

Research Article Physicochemical Properties and Surface Charge Characteristics of Arid Soils in Southeastern Iran

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The majority of previous studies on surface charge characteristics were done on tropical and subtropical soils. Information of such studies in the arid regions is limited. A study was conducted to investigate the relation between soil chemical and mineralogical properties and surface charge characteristics of an arid region in Southeastern Iran. Eight soil pedons, representing the alluvial and the colluvial deposits, were described, and their mineralogical and physicochemical properties were examined. The common clay minerals in the studied area are smectite, palygorskite, kaolinite, chlorite, and illite. The point of zero charge (pH₀) values are low (2.85–3.35) in all soils mostly affected by organic carbon (OC) and free iron oxide (Fe_d). pH₀ has a significant negative correlation with pH under field conditions ($r = -0.45^*$, P < 0.05). The point of zero net charge (PZNC) levels for all the soils were <2, due to the excess negative charge in these soils. The estimated PZNC values were less than pH₀ in all soils because of the high permanent negative charge in these soils. The permanent negative charge (σ_p) of the soils studied is high and it has a significant positive correlation with pH, CEC, Na, Mg, SAR, clay content, palygorskite, OC, and Fe_d.

1. Introduction

Soil surface charges affect the chemical properties of soil by varying the quantity of electric and surface charge density. Surface charge properties have an important bearing on the migration of ions in soil, the formation of organomineral complexes, soil structure, plant nutrition, and the dispersion, flocculation, swelling, and shrinkage of the soil fractions [1]. Based on differences in the surface properties, soils can be classified into two basic categories: permanent-charge soils and variable-charge soils [2, 3].

Point of zero charge (PZC) often denoted as pH_0 is one of the most important parameters used to describe variablecharge surfaces [4]. Uehara and Gillman [5] indicated that pH_0 is the pH where the amounts of negative and positive charge of variable charge components where these are equal. The pH₀ value for the temperate region of Iran was reported in the range of about 2.6 to 3.75 [6]. Anda et al. [7] reported that the pH₀ of three Oxisols in Malaysia was about 3.9 to 5.7. The previous studies showed that the pH₀ values decrease with increasing organic matter content and increase with increase in sesquioxides [6-8]. Taubaso et al. [9] reported that the pH₀ values of Argentinean provinces soils were smaller than the pH in water, indicating that these soils had negative charge under natural conditions.

Gonzales-Batista et al. [10] reported that for systems free of permanent charge, the point of zero net charge (PZNC) should coincide with pH_0 , but for systems where permanent and variable charges coexist, PZNC may differ from pH_0 . Usually in the young soils (Entisols or Inceptisols) PZNC is lower than its pH_0 and higher than pH_0 if the soils are highly weathered, such as Oxisols [9]. In addition, the model of Uehara and Gillman [11] and Yu [2] predicts that in soils having permanent negative charge, the PZNC value is lower than the pH_0 and vice versa.

Most studies on soil surface charge properties were conducted in tropical and subtropical regions where the soils are poor and low in negative charge. In Iran, Sharami et al. [6] conducted similar study for temperate soils of the Northern region but no study was done on arid regions of Southern Iran or elsewhere in the world. The electrochemical properties of soils are useful fundamental knowledge in solving the fertility problems of soils of the arid regions. For example, in the arid regions, the NH₄⁺ fixed by soil particles and leached out as NO₃⁻ form due to high permanent negative charge in the surface of soil particles [12] in comparison with highly weathered soils where NO₃⁻ leaching because of high positive charge present in the soils [13]. The objectives of this study were to determine the physicochemical and mineralogical properties, the pH₀, PZNC, and permanent negative charge (σ_p) and to determine the relation between pH₀ and σ_p with characteristics of arid soils in Southeastern Iran.

2. Materials and Methods

2.1. Description of the Study Area. The studied area is located in the province of Hormozgan, Southeastern Iran, between latitude 28°8' and 28°15' North and longitudes 56°5' and 56° 15' East (Figure 1). The climate is arid with an average annual precipitation of about 162 mm and evaporation of 4243 mm. Burdon [14] reported that the estimated potential evapotranspiration could be in excess of 50 times the mean annual precipitation. The temperature regime is hyperthermic with an aridic and ustic moisture regimes [15]. The sedimentary rocks accompanying marine deposits of the Tertiary age formed the catchment area, which is predominantly composed of thick alluvial and colluvial materials occasionally deposited by the Dehshaykh River for the past thousands of years. The river is dry most of the time except during heavy downfall. The catchment is currently cultivated with wheat, maize, potato, and watermelon as important agricultural crops [16].

Eight pedons were selected among the dug profiles representing alluvial fan and colluvial deposits along the slope area of the catchment by geopedology approach and different soil horizons were sampled for laboratory analysis. The morphological properties of the soils were described in the field [17] and were classified according to the USDA Soil Taxonomy [18].

2.2. Methods

2.2.1. Physical and Chemical Analyses. Field study and samples collection were carried out in the summer season of 2009 (August to September). The soil samples were air-dried and sieved with a 2 mm sieve and kept in plastic bags prior to analysis.

