer adsorption has not yet commenced. It is within these limits that the B.E.T. equation is generallv valid and deviations from this range of linearity reflect unusual surface properties.

The pore volume measured by nitrogen adsorption is 0.494 cm^3/g. The pore size distribution of the soil, shown in Figure 4, is calculated by applying Kelvin equation [17]. The distribution curve indicates one sharp peak at ~ 25 Å, showing the mesoporous character of the clay. The mesopore volume determined from nitrogen adsorption, by the method reported by Guzel and Tez [18], is 0.4826 cm^3/g. The major contribution (97.8%) to total pore volume comes predominantly from mesopores of radius ~ 25 Å. The distribution was cut off on lower end at 15 Å, since the Kelvin equation is considered valid for pore radius no smaller than 15 Å [19].

Experimental

X-ray fluorescence study

An energy dispersive X-ray fluorescence spectrometer XR-500 from Links System, U.K. was used for the chemical analysis of the soil. The system is equipped with 860 analyzer, 100 mm^2 x 3 mm deep Si(Li) detector with 155 eV resolution determined with ^{55}Fe isotope standard and measured at 5.9 keV. The X-ray tube used during the study was K 5012 SV with tungsten anode. The soil sample was presented to the spectrometer in a sample cup with ultra thin mylar film beneath it for minimization of X-ray attenuation [20]. The data was collected under the conditions given in Table-1 and processed with the help of a dedicated computer using the XFF/FLS computer software prepared by M/s Links System, U.K. The determined composition of the soil is given in Table-2.

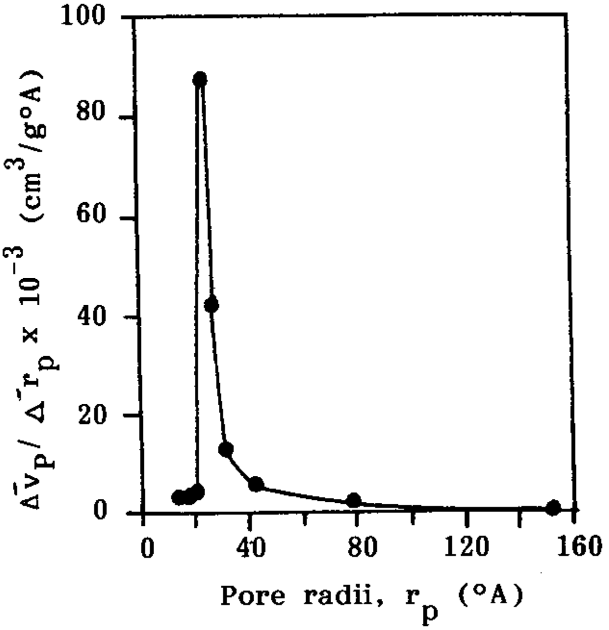

Fig.4: Pore size distribution curve for Ludwa soil.

X-ray diffraction study

Diffraction pattern of the soil was obtained with a Philips PW 1060/70 diffractometer goniometer. The detector was an argon filled proportional counter linked to a PW1390 rate meter and channel analyzer. The radiation was CuKα (1.5418 Å) generated in a Philips PW 1730 generator operated at 36 kV and 30 mA. Diffraction pattern reproduced in Figure 1 was obtained by reflection from the surface of powder sample spread on cellophane tape.

Table-1: Instrumenal parameters.

Instrument	EDXRF - XR-500
Detector	Si(Li)
Tube	W
Voltage	20 kV
Current	0.01 mA
Collimator	Fine
Vacuum	On
Dc Pulse mode	On
Spinning mode	On
Range	20 keV
Peak time	20 µ sec.
Software	XFF/FLS.

Table-2: Chemical composition of Ludwa soil determined by EDXRF spectrometer.

SiO_2	88.44%
Al_2O_3	10.25%
CaO	0.24%
CuO	0.28%
Fe_2O_3	0.15%
CoO	0.03%
MnO	0.01%

Nitrogen adsorption

The nitrogen adsorption study on soil surface was carried out using Quantasorb sorption system (M/S Quanta Chrome Corporation N.Y.) by continuous flow method [21]. The processes of adsorption and desorption were monitored by measuring the change in the thermal conductivity of the gas mixture (N_2/He). The thermal conductivity of the gas mixture was monitored differentially by thermal conductivity cell place before and after the sample cell. A mixture of nitrogen (adsorbate) and helium (carrier) of known concentration was passed over a sample previously outgassed at 100°C by heating. The adsorption was started by immersion of the sample cell containing known amount of soil in a liquid nitrogen coolant. The adsorption peak was produced by the change in the thermal conductivity of the gas mixture resulting from a decrease in nitrogen concentration due to adsorption on soil. The adsorbed nitrogen was then desorbed by removing the coolant and the liberated nitrogen monitored by thermal conductivity detector. The volume of adsorbed nitrogen was calculated. The same measurements were carried out at different N_2/He ratios obtained by adjusting the gas flow rates and data points were obtained to construct the entire adsorption/desorption isotherm shown in Figure 2.

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