EFFECT OF pH AND ELECTROLYTES ON CHARGE DISTRIBUTION IN SOILS AND RELATIONSHIP BETWEEN pH, CEC AND SAR

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Soils carry positive and negative charges simultaneously but vary in space and time. Samples from the A and B horizons of a normal (Typic Calciargids having natric horizon) and a saline-sodic (Calcic Haplosolids) soils were collected. Positive and negative charges were determined by saturating the soils with *IN* KCl at soil-suspension pH 6, 8 and 10. The soils were extracted with 0.2 and *0.5N* $MgS0_4.7Hp$ or Na_2S0_4 solutions. Negative charges statistically increased with an increase in pH of both the soils. The increasing concentration of extracting solutions increased the negative charge, increase being more with $MgS0_4.7Hp$ than that with Na_2S0_4. Response of positive charge to pH, concentration and nature of electrolytes was almost similar to that for negative charge for these soils. Negative charge was significantly higher in the A than that in the B horizon. An increase in pH or farm yard manure addition increased CEC and thus may decrease the rate of Ca-Na exchange, Le. soil sodication.

Key words: horizon, charge, salinity, adsorption, dispersion.

INTRODUCfION

Concentration and valence of electrolytes and pH could influence the diffuse double layer (DDL). According to the DDL theory, divalent ions are attracted much more strongly to the charged surface than are monovalent ions. As a result, the DDL is more compressed in the case of Ca- than that in aNa-saturated soil. In the latter case, the soil will disperse because mono-valent ions, like Na", are weakly adsorbed and increase the thickness of the DDL and hence promote dispersion (Sumner, 1993). Organic matter has a favourable effect on Na-Ca exchange during reclamation of low cation exchange capacity (CEC) soils as it could increase CEC and promote aggregation of soil particles for improved leaching (Naidu and Rengasamy, 1993). However, investigations are needed to quantify the amount of organic matter required in conjunction with inorganic amendments to economically reclaim the sodic soils. The objectives of the present investigations were to study the effect of pH, concentration and nature of electrolytes on the electrochemical properties, and relationship between pH", CEC and sodium adsorption ratio (SAR) during reclamation of arid .region calcareous saline-sodic and normal soils.

MATERIALS AND METHODS

Soil samples were collected from the A and B horizons of normal (nonsaline-nonsodic) and saline-sodic soils (Table 1). Particle-size analysis was carried out by the Bouyoucos method. The pH of the saturated soil paste (pH,), electrical conductivity of the saturation extract (EC), soluble ions, exchangeable cations, lime and CEC were determined by the methods of Richards (1954). Organic carbon was determined by the method described by Nelson and Sommers (1986). Positive and negative charges at 0.2 and *0.5N* of $MgS0_4.7Hp$ and Na_2S0_4 at pH of 6, 8 and 10 were determined. In each centrifuge tube, 2.5 g soil sample was mixed with 25 mL *IN* KCl solution by adjusting pH of the soil-KCl suspension with *O.IN* HCl or KOH at 6, 8 and 10. Next day after readjusting the pH, samples were centrifuged and supernatant was discarded: This step was repeated for four more times, every time adjusting the pH of each sample as was maintained in the first step. Then KCl was removed by washing the samples with 95% ethanol.. Adsorbed K+ and Cl- ions were replaced by using 0.2 and *0.5N* solutions of $MgS0_4.7Hp$ and Na_2S0_4 as extractants. In the extract, Cl- was determined by titration with $AgN0_3$ using K_2Cr0_4 indicator and K+ by flame photometer. The amounts of K+ and Cl- were taken equal to negative and positive charges, respectively (Morais *et al., 1976).* The correlation coefficients between pH", CEC and SAR during reclamation of a saline-sodic soil were also derived.

Table 1. Characteristics of the Hafizabad (Hf) and Khurrianwala (Kw) soil series

Soil property	Ustalfic Haplargids (Ht) A horizon	B horizon	Typic Halorthids (Kw) A horizon	Bhorizon
ECe,dSm'!	4.02	3.24	14.63	4.35
SAR	13,22	11,86	130.00	15.43
ESP	22.00	25.00	89.00	58.00
$CaCO_3$(%)	4.32	3.54	5,40	4.78
Organic carbon (%)	0.52	0.24	0.25	0.15
Textural class	Clay loam	Clay loam	Clay loam	Clay loam

RESULTS AND DISCUSSION

Effects of pH and electrolyte concentration on charges:

The data (Table 2) show that negative charge statistically increased with increasing pH of both the soils, the increase being greater in the A than that in the B horizons. However, total charge was higher in the Hfthan that in the Kw soil series. Increasing concentration of $MgSO_4.7H_2O$ and Na_2SO_4 increased the negative charge (Table 2), the effect being greater with $MgSO_4.7H_2O$ than that with Na_2SO_4.