The particle size analysis was carried out by the pipette method [19]. Organic matter content of the soil was determined by the wet combustion procedure of Walkley and Black [20] and Fe₂O₃ was estimated by the dithionite-citratebicarbonate method [21]. The pH was measured in the supernatant suspension of 1:1 soil : water suspension pH [17], 1:2.5 liquid 0.01 M CaCl₂ solution (pH_{CaCl₂}) [22] and 1:2.5 soil : H₂O (pH_{H₂O}), and 1:2.5 soil : 1 M KCl solution (pH_{KCl}) [23]. The bulk density (ρ_b) was estimated by core method [24], and the electrical conductivity (EC) analysis was measured in the saturated extract [25]. The calcium carbonate equivalent (lime) was measured by acid neutralization [26]; exchangeable cations content and the cation exchange capacity (CEC) of the soils were determined by the 1 M ammonium acetate



FIGURE 1: Location of the study area.

(pH 7) method. The exchangeable cations (Ca²⁺ and Mg²⁺) in the leachate were determined by atomic absorption spectrophotometer (AAS, Perkin-Elmer, 047-1705), whereas K⁺ and Na⁺ were measured by flame spectrophotometer. The soil solution data (Na⁺, Ca²⁺, Mg²⁺ given in cmol_ckg⁻¹) was used to calculate the sodium adsorption ratio (SAR), where SAR = Na⁺[(Ca²⁺ + Mg²⁺)/2]^{-0.5}.

2.2.2. Determination of Point of Zero Charge. Point of zero charge (PZC), denoted as pH_0 , is defined as the pH at which the net charge on the variable charge components is zero and was determined according to the method of Gillman and Sumner [27]. Six portions of 2 g of 2 mm air-dried samples were weighed into 50 mL plastic centrifuge tubes and shaken with 20 mL of 0.1 M CaCl₂ for 2 h to saturate the soil with Ca. The suspension was centrifuged (3000 rpm, 10 min) and the supernatant was discarded. The Ca saturated soil was washed twice with 20 mL of 0.002 M CaCl₂ and after the third addition of 20 mL of 0.002 CaCl₂, the pH was adjusted to six values of 0.1 M HCl in the range of 3.5 to 6 mL by dropwise addition. Equilibration of the pH took several days. When equilibrium occurred for 0.002 M CaCl₂, the pH was recorded as $pH_{0.002}$, then 0.5 mL of 2 M CaCl_2 was added to each sample and shaken for 3 h, and pH was recorded thereafter and designated as $pH_{0.05}$. For each tube, δpH was calculated as $(pH_{0.05} - pH_{0.002})$. The pH_0 was obtained from the plot of δpH against $pH_{0.002}$. The pH_0 was identified as the point where δpH was zero.

2.2.3. Determination of Point of Zero Net Charge. The point of zero net charge (PZNC), the pH at which net surface charge of the whole system (taking into account both permanent and variable charge colloids) is zero, was obtained by interpolation of the data from the measurement of charge variation with pH. Charge variation with pH was determined by the fingerprint method of Gillman and Sumner [27]. Two-gram air-dried soil samples in 50 mL preweighed plastic centrifuge tubes were shaken with 20 mL of 0.1 M CaCl₂ for 2 h to saturate the soil with Ca. The suspension was

Pedon	Soil classification	Relief	Physiography	Land use	Parent material	Drainage
1	Fine loamy, mixed (calcareous), hyperthermic, Calcic Haplosalids	Flat	Piedmont alluvial plain	Saline pasture	Calcareous alluvium	Imperfectly drained
2	Coarse loamy, mixed (calcareous), hyperthermic, Aridic Ustorthents	Almost flat	River alluvial plain	Bare	Calcareous alluvium	Well drained
3	Fine loamy, mixed (calcareous), hyperthermic, Aridic Ustifluvents	Almost flat	Piedmont alluvial plain	Plowed	Calcareous alluvium	Moderately well drained
4	Loamy skeletal, mixed (calcareous), hyperthermic, Aridic Ustifluvents	Almost flat	Piedmont alluvial plain	Harvested wheat	Calcareous alluvium	Well drained
5	Sandy skeletal, mixed (calcareous), hyperthermic, Aridic Ustifluvents	Almost steep	Alluvial-colluvial fan	pasture	Calcareous alluvium	Well drained
6	Coarse loamy, mixed (calcareous), hyperthermic, Aridic Ustorthents	Flat	River alluvial plain	Plowed	Calcareous alluvium	Moderately well drained
7	Fine loamy, mixed (calcareous), hyperthermic, Aridic Ustifluvents	Almost flat	Piedmont alluvial plain	Plowed	Calcareous alluvium	Well drained
8	Sandy skeletal, mixed (calcareous), hyperthermic, Aridic Ustorthents	Almost steep	Alluvial-colluvial fan	Pasture	Calcareous alluvium	Well drained

TABLE 1: General information on the studied pedons.

centrifuged (3000 rpm, 10 min) and the supernatant was discarded. The Ca saturated soil was washed twice with 20 mL of 0.002 M CaCl_2 and after the third addition of 20 mL of 0.002 M CaCl_2 soil suspension was recorded, and thereafter the pH was adjusted to different values by dropwise addition of 0.1 M HCl or saturated Ca(OH)₂. The equilibration of the pH took several days. After the pH was stable, the suspension was centrifuged and the supernatant was collected to determine Ca, Al, and Cl in the entrained solution. The tubes were then weighed to estimate the volume of entrained 0.002 M CaCl₂.

