Research Journal of Chemical Sciences ISSN 2231-606X
Vol. **3(9),** 10-17, September **(2013)** *Res. J. Chem. Sci.*

Spectro-Chemical Characterization of Rangpur (Sabjibari) Soil Fractions of Bangladesh

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Available online at: www.isca.in
Received 9th July 2013, revised 27th August 2013, accepted 12th September 2013

Abstract

Rangpur (Sabjibari) soil was fractionated to three different fractions as sand (≥140 μm), silt (53~140μm) and clay (≤53μm) based on particle size using hydrometer method. These three fractions were characterized by LIBS (Laser induced breakdown spectroscopy), XRD (X-Ray diffraction) and FT-IR (Fourier transform infra-red spectroscopy). pH_{zpc} (Zero point charge pH) of clay and silt were also determined by titrimetric method. According to the results of LIBS Fe, Si, Cu, and Na are present in all fractions with different oxidation state. Ti is the only element which is present in clay fraction. XRD analysis indicates that d-values of the soil fractions are not similar to the d-values of any of clay minerals kaolinite, quartz, chlorite and illite. FT-IR spectra of all fractions show the presence of Zn=O, O-H, Al-O-Si, Fe-O, Al-OH and Si-O bonds with different vibrational modes. The pH_{zpc} value of silt and clay were obtained as 6.35±0.02 and 5.98±0.02 respectively suggesting that silt surface is neutral but the surface of clay is slightly acidic.

Keywords: Rangpur (Sabjibari) soil, sand, silt, clay, characterization, LIBS, FT-IR, XRD, pH_{zpc}.

Introduction

Many investigators[1-3] fractionated soil into different categories. Based on particle size, three different fractions as sand, silt and clay can be obtained from soil. Clay minerals are generally defined as very fine grained, natural, earthy material aggregates consisting essentially of the hydrous silicate of alumina. This hydrous silicate becomes hard when dried or fired. Sometime the aluminum silicate contains variable amounts of iron, magnesium, alkali metals, alkaline earths and other cations having structural similarity to the micas and form flat hexagonal sheets[4]. Sand is a naturally occurring granular material composed of finely divided rock and mineral particles. The composition of sand is highly variable, depending on the local rock sources and conditions, but the most common constituent of sand in inland continental settings and non-tropical coastal settings is silica (silicon dioxide, or SiO_2), usually in the form of quartz[5]. Sand is generally non-toxic but sand-using activities such as sandblasting require precautions. Bags of silica sand used for sandblasting now carry labels warning the user to wear respiratory protection to avoid breathing the resulting fine silica dust[6]. Silt is created by a variety of physical processes capable of splitting the generally sand-sized quartz crystals of primary rocks by exploiting deficiencies in their lattice[5]. These involve chemical weathering of rock and regolith, and a number of physical weathering processes such as frost shattering and holoclast[7]. The main process is abrasion through transport, including fluvial comminution, aeolion, attrition and glacial grinding[8]. Mineralogically, silt is composed mainly of quartz and feldspar. Clays are formed by alteration, through aging and weathering of rocks such as granite and other igneous rocks containing feldspar, mica, quartz and accessory minerals including kaolinite, quartz, calcite, limonite, gypsum and muscovite. At their origin they are known as residual or primary clays[9]. In recent years, soil's fractions are important in many different fields such as agriculture, oil drilling and the building industry. Owing to some physicochemical characteristics like high surface area, high cation exchange capacity, clay minerals adsorb pollutants very easily. Among the studied clays, the montmorillonite have received considerable attention of scientists as adsorbent[10-13]. Soil can be characterized by several analytical techniques. Biswas and Basak characterized Bijoypur soil by IR spectra[14]. Many researcher characterized soil fractions by different analytical techniques[15-22].

The objective of the present work was to characterize the sand, silt and clay obtained after fractionation of locally collected Rangpur (Sabjibari) soil by LIBS, FT-IR, XRD and to characterize the surface of silt and clay by pH_{zpc}.