Table 2. Charge distribution (cmol, kg-I) in soils at different pH and eleetmlyte concentrations

Soil	pH	Cone:	[illegible] Positive	Negative	MgS~~O Positive	Negative
Hf A horizon	6	0.2N	'2.8Ofm*	4.70ko	3.8100	4.76in
	8	"	2.4Qjm	5.02gl	3.90ac	5.39dg
	10	"	2.4Qjm	5.67bd'	3.25aj	5.84ac
	6	0.5N	2.65im	4.68kp	3.ISbk	4.270s
	8	"	2.4Qjm	5.18ej	4.05a	5,5Sbf
	10	"	3,l0cl	5.93ab	3.95ab	6.16a.
HfB horizon	6	0.2N	2.6Oim	3.94s	235km.	4.33ns
	8	"	235km.	4.23ps	2.5Okm	5.20ei
	10	"	2.6Oim	4.87hm	·3.30ai	5.4Ocg
	6	0.5N	2.25lm	4,47mr	3,30ai	4.581q
	8	"	2.95el	4,42mr	3.95ab	5.21ei
	10	"	3.60eg	5,5600	3.65af	5,5lbf
Kw A horizon	6	0.2N	2.4Qjm	337t	2.6Oim	4.561q
	8	"	3.00dl	4.02rs	2.65im	4.74jm
	10	"	2.70hm	4,54mq	2.75gm	5.01gl
	6	0.5N	3.60ag	4.oors	3.lObI	4.41mr
	8	"	3.55ah	4,4lmr	3,35ai	4.70ko
	10	"	2.55im	5.25dh	3.70ae	5.51bf
KwB horizon	6	0.2N	2.05m	3.03t	2.5Oim	4.23ps
	8	"	2.25lm	3.88s	2.5Oim	4.40nr
	10	"	2.lffin.	4.70ko	2.9Oem	5.l1ek
	6	O.5N	2.05m	3.90s	3.05cl	4.19qs
	8	"	2,55im	4.46mr	3.lObI	4.611q
	10	"	2.9Oem	5.21ei	3.25aj	5.10£

*fm = fghijklm and alphabet allocation is for soilxconc.xpHxelectrolyte sub-table.
Figures sharing same letters are statistically similar at P = 5%.

An increase in negative charge at higher pH occurred due to proton exchange from organic matter and clay minerals (Hingston *et al*, 1972). Higher charge in the A than that in B horizon was attributed to higher organic matter (Table 1) in the A horizon. Organic matter can contribute large amounts of pH-dependent charge (Anderson and Sposito, 1992).

Positive charge in-consistently changed with pH for both the soils (Table 2), though the extent of change was less compared to that of the negative charge. Total positive charge was generally greater at higher concentrations of extracting solutions (Table 2). The thickness of DDL decreases with increasing soil solution concentration. Since the concentration of extracting solution increased soil solution concentration as well, the DDL thickness decreased. This shift in DDL thickness caused redistribution of ions in the new developed DDL, with counter ion (cations) being more closely packed near the negatively charge surface than those before adding the extracting solution.

The clay fraction of test soils was dominated by illite with minor quantity of kaolinite and traces of smectite/vermiculite/chlorite. Negative and positive charges measured with $MgSO_4.7H_2O$ were higher than those with Na_2SO_4 (Table 2). This is due to higher fixation of K^+ in illite clays than that in the montmorillonite or vermiculite (Niazi, 1994), and/or more replacement of adsorbed K^+ with Mg^{2+} than with Na^+ (Morais *et al.*, 1976). The higher values of charge with Mg^{2+} than that with Na^+ could be due to its higher replacing power and/or ionic size than that of Na^+. The size (unhydrated) of Mg^{2+} is 0.65 A° and Na^+ is 0.96 A°. These findings are in agreement with those of Morais *et al.* (1976) and van Raij and Peech (1972) who found that positive and negative charges determined by divalent ions were higher than those with monovalents.