The soil was then extracted with 20 mL of 1 m NH_4NO_3 , and Ca, Al, and Cl were determined in the extract. Allowing for entrained Ca, Al, and Cl, the amounts of cation ($Ca^{2+} + Al^{3+}$) and anion (Cl^-) adsorbed were calculated and equated with total negative (CEC_T) and positive (AEC) charge, respectively. The amount of Ca adsorbed was equated with basic cation exchange capacity (CEC_B). Aluminum and Ca were determined by AAS and Cl measured by silver nitrate titration method [28]. The PZNC was identified as the pH value where total negative and positive charges are equal. The permanent charge was estimated as the difference between AEC and CEC_T values at pH_0 [29].

2.2.4. Mineralogical Analyses. Removal of chemical cementing agents and separation of the different size fractions of soils were carried out according to Mehra and Jackson [21], Kittrick and Hope [30], and Jackson [31]. Organic matter and carbonate were removed with 30% H_2O_2 and 1 N HCl, respectively. X-ray diffraction (XRD) studies were carried out on both fine and coarse clay fractions, while equal concentrations of clay suspensions were used for all samples in order to allow for a more reliable comparison between relative peak intensities for different samples. Two drops of the prepared suspension were used on each glass slide. The clay samples were finally examined by XRD analysis using a Philips diffractometer with Co Ka radiation in order to allow for a more reliable comparison between the relative heights of peaks in the XRD data. The K-saturated samples were studied both after drying and heating at 500°C for 4 h to identify kaolinite in the presence of trioctahedral chlorite, and samples were also treated with 1 N HCl at 80°C, overnight. Semiquantitative estimation of clay minerals was made by directly converting the diffraction peak areas using the method of Karanthanasis and Hajek [32]. Selected dried clay particles of the soils were studied under a transmission electron microscope (TEM, LEO 912 AB). The samples dispersed in 100% alcohol and 100 μ L of the suspension was dropped on formvar-coated Cu grids.

The soil chemical and mineralogical properties and their relationship with the surface charge characteristics were analyzed by multiple and simple linear regression using SAS and Excel softwares.

3. Results and Discussion

3.1. Field Observation and Soil Classification. The soil chemical data are shown in Table 1. Pedons 1, 3, 7, and 4 are soils developed on the piedmont alluvial plains while pedon 2

Soil number	Depth (cm)	Clay	Silt (%)	Sand	Texture ⁺	Structure*	$\rho_b (\mathrm{gcm^{-3}})$	Gravel (%)
	0-25	34	56	10	SiCL	WP	1.54	_
1	25-78	14	36	50	L	Ma	1.50	_
1	78-110	32	48	20	CL	WG	1.53	—
	100-150	12	22	66	SL	Ma	1.51	—
	0-20	10	40	50	L	WP	1.52	_
2	20-50	10	8	82	LS	Sg	1.53	—
2	50-100	12	16	72	SL	Sg	nd	35
	100-150	8	2	90	S	Sg	1.36	—
	0-30	18	38	44	L	WG	1.44	_
3	30-80	16	37	47	L	WG	1.40	—
	80-150	16	12	72	SL	Sg	1.49	—
	0-20	10	16	74	SL	Sg	nd	30
4	20-70	8	16	76	SL	Sg	nd	50
7	70-95	14	12	74	SL	Sg	nd	10
	95-150	12	4	84	LS	Sg	nd	50
5	0-45	18	20	62	SL	Sg	nd	85
5	45-150	24	20	56	SiL	Sg	nd	65
	0-42	16	34	50	L	WG	1.41	_
6	42-88	10	12	78	SL	Ma	1.37	—
	88-150	12	26	62	SL	Ma	1.41	—
	0-36	24	42	34	L	WG	1.35	_
7	36-86	30	50	20	CL	WG	1.39	_
	86-150	26	38	36	L	WG	1.41	—
	0-30	12	14	74	SL	Sg	nd	70
8	30-70	10	8	82	LS	Sg	nd	75
	70–150	14	14	72	SL	Sg	nd	80

 TABLE 2: Some physical properties of the representative profiles.