Material and Methods

Fractionation of Soil: The soil sample was collected from Sabjibari, Rangpur which is situated in North-West part of Bangladesh. Sample was sundried, powdered and stored in a plastic bottle. Sand, Silt and Clay were obtained from the fractionation of soil sample using Hydrometer method[1]. Due to the diffuse boundary between clay and silt, the separation of these two fractions with 100 percent accuracy was not practically possible. Clay might contain about 5 % silt when physically separated from silt.

Characterization of Sand, Silt and Clay: LIBS: To prepare the sample for LIBS, about 0.5-1.0g of sample (sand, silt and clay) was mixed with 1-2 drops of glue and small pellet was made. This was air dried before use. LIBS spectra were taken in the spectral range of 200-900 nm using two gratings. One was 2400 ruling/mm grating blazed at 240 nm (for 200-350 nm) and the second one was 600 ruling/mm grating blazed at 500 nm (for 350-900 nm). These data are shown in table 1.

FT-IR: FT-IR spectra of sand, silt and clay were taken from the Centre of Excellence, University of Dhaka. This was carried out by Shimadzu-FT-IR spectrometer (IR Prestige-21) equipment using potassium bromide pellet. The pellet was prepared by mixing 1.0 mg of finely ground dry sample and 200.0 mg of spectroscopic grade dry KBr. The spectra were recorded over the range of 400 - 4000 cm^{-1} with 2 cm^{-1} resolution. Normally, 10 scans were recorded. Spectrum and date are presented in figure 1-3 and table 2.

XRD: X-ray powder pattern of samples (sand, silt and clay) were obtained from Philips PW-1380 X-ray generator operating at 40 kV and 30 mA and an XDC-700 Guinier- Hägg focusing camera using $Cuk_{\alpha 1}$ radiation. An exposed time of 1 hour was used and the films were processed using commercially available developer and fixer. The d-values of the diffraction lines in the films were calculated manually and presented in table 3.

Determination of zero point charge pH: The pH of silt and clay surface at zero point charge (pH_{zpc}) was determined by the method suggested by Huang and Ostovic[23]. The zero point charge pH of solid substance (pH_{zpc}) means the pH at which the positive and negative charges in the surface are equal. 0.1 g of sample was added to four identical portions of 40 mL 0.1 M NaCl solution of pH 7 (pH measured by pH meter, HM-26S, TOA Electronics Ltd, Japan; with a combination GST-5311C,TOA electrode) and bottles were agitated for 24 hours in thermo mechanical shaker (SWB-20, HAAKE, Fisons Ltd, Germany). Two bottles of suspension were titrated with 0.05 M HCl and 0.05 M NaOH separately using micro burette (±0.01 mL). During the titration, the constant pH reading was taken carefully. From other two bottles, the supernatants after filtration were titrated with acid and alkali as described above. pH data both for filtrate and supernatant were plotted against the volume of acid and alkali in the same graph. From the graph, pH and corresponding mean volumes were estimated. Mean volumes were the differences between either the volume of acid and alkali or vice versa. The experiment was repeated with 0.01 M NaCl solution. The plot of pH versus mean volume of acid and alkali added producing two titration curves as shown in figure 4 and 5, meeting at a point defined as zero point charge pH.

Results and Discussion

Elemental analysis by LIBS: LIBS was used to know the presence of elements with different oxidation states in the sand, silt and clay. Table 1 shows the list of elements present in sand, silt and clay fractions (NIST Atomic Spectra ref. data 2010)[24].

Table-1
Characteristic emission lines of elements present in Rangpur (Sabjibari) soil fractions