Relationship between pH, CEC **and** SAR: An increase in pH, tends to increase soil CEC and the same was observed for the Khurrianwala soil (Murtaza *et al.,* 1997). Increased CEC favours Ca^{2+} adsorption at the expense of Na^+ (Pratt *et al.,* 1962). Hence an improved Na-Ca exchange which is primary for cost-effective reclamation of saline-sodic/sodic soils. An increase in pH. upon leaching with brackish water of saline-sodic soils without a Ca-source has been observed (Muhammed, 1983). In our studies there was a slight increase in soil CEC with all the treatments, increase being more with FYM than that for the other treatments (Table3).

The comparison of data (Table 3) indicate that steady-state with respect to SAR or pH. was achieved earlier for the drainage water treatment followed by gypsum @ 50 % gypsum requirement (GR), gypsum @ 100 % GR and FYM. However, the process of re-sodication was the slowest with FYM followed by gypsum 100 %, gypsum 50 % and drainage water. Such a slow increase in SAR with FYM is important for the management of high SAR waters on productive as well as on saline-sodic soils. The higher CEC of. soil after the addition of organic matter attracts stronaty the polyvalent cations that reduces their exchange b,. low-valent cation, like Na^+. Polysaccharides in organic matter link clay particles together and resist the dispersiv.. forces of Na^+ (Rengasamy and Olsson, 1991), thus infiltration rate is sustained to promote leaching 0: Na^+. This mechanism is responsible for the low Ca-Na exchange with FYM.

CONCLUSIONS

Positive and negative charges in soils determined by di-valent extracting ions remained higher than those with mono-valent ions. At higher concentration of the extracting solution, the amount of both negative and positive charges was more than that at lower concentration. Both the types of charge was found higher for the A than that for the B horizons. However, salinity and/or sodicity of soil (Kw soil series) resulted in lower magnitude of negative and positive charges than that in the normal Hf soil series. There was an increase in soil CEC with all the treatments, increase being the highest with FYM. The process of re-sodication was the slowest with FYM followed by gypsum @ 100 % and 50 % GR and the control.

Table 3. Relationship between pH,. CEC and SAR during reclamation

Treatment	Property	OS 1993	PW 1993-94	PW 1994-95	PW 1995-96
Drainage water	pH,	8.22	8.09	8.04	8.43
	SAR	60.80	16.90	30.03	36.33
	CEC	7.83	—	—	8.21
Gyp. @ 50% GR	pH,	8.23	8.04	8.08	8.25
	SAR	77.50	13.44	30.31	27.00
	CEC	7.83	—	—	7.83
Gyp. @ 100% GR	pH,	7.95	7.95	8.07	8.22
	SAR	61.60	13.26	24.93	21.33
	CEC	7.83	—	—	8.36
FYM @ 25 Mg ha^{-1}	pH,	8.35	7.96	8.02	8.18
	SAR	56.90	25.21	23.22	21.66
	CEC	7.83	—	—	8.88

OS = Original soil, PW = Post wheat, CEC as $cmol_c kg^{-1}$

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PREPARATION AND BIOLOGICAL EVALUATION OF 'WHOLE SOYMILK

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Soymilk was prepared from indigenous soybean by two different methods and its protein quality was evaluated by conducting a feeding trial on Albino rats. Results showed protein efficiency ratio 2.595, 1.650; net protein utilization 69,405, 57.615; true digestibility 90.305, 87.905 and biological value 76.855, (i5.560 for dehulled soymilk and whole soymilk respectively, while these values for skim milk were protein efficiency ratio 2.785, true digestibility 91.730 and biological value 80.980.

Key words: Biological value, net protein utilization, protein efficiency ratio, true digestibility

INTRODUCTION

Use of vegetable protein in weaning food for infants and children may be recommended due to shortage' and higher cost of animal protein sources. Among vegetable sources of protein, soybean is ranked at the top due to its better amino acid profile and availability of vitamins and minerals (Pyler, 1988). Very small amounts of whole soybeans are consumed as food. It is used as canned soybean in tomato sauce, canned green soybean, soymilk based infant formulae and beverages. The largest use of soybean is in the preparation of the soymilk, tofu, misoand tempeh. Whole soymilk may serve as a good nutritive source for the babies who are malnourished and for those who do not tolerate cow milk and lactose of milk. Evidence suggests that soy protein may be less allergenic 'than heat treated cow's milk protein and is probably a better source of nutrition in allergy prone infants (Anon., 1983). Several methods of the soymilk preparation have been tried in developed countries but they are rarely used in Pakistan. The aim of the present investigation was to prepare whole soymilk and dehulled soymilk from indigenous soybean and to evaluate the quality of whole soymilk products by chemical and biological methods.