Texture⁺: SL: sandy loam, LS: loamy sand, L: loam, S: sand, SiL: silty loam, SiCL: silty clay loam. Structure^{*}: Ma: massive, Sg: single grain, WP: weak platy, WG: weak granular, nd: no determine.

and 6 are formed on river alluvial plains. Pedons 5 and 8 are formed on alluvial colluvial fans and sited on a higher slope area. All pedons were dug with a maximum depth of 150 cm and obvious textural changes throughout the profile were observed. Since the plain is part of an alluvial and colluvial fan, the deposition of materials from the alluvial and colluvial wash varies from time to time creating different textural layers. This was observed in all the soils studied where the soils textural changes were extreme, particularly for the silt and sand content. There were also variations in their structures, which is also associated with the amount of sand and silt in the soils. The soils tend to be massive when the silt content is high, otherwise the structures would be single grain when the sand content is high. The rounded nature of these gravels suggests that they were washed and deposited along part of the plain. All soils were weakly developed and evidenced by weak horizon formation in the profiles. Under the arid environment with annual precipitation value of less than 200 mm and evaporation of more than 4000 mm, one would surely expect to see slow rate of soil pedological development because of very low rate of P/ET⁰ [33].

The eight representative profiles were classified using the USDA Soil Taxonomy [18]. All soils are young and differentiated by their moisture regime. They were identified as Calcic Haplosalids, Aridic Ustorthents, and Aridic Ustifluvents (Table 1).

3.2. Physical Properties. The soil physical data are presented in Table 2. None of the soil physical characteristics show any clear trend with depth. In pedon 1, the clay content distribution was irregular. In pedons 4, 5, 7, and 8, clay increases with depths, while in pedon 2, it increased only until the top 100 cm. In contrast to the above observations, pedon 6 exhibits a remarkable decrease in clay content with soil depth. In pedons 3 and 4, the silt content decreases with depth. The sand size particles are dominant in all pedons except for pedons 1 and 7, but their distribution throughout the profile was very irregular. The results are consistent with the nature of alluvial and colluvial deposition that varies from time to time. Khresat and Qudah [34] also observed a similar deposition trend on studying the Azraq Basin in Northeastern Jordan, which is also formed from alluvial and colluvial deposition.

3.3. Chemical Properties. The soil chemical data of the representative profiles are presented in Table 3. The soils are alkaline and calcareous in nature, containing 19.83% to 61.45% CaCO₃ throughout the profiles. All soils have pH values above 7.0 showing that they are alkaline. The average electrical conductivity values exhibited some variations among the soils studied, placing these soils from slightly saline to saline level. In pedons 2, 4, 5, and 8, the soils were noted to be nonsaline with EC values ranging from 0.4 to 2.64 dS m^{-1} , while soils in pedons 3, 6, and 7 were slightly saline with EC values ranging from 2.1 to 7 dS m⁻¹. Pedon 1 soil was observed to be saline with EC values ranging from 18.11 to $30.5 \,\mathrm{dS}\,\mathrm{m}^{-1}$. The Na content showed slight variability among the soils studied. In pedons 2, 5, and 8, the amount of Na was between 0.4 and $6.8 \text{ cmol}_{c} \text{kg}^{-1}$ as compared to pedons 1, 3, 4, 6, and 7, which Na ranges between 1.84 in 20 cmol_ckg⁻¹. The soils, however, are nonsodic with SAR values ranging from 0.3 to 7.7. The cation exchange capacity ranges from 1.7 to 41.4 cmol_ckg⁻¹. In pedons 1, 3, 6, and 7, the CEC was between 19.5 and 41.1 cmol_ckg⁻¹ as compared to pedons 2, 4, 5, and 8, with values of 11.7 to 21.5. The organic carbon content was low in all soils, which is common for soils of these regions where the vegetation is scarce.

The variability of the soil chemical properties again reflects the alluvial and colluvial nature of soil deposition and their rocks origin. According to Navai [35], the predominant rocks surrounding the study area are limestone, dolomite (Jahrom Formation), limestone, marl (Aghajari Formation), limestone, green marl (Mishan Formation), salt domes (Hormoze Formation), and conglomerate (Bakhtiari Formation). The weathered rock materials from these formations were washed to the catchment areas and these contributed to the variability in the soil physicochemical properties.

3.4. Clay Mineralogy. The clay minerals of the examined soils are presented in Table 4. Based on *d*-spacing the minerals identified through XRD diffractograms are as follows: smectite (14.02–15, 3.18–3.20 Å), palygorskite (10.4–10.6, 6.34–6.4, 3.23, and 4.25–4.47 Å), chlorite (7.01–7.11, 3.53 Å), illite (9.97–10.09, 4.98–5.02 Å), kaolinite (7.2–7.3, 2.28 Å), and sepiolite (12.10–12.11). The presence of smectite was proven by Mg-saturated clay samples solvated by ethylene glycole, which expanded due to treatment with Mg-saturated.

The common minerals in all samples of the studied area are smectite, palygorskite, illite, chlorite, and kaolinite. Kaolinite is found in all soils with the exception of pedon 8. Sepiolite exists in pedons 3, 4, 6, and 7. The dominance of these minerals in the arid regions agrees with the results obtained by Owliaie et al. [36] and Emadi et al. [37]. Palygorskite and sepiolite are fibrous clays and are considered to be of authigenic origin, inherited from weathered parent materials of the surrounding hills and plateaus [33]. The presence of kaolinite in most soils is probably due to inheritance from the weathering of coarse and fine materials transported from the surrounding upland zones. It may also suggest the occurrence of palygorskite and sepiolite kaolinization that apparently may be due to the effect of organic matter decomposition and fibrous clay destabilization caused by Mg uptake by plants [38].