Soil fraction	Element*	Characteristic emission lines (wavelength, nm)
Clay	Si(0)	212.39, 221.65, 243.49, 263.12, 568.86
	Ti(0)	334.74, 453.41, 498.12, 720.78
	Cu(II)	518.26, 766.36
	Na(I)	285.28, 588.88, 589.50, 818.15, 819.29
	Fe(0)	251.63, 293.68, 296.68, 297.31
	Fe(II)	234.34, 234.82, 238.20, 241.05, 252.87, 274.94, 275.58
Silt	Si(II)	205.84, 212.39, 221.65, 243.49, 263.123
	Fe(0)	251.67, 293.68, 296.67, 297.31, 373.63
	Fe(II)	234.34, 234.82, 238.20, 241.03, 252.89, 274.94, 275.58
	Cu(II)	518.26, 766.37
	Na(I)	285.25, 589.23, 818.20, 819.33
Sand	Si(0)	212.39, 221.08, 221.65, 243.49, 263.12, 298.76
	Si(II)	205.84, 207.25, 438.22
	Fe(0)	237.36, 251.67, 252.44, 293.68, 296.67, 297.31, 373.63, 375.78, 794.69
	Fe(II)	234.34, 234.82, 238.20, 241.03, 243.48, 274.94, 275.58
	Cu(II)	518.23, 766.39
	Na(I)	588.88, 589.50, 769.75, 818.20, 819.35

* 0, I, and II imply neutral, single and double ionized states of the atoms respectively

Table-2
Comparative FT-IR analysis for Rangpur (Sabjibari) soil fractions

Functional group	Sand (Present research) (cm^{-1})	Silt (Present research) (cm^{-1})	Clay (Present research) (cm^{-1})	Standard FT-IR spectra[25-26] (cm^{-1})	Kaolinite[27] (cm^{-1})	Quartz, Bijoypur Sand[22]
O-H (stretching vibration)	-	3623	3471, 3416	3710-3200	3694, 3671, 3652, 3620	-
Zn=O (plane bending)	1617	1623	1639, 1624	1650-1350	-	-
Si-O (plane bending)	1080, 1033	1078, 1024	1026	1150-900	1116, 1099, 1035, 1011	1031, 1006
Al-OH (bending)	-	912	-	950-900	913	-
Gibbsite-like vibration	778, 694	759, 691	778, 694	800-690	797, 701	-
Al-O-Si (skeletal vibration)	462	530,466	530, 489	550-450	544, 473	-

Table-3
XRD data of Rangpur (Sabjibari) soil fractions along with the data from JCPDS for kaolinite, quartz, chlorite and illite

d-values of sand A^o	*d*-values of silt A^o	*d*-values of clay A^o	*d*-values of Kaolinite A^o	*d*-values of Quartz A^o	*d*-values of Chlorite A^o	*d*-values of Illite A^o
6.65	4.34	4.33	7.10	4.32	7.70	10.0
4.35	4.21	4.23	4.41	3.38	4.78	5.02
4.21	3.34	3.31	3.56	2.50	4.44	4.48
2.49	2.53	1.98	2.55	2.30	3.50	4.44
1.99	2.33	1.42	2.49	2.16	2.56	3.46
1.85	2.26	-	2.43	2.01	2.50	3.34
1.71	2.17	-	2.38	1.84	2.34	3.20
1.54	2.01	-	2.33	1.70	1.98	2.99
1.40	1.87	-	2.20	1.57	1.66	2.56
-	1.75	-	1.98	-	-	2.00
-	1.58	-	1.79	-	-	1.49
-	1.41	-	1.67	-	-	-
-	-	-	1.66	-	-	-
-	-	-	1.54	-	-	-
-	-		1.49	-	-	-

It can be concluded from the qualitative study of the emission spectra in table 1 that, sand fraction contains a high proportion of Si (0 and II), Fe (0 and II), Cu (II) and Na (I). Silt fraction also contains a high proportion of Si (II) and Fe (0 and II). Cu (II) and Na (I) are also present in silt. Clay fraction contains a high proportion of Si (0) and Fe (0 and II). Ti (0), Cu (II) and Na (I) are also present in clay. Comparing these results with that of Bijoypur soil fractions[20-22] the remarkable differences are found in elemental analysis between both the soil fractions. Rangpur soil fractions spectra show lesser number of lines for Ti, Si and Fe than Bijoypur soil fractions. Characteristic emission lines for F, I, Tc, Pu and Ni are observed in Bijoypur sand and spectral lines of Zn (I) are found in Bijoypur silt but those are not found in any fraction of Rangpur soil. Zn (I), Sn (0) and Co (0 and II) are present in Bijoypur clay but not in Rangpur clay.