MATERIALS AND METHODS

The indigenous raw soybean was procured from Ayub Agriculture Research Institute, Faisalabad. It was dried and ground to uniform size and subjected to proximate analysis by AOAC methods (1990). The experiment was conducted at AnimalNutrition Laboratory, University of Agriculture, Faisalabad.

Preparation of Soymilk: Soymilk was prepared from indigenous soybean by the following two precesses:

A: One kilogram of the soybean was placed in a two-litre stainless steel bowl and excess of boiling water was added. The container was allowed to stand overnight. Thereafter, the whole material was blended for 5 min and filtered through cheesecloth under suction. The milk thus, obtained was dried in an air oven initially at 1000e for one hour and then the temperature was decreased to 60°C to attain a constant weight.,

B: Soybean was soaked for 6 hand dehulled with smooth maceration with hands. Whole material was blended for 10 min at 80°C. To obtain a blend soymilk, it was filtered through cheese cloth, dried initially at 100°C in an air oven for one hour and then the temperature was decreased to 60°C till a constant weight was obtained. This method was described by Wilken's et al. (1967) cited in Smith and Circle (1980).

Biological Evaluation: Whole soymilk and dehulled soymilk was evaluated on weanling Albino rats following the methods described by Pellet and Young (1980). Thirty Albino rats were selected at the age of 21 days. The rats were fed a stock diet for 7 days before the start' of experiment and then divided into 10 groups of 3 rats each with a weight difference of ± 5 g. Each group of rats was weighed prior to the feeding trial and thereafter daily. The rats were housed in wire screen mesh bottomed cages. A sheet of filter paper was used under each cage for the collection of faeces and spilt diet. Water and feed were provided adlibitum to the rats. The temperature of animal room was maintained at 28 ± 2°C. Five diets were prepared as shown in Table 1.

Table 1. Composition of experimental diets

Ingredient	Diet				
	A	B	C	D	E
	--------------		(g) -------		
Whole soymilk	—	—	212.77	—	—
Dehulled soymilk	—	—	—	204.08	—
Skimmedmilk	260	—	—	—	—
Cerelac	—	666.60	—	—	—
Corn starch	340	333.40	387.23	359.92	6X)
Cornoil 100	—	100	100	1000	
Glucose	150	—	150	150	150
Potato starch	100	—	100	100	100
Mineral mixture	40	—	40	40	40
Vitaminmixture	10	—	10	10	10
Total	1000	1000	1000	1000	1000

These diets were assigned randomly to ten groups of rats in such a way that there were two groups of rats on each diet. The diets were fed for 10 days. The spilt feed and faecal materials were collected daily from each. cage, oven dried, weighed and stored separately. The dried faeces were ground and analyzed for total nitrogen (Miller & Bender 1995). At the end of the experiment, the rats were anaesthesized with an over dose of chloroform. Their cranial as well as abdominal cavities were opened. Each group of carcasses was weighed after oven drying at 105°C to a constant weight. The dried carcass was ground and analyzed for nitrogen. The protein quality of diets was expressed in terms of following formulae described by Pellet and Young (1980).

1. Protein efficiency ratio (pER)
   = Gain in body wt./protein intake of test diets
2. Net protein utilization (NFU)
   $= [B - (B_2 - It)] / [1 \times 100]$
3. True digestibility (TO)
   $= [I - (F_n - Ft)] / [1 \times 100]$
4. Biological value (BY)

$$= \frac{\text{Net protein utilization}}{\text{true digestibility}} \times 100$$

RESULTS AND DISCUSSION

The nutrient composition of raw soybean, whole soymilk and dehulled soymilk is shown in Table 2.

Table 2. Proximate composition of raw soybean, whole soymilk and dehulled soymilk

Composition (01Q)	Raw soybean	Whole soymilk	Dehulled soymilk
Moisture	7.00	5.35	5.40
Crude protein	34.00	47.00	49.00
Ether extract	22.50	24.00	27.75
Crudefiber	4.25	0.00	0.00
Ash	5.50	7.25	6.50
Nitrogen free extract	26.75	16.40	11.35

N Factor: 5.71 for soybean product, 6.38 for skimmed milk, 6.25 wheat (Cerelac).