3.5. Soil Electrochemical Properties

3.5.1. Point of Zero Charge Characteristics. The pH₀ values varied from 2.8 in subsurface horizon of pedon 2 to 3.35 in the topsoil horizon of pedon 1 (Table 4) and were positively correlated with the Fe_d content ($r = 0.87^{**}$, P < 0.01) which was far more than its correlation with the OC percentage ($r = -0.83^{**}$, P < 0.01). The pH₀ also has a negative significant correlation with pH_{H₂O} ($r = -0.45^*$, P < 0.05). Hence, the Fe_d content in the soils studied. The respective pH₀ values of organic matter and sesquioxides have been reported to decrease and increase, respectively [8, 39].

Li and Xu [40] reported that the layer silicate clays (2:1 clays) decreased the pH_0 values, while the 1:1 clay minerals as kaolinite increased the pH_0 . Besides, Uehara and Gillman [5] reported that the oxides of Fe and Al have high pH_0 values (pH7-9), while silica (SiO₂) and organic matter have low pH_0 values. Therefore, the low levels of pH_0 in the present study were probably related to layer silicate clays (2:1 clays) and high pH in all the pedons.

The values of $\delta pH (pH_0 - pH_{CaCl_2})$ indicate the evolution of positive and negative charges on the variable charge components [11]. The greatest values of $\delta pH (pH_0 - pH_{CaCl_2})$ were related to subsurface horizon of profile 2 (-5.10 units), which agreed with its strongly negative net charge in the field conditions (Table 4). The mineralogical data also confirmed the occurrence of significant amounts of layer silicate minerals (smectitic type) in this profile (Table 4). Generally, the variations of $\delta pH (pH_0 - pH_{CaCl_2})$ for all the studied horizons showed a rather high level (between -4.25 and -5.10 units) (Table 4), which was in accordance with their CEC levels (Table 3). However, because of a large quantity of layer silicate minerals (2:1 clays) and a scarcity of 1:1 clays and Fe_d, this rising trend from surface to subsurface horizons was not so noticeable.

3.5.2. Point of Zero Net Charge (PZNC). For all the studied soils, the PZNC levels were <2, which was probably due to the excess negative charge in these soils. Gonzales-Batista et al. [10] reported that for systems free of permanent charge, PZNC should coincide with pH₀, but for systems where permanent and variable charges coexist, PZNC may differ from pH₀. Usually, in the young soils (Entisols or Inceptisols) PZNC is lower than its pH₀ and higher than pH₀ if the soils are highly weathered, such as Oxisols [41]. In addition, the model of Uehara and Gillman [11] and Yu [2] predict that in soils having constant negative charge, the PZNC value is lower than pH₀ and vice versa. None of the charge variation curves of the samples indicated the PZNC in pH between ranges of 2.6 and 6, which was due to the excessive amount of negative charge compared with the positive charge in these ranges of pH. Besides, the amount of estimated ZPNC in all the samples was lower than the pH_0 , confirming the presence of the permanent negative charge in these soils.