Bond patterns and vibrational mode analysis by FT-IR: Figure 1-3 shows the FT-IR spectrum of sand, silt and clay respectively. Vibrational modes for different functional groups are compared with standard FT-IR data[25-26] and are presented in table 2. The spectral data are also compared with that of Kaolinite obtained from Adrian and Kelleher[27] (column 6) and Quartz (Bijoypur Sand)[22] (column 7). The results in columns 2, 3 and 4 of table 2 shows the data of sand, silt and clay respectively and these are compared with the standard spectral data.

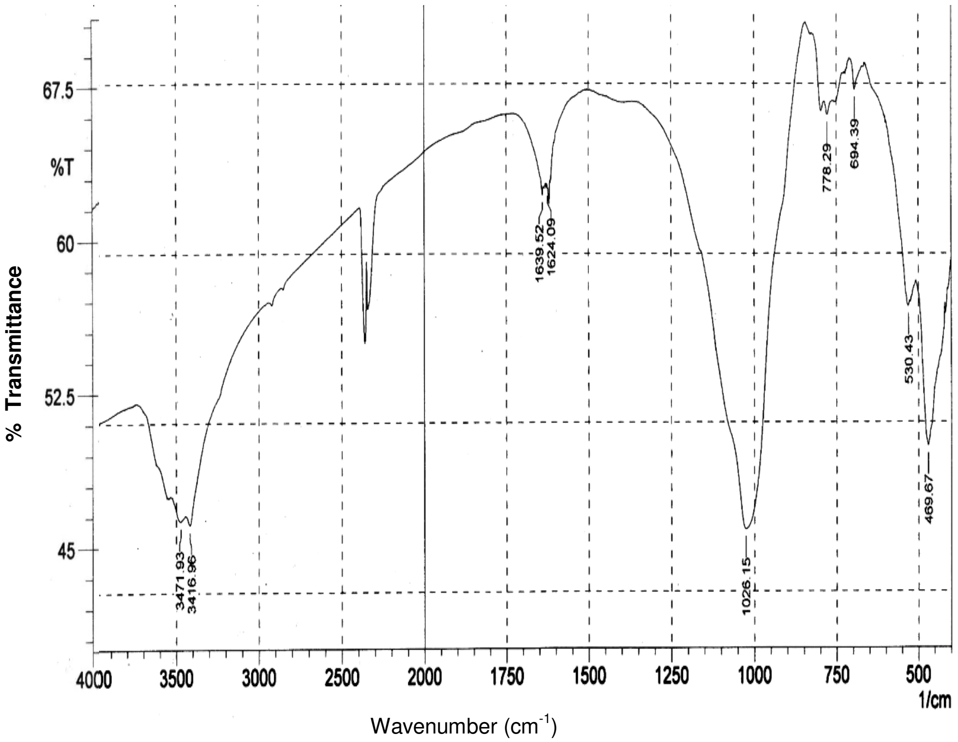

Figure-1
FTIR spectra of Rangpur (Sabjibari) clay fraction

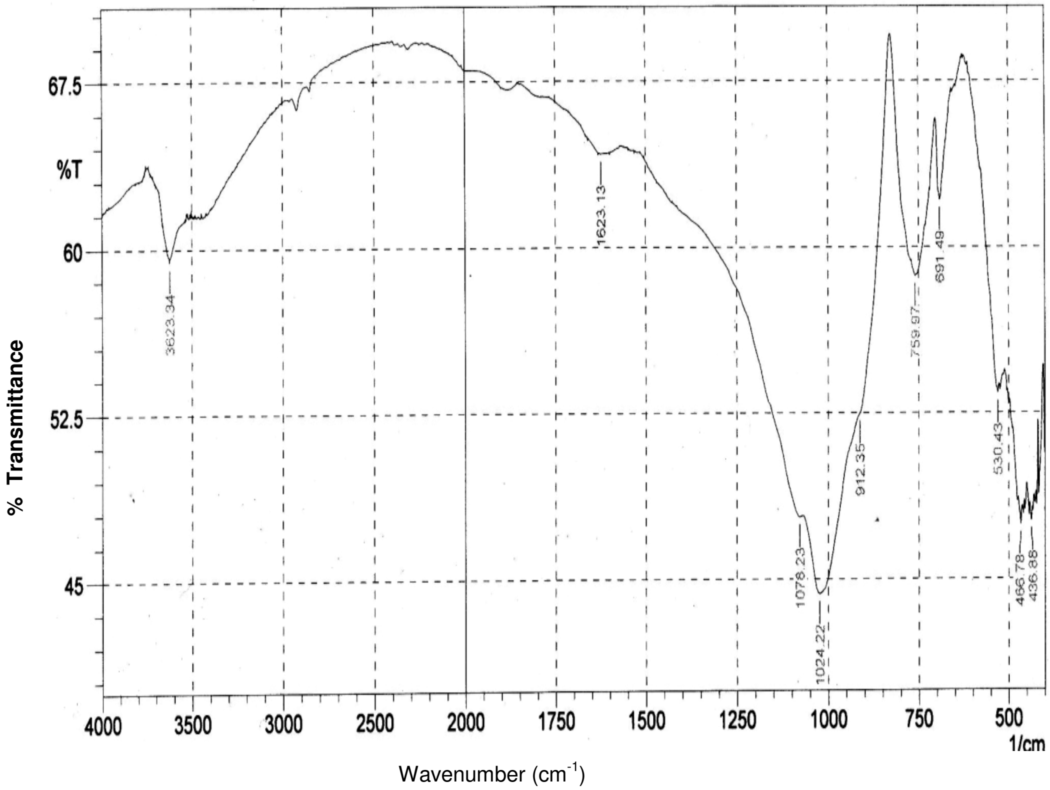

Figure-2
FTIR spectra of Rangpur (Sabjibari) silt fraction

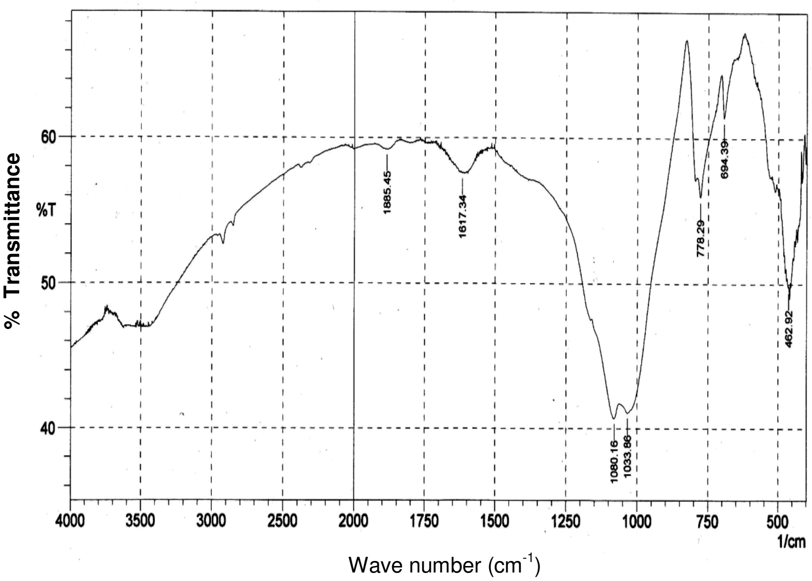

Figure-3
FTIR spectra of Rangpur (Sabjibari) sand fraction

Two peaks for clay corresponding to 3471 cm^{-1} and 3416 cm^{-1} and one peak for silt corresponding 3623 cm^{-1} are due to stretching vibration of O-H bond. The plane bending vibration due to the presence of Si-O bond is indicated by the presence of peaks 1080 cm^{-1} and 1033 cm^{-1} for sand, 1078 cm^{-1} and 1024 cm^{-1} for silt and 1026 cm^{-1} for clay. The bending vibration of Al-OH corresponds to 912 cm^{-1} in silt. Gibbsite like vibration is also present in all fractions corresponding to 778 cm^{-1} and 694 cm^{-1} in sand, 759 cm^{-1} and 691 cm^{-1} in silt and 778 cm^{-1} and 694 cm^{-1} in clay. Skeletal vibration due to Al-O-Si bond is suggested by the presence of peaks 462cm^{-1} in sand 530 cm^{-1} and 466 cm^{-1} in silt and 530 cm^{-1} and 