Mean values for the biological evaluation of the protein quality of skimmilk, Cerelac, whole soymilk and dehulled soymilk are given to Table 3.

Table 3. Biological evaluation of diets (mean values for diets containing 10% protein) ~nalysis

Analysis	A Skim	B Cerelac milk	C Whole Soymilk	D Dehulled Soymilk
Wt. gain	37.170	44.750	18.915	31.165
PER	2.785	3.140	1.65	2.595
NPU(%)	74.285	65.630	57.615	69.405
TO(%)	91.730	92.115	87.905	90.305
BV(%)	80.980	71.250	65.560	76.855

Weight Gain: Weight gain of rats fed on dehulled soymilk was less than those on skimmilk, indicating deficiency of certain essential amino acids. Khader (1983) found similar results in rats on shoyu (a fermented soybean sauce). Weight gain with dehulled soymilk diet was less than that with Cerelac (wheat based food). It may be due to that Cerelac is a commercial baby. food and it contains wheat, skimmilk and flavours. In case of whole soymilk the weight gain was lower than that with other three diets, indicating that it contains more trypsin inhibitors due to hulls. A1i(1995) reported that higher trypsin inhibitors impaired the quality of soybean.

Non-significant difference was observed among the consumption of four diets. It means that acceptability of four diets. was the same. Present study showed that acceptability of soymilk was somewhat higher than skimmilk.

Similar results were observed by Cook et al. (1985). They found that litters ate 3 different levels of soyprotein and avoided casein diet. Kinik and Akbulut (1996) also found that yogurt containing 50% soymilk along with .50 % cow milk was highly acceptable.

Diet consumption of Cerelac was slightly higher than soymilk. It was probably due to the reason that Cerelac isa commercial baby food and its organoleptic characteristics have been improved by addition of some flavours. It is therefore, suggested that if soymilk would be prepared commercially, addition of some fllavours, is a must to increase the organoleptic characteristics. Singh et al. (1996) concluded that acceptability of soymilk was increased by addition of 0.1 % salt, 0.5 % sugar and 0.25 mLl L vanilla essence. The difference between the PER values of the two soymilks was due to the presence of hull and trypsin inhibitor in whole soymilk. The time for blending was also different. Arshad et al. (1985) found that PER for dehulled soybean was 2.30 compared to whole raw soybean for which PER was 1.34. Ali (1995) found that trypsin impaired protein quality of soybean. The PER value of dehulled soymilk was 2.59, which was comparable with PER of skimmilk (2.78). Heat treatment may have improved the protein quality of dehulled soymilk because it was given 10 min blending at 80°C. Liener (1976) and Lowgren and Hambraeus (1988) found PERs of soymilk diets lower than Cerelac. It may be due to the reason that Cerelac is a commercial baby food and its organoleptic characteristics have been improved by the addition of flavours.

The digestibility of all the diets showed non-significant differences, indicating high digestibility because of low fibre contents. The proximate analysis (Table 2) of both the soymilks showed no fibre in it. This suggested that soymilk prepared form two different methods did not affect the digestibility of its protein. Liener (1976) and Lowgren and Hambraeus (1988) found that protein digestibility was not affected by heating.

The NPU and BV of dehulled soymilk was significantly lower than skimmilk indicating that it was deficient in sulphur containing amino acids; this deficiency was also reported by Sarwar (1991) and Young (1991). The NPU and BV of dehulled soymilk was higher compared to that of Cerelac. It could be due to lack of lysine in cereal based foods. Legumes were reported higher in thiamin, nicotinic acid,itryptophan and minerals along with lysine compared to cereals. Pyler (1988) showed that soybean had better essential amino acids profile than cereal based foods. The NPU and BV of dehulled soymilk was also higher than that of the whole soymilk. This difference was found in the studies of Arshad et al. (1985). It may be due to overnight soaking of whole soybean which resulted in losses of nutrients. Albrecht et al. (1966) found 3-4 % losses of nutrients in soybean due to overnight soaking and 10 % losses were found in the studies of Borhan and Snyder (1979).

CONCLUSIONS

It .may be concluded that dehulled soymilk is a good source of protein. The higher values of NPU and BV showed that it can be cost-effective to replace Cerelac and nutritious baby food. If sulphur containing amino acids (methionine, cystein) and flavours are added, it will improve its quality and organoleptic characteristics.

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