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Soil number	Depth (cm)	$\mathrm{pH}_{\mathrm{CaCl}_2}$	$pH_{H_{2}O}$ (1:2.5)	pH_{KCI}	$\Delta pH (KCl - H_2O)$	0C%	SAR	CCE%	EC dSm ⁻¹	CEC	5 K	Na⁺ mol kg ⁻¹	Mg ²⁺	Ca⁺⁺	Fe _d (%)
	0-25	7.65	7.79	7.60	-0.19	0.34	7.4	21.37	29.85	41.4	0.67	20	8.5	6.5	0.16
-	25-78	7.60	7.76	7.55	-0.21	0.20	7.0	24.98	27.5	26.3	0.22	14	4.5	3.5	0.15
I	78-110	7.55	7.68	7.50	-0.18	0.23	6.6	19.83	32.5	33.4	0.36	16	7.2	4.3	0.14
	100 - 150	7.70	7.87	7.62	-0.25	0.12	7.7	23.70	18.11	31.3	0.17	15.4	5.2	3.3	0.15
	0-20	7.85	7.97	7.80	-0.17	0.18	3.6	27.04	0.96	21.5	0.23	6.8	4.8	2.5	0.09
ç	20-50	7.90	8.03	7.86	-0.17	0.14	3.7	27.55	0.40	18.2	0.22	5.7	4.6	2.2	0.10
4	50 - 100	7.80	7.95	7.73	-0.22	0.13	1.8	28.32	1.20	15.4	0.20	3.4	4.3	2.4	0.09
	100 - 150	7.90	7.94	7.74	-0.20	0.16	0.7	24.46	0.93	11.7	0.17	1.4	1.7	2.3	0.10
	0-30	7.75	7.90	7.70	-0.20	0.37	3.5	51.5	4.28	23.3	0.40	7.7	6.7	2.8	0.11
3	30-80	7.79	7.93	7.74	-0.19	0.20	4.6	57.16	7.00	34.7	0.25	12.1	10	3.2	0.13
	80-150	7.83	7.97	7.78	-0.21	0.17	4.5	58.97	5.48	29.5	0.22	10.8	8	3.7	0.09
	0-20	7.85	7.94	7.80	-0.14	0.33	2.4	28.84	2.64	17.6	0.51	5.2	4.7	5.3	0.10
~	20-70	7.93	8.02	7.92	-0.10	0.35	3.0	28.85	1.45	16.1	0.18	5.2	1.3	4.6	0.12
۲	70-95	7.80	7.92	7.75	-0.17	0.30	1.0	27.29	1.03	14.4	0.18	1.84	1.5	4.8	0.11
	95-150	7.94	8.01	7.90	-0.11	0.43	1.6	27.98	1.21	11.7	0.15	2.6	0.8	4.3	0.15
Ľ	0-45	7.75	7.88	7.72	-0.16	0.35	1.5	58.20	1.54	15.1	0.21	2.8	0.6	6.5	0.12
C	45 - 150	7.90	8.04	7.85	-0.19	0.38	0.3	56.45	0.37	13.2	0.20	0.4	0.5	6.4	0.13
	0-42	7.78	7.9	7.71	-0.19	0.29	3.9	28.24	5.16	27.5	0.39	9.7	6.6	6.5	0.09
6	42–88	7.90	8.08	7.86	-0.22	0.33	2.6	23.53	2.10	19.5	0.17	5.7	4.8	5.0	0.11
	88-150	7.89	8.06	7.87	-0.19	0.16	4.8	25.36	4.92	25.8	0.23	10.8	5.8	4.5	0.12
	0-36	7.68	7.81	7.57	-0.24	0.37	2.9	61.45	4.55	24.3	0.22	6.9	5.1	6.7	0.10
7	36-86	7.80	7.95	7.72	-0.23	0.39	2.1	60.41	5.25	26.7	0.24	5.4	6.1	6.4	0.09
	86-150	7.84	7.98	7.80	-0.18	0.29	2.9	60.67	4.96	25.8	0.26	7.5	8.9	4.5	0.10
	0-30	7.80	7.91	7.76	-0.15	0.24	2.2	31.12	0.57	16.8	0.36	4	2.6	4.3	0.09
8	30-70	7.85	7.89	7.83	-0.06	0.25	2.1	31.90	0.80	18.4	0.24	3.8	2.2	4.8	0.06
	70-150	7.81	7.85	7.78	-0.07	0.26	3.3	28.5	0.66	17.5	0.18	9	2.7	4.3	0.07
OC: organic car	bon; SAR: sodium	adsorption r	atio; CEC: cat	ion exchang	e capacity; Fe _d : dithionite	citrate bica	rbonate; C	CE: calcium c	arbonate equiv	/alent; EC:	electrical	conductiv	vity.		

TABLE 3: Chemical properties of the representative profiles.

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			TABLE	4: Relati	ive abun	dance of	clay min	eral and sc	ome electr	ochemical characterist	ics of the soils studied.		
Soil number	Depth (cm)	Chl	Sme	Pal	III %	Kao	Sep	Ill-Sme	pH_0	$\delta pH (KCl - H_2O)$	δpH (pH ₀ – CaCl ₂)	$\sigma_p (\mathrm{cmol}_\mathrm{c} \mathrm{kg}^{-1})$	$\sigma_{ m max}~(m cmol_ckg^{-1})$
	0-25	17	8	38	16	13		8>	3.35	-0.19	-4.65	-38	-48
F	25-78	15	13	37	11	24			3.20	-0.21	-4.40	-27.3	-35
T	78-110	22	18	35	7	18			3.30	-0.18	-4.25	-35.7	-43
	100 - 150	20	22	31	Ŋ	22		Ι	3.20	-0.25	-4.50	-29.2	-38.9
	0-20	16	16	25	18	25			3.15	-0.17	-4.70	-21.2	-29.5
ç	20 - 50	37	22	24	12	Ŋ			2.90	-0.17	-5.00	-19.1	-27
7	50 - 100	31	25	18	8	8		<10	3.00	-0.22	-4.80	-14.3	-22
	100 - 150	30	29	17		6		8	2.80	-0.20	-5.10	-15.4	-22.7
	0-30	10	15	33	26	6		<10	3.00	-0.20	-4.75	-22.1	-32
3	30-80	21	21	30	20	8	I	I	3.15	-0.19	-4.69	-29.7	-41
	80 - 150	11	26	29	15	4		<12	3.10	-0.21	-4.46	-31.8	-42
	0-20	23	8	16	35	8	5	<5	2.95	-0.14	-4.90	-18.1	-34
-	20 - 70	20	14	14	24	18	10		2.87	-0.10	-5.06	-11.2	-25.5
4	70-95	36	16	10	20	6	6	I	3.20	-0.17	-4.60	-13.2	-22
	95–150	27	20	6	15	6	8	<12	3.14	-0.11	-4.80	-17.2	-20.9
 	0-45	18	15	14	33	7		<13	3.11	-0.16	-4.64	-15.9	-24.1
C	45 - 150	25	24	21	30	I		Ι	3.25	-0.19	-4.65	-14.2	-22.4
	0-42	20	15	23	30	7	5		3.01	-0.19	-4.77	-24.5	-32
6	42-88	19	21	15	24	8	8	~ 5	2.87	-0.22	-5.03	-20.1	-28.9
	88-150	25	25	12	20	6	6		2.90	-0.19	-4.99	-24.3	-32.5
	0-36	28	14	32	26			Tr	3.15	-0.24	-4.38	-25.3	-35
7	36-86	24	20	30	20	9		I	3.10	-0.23	-4.70	-23.4	-32
	86 - 150	19	26	18	17	6	11	Tr	3.15	-0.18	-4.54	-24.3	-34
	0-30	30	18	27	25			1	3.17	-0.15	-4.63	-17.3	-24
8	30-70	33	26	23	18			I	3.10	-0.06	-4.75	-19.2	-25.5
	70–150	34	30	20	16	Ι	I	I	2.98	-0.07	-4.83	-18.4	-23.8
Chl: chlorite, Sm	e: smectite, Pal: p	alygorskit	e, Ill: illite	, Kao: ka	olinite, S¢	p: sepioli	te, Ill-Sme	: illite-smec	tite.				