489 cm^{-1} in clay. The presence of plane bending vibration due to Zn=O bond corresponding to 1617 cm^{-1} and 1623 cm^{-1} in sand and silt respectively. The presence of plane bending vibration due to Zn=O bond corresponding to 1639 cm^{-1} and 1624 cm^{-1} in clay. These information suggest that the frequency of O-H stretching vibration present in silt and clay are comparable with that present in kaolinite. The frequencies of plane bending vibration due to Si-O found in all fractions of soil are close to that observed in quartz. The frequency of Al-OH bending found in silt is very close to that present in kaolinite. Gibbsite like vibration frequency and Al-O-Si vibration frequency found in all fractions are comparable to that present in kaolinite. Observing these it can be inferred that kaolinite is present both in silt and clay. Quartz is found in all fractions of soil. Sand, silt and clay show the presence of plane bending vibration of Zn=O bond but this was not found neither in kaolinite sample by Adrian and Kelleher[27] nor in Quartz (Bijoypur sand)[22].

Phase analysis of sand by XRD: XRD method was used to identify the crystalline property of the samples. The d-values of XRD pattern of sand, silt and clay were estimated and compared with the standard values of kaolinite, quartz, illite and chlorite supplied by JCPDS (Joint Committee on Powder Diffraction Standards)[28]. The values are shown in table 3.