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3.5.3. Permanent Negative Charge (σ_p) . The σ_p has a positive significant correlation with Fe_d $(r = 0.63^{**}, P < 0.01)$. Earlier, the effects of Fe_d on the surface charge properties were discussed. Hamdan et al. [42] showed that charge characteristics were significantly correlated with soil organic matter, free iron oxides, and clay content. Sesquioxides have amphoteric properties; that is, their surface charge can bear either positive charge in an acid condition or negative charge in an alkaline condition [43].

The σ_p has a positive significant correlation with clay content ($r = 0.54^{**}$, P < 0.01). The results agree well with those of Sharami et al. [6]. At high pH, OH⁻ ions interact with the edge of the clay particles, making them neutral or negatively charged [44].

The mineralogical compositions in these soils were mixed and each clay mineral plays an important role in the total permanent charge. Although all soils are a mixture of permanent and variable-charge components, whether one or the other dominants depends largely on its mineralogy [45]. For instance, palygorskite has a positive significant correlation with σ_p ($r = 0.60^{**}$, P < 0.01). Structurally, palygorskite includes alternation of blocks and tunnels that grow along the length of the fiber. Each structural block is composed of two discontinuous tetrahedral sheets of silica that a central octahedral sheet sandwiched between them. Because of the discontinuity of the silica sheets, silanol groups (Si-OH) are present on the surface of the fiber.

The σ_p has a positive significant correlation with OC ($r = 0.60^{**}$, P < 0.01). Organic matter also acts as an important source of surface negative charge. Oades et al. [46] reported several relationships between surface charge characteristics and organic matter in an Oxisol under rainforest vegetation in Australia. Hydroxyl groups of organic matter can also contribute to negative charge [2]. Shamshuddin and Anda [47] showed that organic carbon in soils is responsible for lowering the pH₀ because of the creation of negative surface charge and/or masking of positive surface charge.

The SAR, exchangeable Na and exchangeable Mg also have a positive significant correlation with σ_p with *r*-values of 0.84^{**}, 0.92^{**}, and 0.82^{**}, respectively. Through alteration of the crystal lattice structure of soil colloids, permanent charge develops when ions of lower valence substitute for ions of higher valence [48]. The mechanisms of the effect of electrolyte on surface charge of soils are rather complex. According to the theory of diffuse double layer, two mechanisms may exist. The surface of variable charge minerals is one kind of reversible constant potential surface. The charge density δ on this type of surface is proportional to the square root of ion concentration *C* of the solution, that is, $\delta = K(C)^{1/2}$, where *K* is a constant [28].

The valence, ionic radius, and thickness of hydrated layer of cations and anions of various electrolytes are different. Morais et al. [49] showed that the nature and valence of the counterions also influenced the magnitude of the electric charges on the soil particles. For example, the quantities of negative surface charge and net surface charge in $MgCl_2$, $MgSO_4$, and K_2SO_4 solutions are lower than those in KCl solution.

Furthermore, the σ_p has a positive significant correlation with CEC ($r = 0.96^{**}$, P < 0.01). This demonstrates that the CEC has the highest effect on the σ_p . Since organic matter is low in the soils, the CEC is affected by the expanding minerals (e.g., smectite) [50] and basic exchangeable cations (e.g., Na). Sollins et al. [45] reported that most of the permanent charge in the soils is on the surfaces of layer-silicate clays, which compose most of the surface area of p-c soils. These clays include the 2:1 layer-silicates (illite, vermiculite, and smectite) and the 2:2 clays (chlorite). The 1:1 group of kaolin clays has a small amount of permanent charge on their surface.