The present sand sample shows 9 (nine) different *d*-values within the range of 6.58 to 1.40 A^o. In case of silt 12 (Twelve) *d*-values are found within the range of 4.34 to 1.41 A^o and for clay 5 (five) *d*-values are found within the range of 4.33 to 1.42 A^o. Some *d*-values are missing in sand and clay. From the comparative table 3, it can be concluded that sand contains dominantly quartz, (Silicon oxide, SiO_2), chlorite, (Sodium Aluminum Silicate Hydroxide Hydrate, $Na_{0.5}Al_6\ (Si,Al)_8\ O_{20}\ (OH)_{10}.H_2O$) and illite, (Potassium Aluminum Silicate Hydroxide, $(K,\ H_3O)Al_2Si_3AlO_{10}(OH)_2$ and trace amount of kaolinite type of mineral (aluminum silicate hydroxide, $Al_2Si_2O_5(OH)_4$). Again from table 3, it can be inferred that present silt is mainly quartz containing poor amount of chlorite and illite, trace amount of kaolinite type of mineral and present clay resembles to silt but some line are missing here due to fractionation . However these observations are in agreement with that obtained from FT-IR.

Zero point charge pH of silt and clay: The pH of zero point charge is the pH of the solution in which the charges on the surface (-ve or +ve) are balanced by the addition of acid or alkali. In figures 4 and 5 the point of intersection of two curves is the pH_{zpc} of silt and clay. These were estimated as 6.35±0.02 and 5.98±0.02 for silt and clay respectively. The values are close to the pH_{zpc} of Bijoypur silt[21] 6.39±0.02 and Bijoypur clay[20] 6.40±0.02.

The pH_{zpc} of silt and clay suggest that the surface of samples acts as a positive charge at pH_{zpc} and below, whereas negative charge at pH higher than pH_{zpc}. The surface of silt and clay are almost neutral and the cationic adsorbate would favor basic medium and anionic adsorbate would favor acidic medium[12-13].