The pH_{H₂O} has a positive significant correlation with the permanent negative charge (σ_p) $(r = 0.72^{**}, P < 0.01)$. The pH_{KCl} also has a positive significant correlation with the permanent negative charge (σ_p) $(r = 0.55^{**}, P < 0.01)$. Rashad and Dultz [51] indicated that at low pH the surface charge of both clay soil samples (original clay and the organic matter removed clay soil) had low negative values, which is due to the protonation of variable charge with increasing pH, where deprotonation of functional groups occurs, the surface charge becomes more negative. Shamshuddin et al. [52] reported that the negative charges on the soil surface were found to increase significantly with an increase in pH. Thus, when the pH is raised, more OH⁻ are adsorbed onto the surface or H⁺ are released into the solution, causing an increase in negative charges.

3.5.4. Charge Variation with pH. Charge (negative and positive) variations with pH (0.002 M CaCl₂) for different horizons of the soils are presented in Figure 2. The inverse relations between both negative and positive charge variation curves both in surface and between subsurface horizons (having small levels of variable charge components) were noticeable. The results showed that all of the samples showed large negative charge over the range of applied pH. The highest level of negative charge was evident in profile 1, which was probably due to high levels of clay content in its surface and subsurface horizons and the relation to 2:1 clay minerals. The charge properties did not show any clear trend with depth. Since the plain is part of an alluvial and colluvial fan, the deposition of materials from the alluvial and colluvial wash varies from time to time creating different textural layers. For instance, the level of negative charge in horizon Cz1 $(-27.3 \text{ cmol}_{c}\text{kg}^{-1})$ of profile 1 (Calcic Haplosalids) was lower than that of horizon Cyz2 (35.7 cmol_ckg⁻¹). Hence, the soil electrochemical properties in profile 1 were different from the other studied pedons.

Profile 4 (horizon C_1) has the lowest negative charge (11.2 cmol_ckg⁻¹), which is probably due to low levels of clay content and the relatively low smectite in this layer. Profile 4 also shows the lowest levels of negative charge in both surface and subsurface horizons compared with the other profiles, due to its lower CEC, clay content, and smectite.

The negative charge of the soils in the present study is influenced by the 2:1 clay minerals where they are prevalent



FIGURE 2: Charge variation with soil pH (0.002 M CaCl_2) for different horizons.

and organic matter accompanied by iron oxide is scarce (Tables 3 and 4). Consequently, pH variations could not have a great influence on the charge curve. Therefore, for soil pH (CaCl₂) of 7.55, the amount of negative charge in the subsurface horizon of profile 1 is more than the above horizon. Naidu et al. [53] studied the clay mineralogy and surface charge characteristics of four basaltic soils from Western Samoa. The level of trace to subordinate amounts of kaolin minerals was present in these soils. The surface charge pH curves followed a constant potential model, indicating the presence of substantial amounts of pH-dependent charge.

In addition, they reported that negative charge was present at pH values as low as 3.0 and small quantities of positive charge were detected at pH values as high as 9.0. Values for PZC ranged from 2.2 to 3.9 and these were generally greater than the pH₀ determined by δ pH method in their study. The permanent negative charge of the soils is high because the majority of parent materials are limestone. The results agreed well with those obtained by Sharami et al. [6].

Generally, for all the soils examined, the ranges of charge variation with pH in the surface horizons were more noticeable than in the subsurface horizons. Most of these variations were observed in the pH ranging from 3.5 to 5.0, where the curves had a descending trend.

The values of anion exchange capacity (AEC) in most of the studied soils showed small levels, which were due to a shortage of materials having variable charge. However, organic matter and kaolinite are present in these soils, but these materials do not enhance the AEC level with respect to their intrinsic characteristics and soil pH. Another reason for this observation (small level of AEC) was negative adsorption (repulsion) of anions from surfaces with variable charge. Adsorption of anions is one of the important characteristics of variable-charge soils. Owing to the properties of variablecharge soils in chemical and mineralogical compositions, adsorption of anions by these soils would have been more significant compared with adsorption by constant-charge soils [54]. Soils having variable charge, occupying large areas in tropical and subtropical regions, are characterized by carrying variable amounts of both negative and positive charges and therefore can adsorb both cations and anions [55]. Hence, the soils of the present study, due to a shortage of materials having variable charge, which is a common property of soils from humid regions, had small capacity levels for anion adsorption.

4. Conclusion

The soils of the studied area are young, dominantly of Aridisols and Entisols. Their mineralogy is dominated by the 2:1 silicate layer clay minerals. Consequently, the pH₀ and the PZNC values in the arid soils are low in comparison with tropical soils. The pH₀ values of all samples are less than pH under the field condition because of the high pH and the presence of high amount of 2:1 silicate clay minerals. Charge variation curves in the soils did not give PZNC values within pH range of 2.6 to 6. The PZNC values are less than pH₀ in all samples. However, permanent negative charge (σ_p) is high in the arid soils because of presence of clay minerals (2:1 and 1:1 types). Hence, the σ_p has a significant positive correlation with pH, CEC, OC, SAR, Na, Mg, clay, and palygorskite. The charge variation curves showed that the AEC values are small with values of <2.83 cmol_ckg⁻¹.

After this study we can recommend the application of fertilizers based on the amount of negative charges in the soils studied.

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