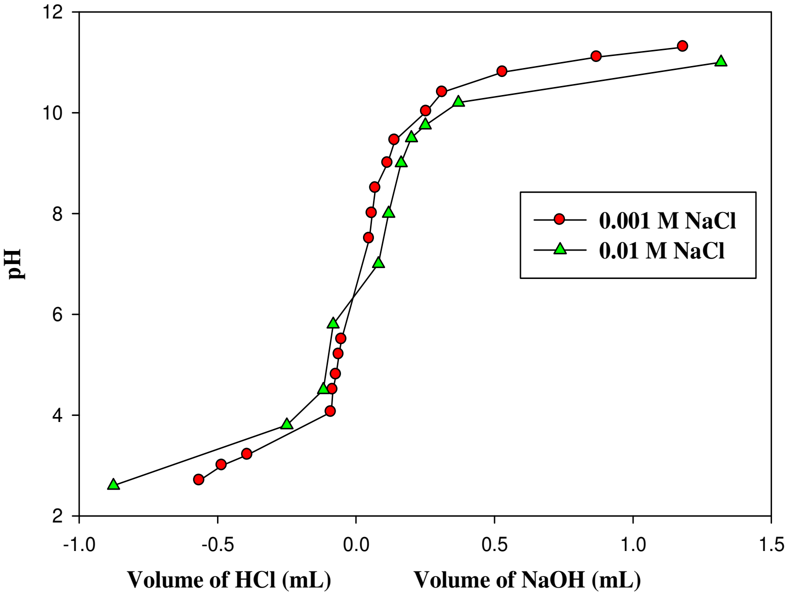

Figure-4
Net titration curves for silt in presence of different concentration of NaCl

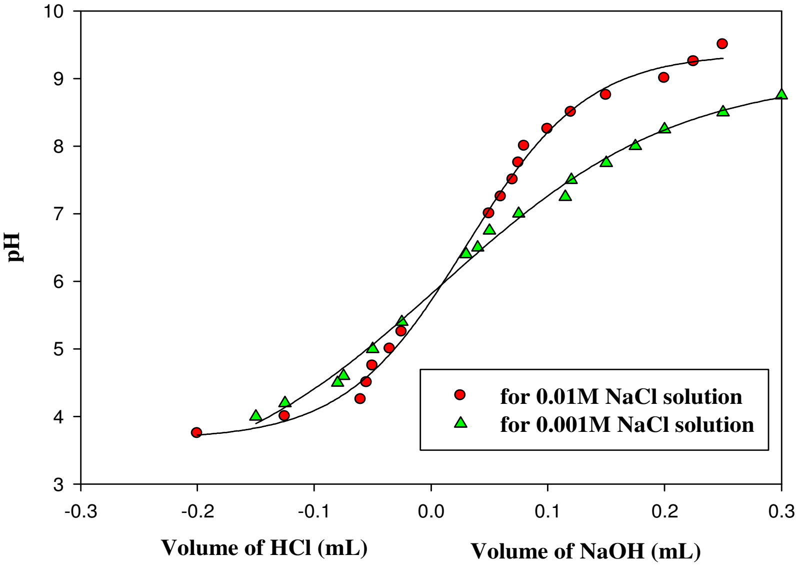

Figure-5
Net titration curves for clay in presence of different concentration of NaCl

Conclusion

The analytical results show that sand, silt and clay obtained from fractionation of Rangpur (Sabjibari) soil contains many metals (Si, Fe, Al and Zn) bonded with oxygen. LIBS spectra show the presence of many elements (Si, Fe, Na, Cu and Ti) with various oxidation states. FT-IR spectra give the evidences of different bonding structure (Si-O, O-H, Al-O-Si, Fe-O, Al-OH and Zn=O). FT-IR spectra, XRD lines and *d*-values indicate that sand fraction of Rangpur (Sabjibari) soil is closely resembled to quartz. This analysis also indicates that silt and clay contain quartz and kaolinite. pH_{zpc} of silt and clay are obtained as 6.35±0.02 and 5.98±0.02 respectively suggesting the poorly acidic nature.

Acknowledgement

The authors are highly grateful to Professor Dr. A F M Yousuf Haider, Department of Physics, University of Dhaka for his co-operation in conducting the LIBS experiments and also highly obliged to Professor Dr. Md. Akhter Hossain Khan, Department of Soil, Water and Environment, University of Dhaka for his co-operation in soil fractionation procedure. The authors are also grateful to the Chairman, Department of Chemistry, University of Dhaka, Bangladesh for provided facilities to performed the research.

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