CHAPTER- 3

EFFECT OF TREATED OIL WELL EFFLUENT

ON

SOIL EXCHANGE CAPACITY

INTRODUCTION

The increasing environmental health issues in developing countries resulted in a concomitant interest in the safe disposal of waste-water beneficially [1]. The use of irrigation as the primary disposal method for the wastewater becomes more difficult as the salinity and total dissolved salts (TDS) of the feed-water increase beyond the fresh water level [2]. The hazardous effect of the use of poor quality water on soils depends on many factors such as soil type, initial salt content in soil, amount and nature of salt in irrigation water, etc. Determination of suitability of water for irrigation is a complex task. It not only involves the composition of the irrigation water, but also the knowledge of how a particular soil reacts to the irrigation over a period of time. The conductivity measurement of soil and water , pH, sodium adsorption ratio (SAR), cation exchange capacity (CEC), Na/Ca+K+Mg ratio, exchangeable sodium fraction and Gappon constant have all been used in several combinations to predict the soil behavior in relation to the quality of the irrigation water. However, the drainage relation of the soil profile and the impact of different farm management regimes are difficult to predict in the laboratory and need field studies. In addition , the salt tolerance of the crops, the rising demand for the agricultural products and environmental regulations on industries to dispose or to use their waste-water are needed to be considered in developing the irrigation guidelines.

Recycling of waste-water is a common practice. Land application of waste-water offers great scope in reclaiming water resources and has proved to be widely acclaimed practice for several decades, especially in the arid countries [3]. Reuse of wastewater for irrigation is beneficial as it is a cheap source of water. Properly planned use of wastewater can reduce the environmental and health related hazards, which have been observed with traditional water disposal practices in developing countries. This is an economical way to dispose waste-water to prevent pollution and salinity problems etc. [1,4]. The use of available water for irrigation without assessing its quality will be hazardous to plants and animal life. Water with high dissolved salts affects the physical and chemical properties of the soil depending on the total salt concentration, properties of various cations and anions and the ion exchange characteristics of the soil surface [5]. The mode of salt transportation and accumulation in the soil depend on the quantity and quality of the irrigation water [6]. While irrigating with saline water, the main exchange is taking place between Na, Ca and Mg ions [7,8,9]. Many workers have mentioned various standards for determining the quality of water for irrigation. However the safe disposal of oil-well effluent is a difficult task. This difficulty varies with various treatment methods currently available. Utilization of this treated effluent for irrigation depends on the salinity level of the treated effluent and the salt tolerance ability of the plants.

It is a well -known fact that high concentration of sodium in the irrigation water will increase the hardness and porosity of the soil [10,11,12]. The clay fraction constitutes the most reactive part of the soil. These clay particles are in colloidal dimension and they can be considered as the complex silicate in which silica is combined with different proportions of alumina and magnesia along with varying proportions of other elements. As the clay colloid is negatively charged , it attracts a large number of positively charged cations. The clay nucleus can be considered as 'Micelle', a negative radical having a swarm of adsorbed cations [10]. Because of this, cations like Ca, Na, K, Mg are adsorbed on the soil. These loosely held cations can be replaced by other cations and this is known as 'cation' exchange.Cation exchange capacity is defined as the number of milli- equivalent of cations that can be held in an exchangeable form by 100g of the soil. This is an important property describing the nutrient availability for plant growth [13,14]. The presence of Ca ions on suitable proportion to other exchangeable cations such as Na , K , H and NH_4^+ is necessary, if the soil is to be suitable for plant root development. The outline of the fundamental forces involved in the clay particle interactions will be given as a background for the consideration of the effect of sodium ions on the structure of the soil and the ways in which the effect of the sodium can be diminished [11]. If the exchangeable sodium occupies more than 15% of the total exchange capacity, the clay and the organic matters will get dispersed due to the flocculating effect of the sodium and these soils will be in an unsatisfactory physical condition [10]. Because of this the plant may no longer be able to take up Ca ions for its needs [15,16]. The effect of sodium ions on the swelling properties of clays is so pronounced that even in sandy loam soils very marked changes in soil permeability are observed, if the soil has an appreciable exchangeable sodium percentage [11]. As the exchangeable sodium increases , increased swelling reduces the size of the microporosity and permeability of the soil [11]. Very large changes in the soil permeability are seen if the soil has an appreciable sodium percentage. When the exchangeable cations are predominantly Ca or Mg, the clay particles interact or repel each other only to a limited extent [11]. This leads to the granulation of clay particles and increases the aeration and drainage [10].

Sandy soils may be affected more adversely than clay soils under continued irrigation with saline water without proper leaching. Once the leaching is provided carefully, these soils can be reclaimed more easily due to better drainability characteristics [17]. The pH of the soil is not liable to constant changes, but only minor fluctuations are seen from season to season. This is a reflection of the buffering capacity of the soil [18,19]. A sudden change in soil pH may seriously affect the higher plants in getting the proper nutrients and also will affect the soil micro organisms.

Studies have also been carried out to see the effect of pH on ion exchange equilibria of soils [16,17]. It has been reported that the sodic soil can be reclaimed and the permeability can be improved by the addition of gypsum to soil or to irrigation water [2,11,20-22]. Addition of gypsum to soil or irrigating water increases the removal of sodium from the soil profile and improves the water infiltration rate [23]. Calcium chloride has also been used for the same purpose [19]

The present irrigation guide lines deal with only narrow range of water with unconventional composition of inorganic electrolytes. It is therefore necessary to carefully investigate and monitor the situation in which the use of irrigation water with unconventional compositions of electrolytes or organic materials are involved. Accordingly laboratory experiments have been conducted to find out maximum concentration of total dissolved salts (NaCl), and the optimum pH at which the treated oil well effluent can be used for agricultural purpose and the extent to which sodium adsorption on exchange complex of soil can be restrained by other chemicals.

EXPERIMENTAL PROCEDURE

All the chemicals used for the studies were of AR grade and obtained from Qualigens, India Ltd.. Systronics India Ltd., make flame photometer(Model 105) was used for the cation analysis. pH adjustments of the effluent were done using with 0.05N HCl and NaOH solutions. The pH of the ammonium acetate solution was adjusted with ammonium hydroxide and acetic acid solutions as per the requirements.

The soil samples (1- 100 cm depth) for the study were collected taken from Mehsana, North Gujarat, India. The treated oil-well effluent taken for the present study contained 15mg/L oil and the total dissolved salts (TDS), mainly NaCl, was around 9000mg/L. This treated effluent and the effluent diluted to contain 5000 mg/L, 3000 mg/L and 1500 mg/L of NaCl were applied to soil after adjusting the pH to 7.5, 5.5 and 4.5.

The soils of Mehsana region are alluvial in nature and have an average composition of 70% sand 10% silt and 20% clay. They are extremely porous with excellent drainage profile and have a pH 8.95. The upper layer of the soil contain small amount of $CaCO_3$ and the free $CaCO_3$ goes on increasing as the depth increases. The clays play an important role in determining the physical characteristic of the soil, soil fertility and degree of soil susceptibility to saline damage.

About 2.5gm of the soil was weighed and mixed with distilled water and stirred for half an hour. The solution was allowed to stand for the time period till soil settled down and then filtered.The filtrate was analyzed flame photometrically to determine the soluble sodium, potassium and calcium ions in the soil (Table 1).

2.5 gm of soil was weighed accurately , washed with 40% alcohol and then with distilled water to remove soluble salts present in the soil. The exchangeable cation present in this soil was determined by extracting with ammonium acetate [22] at pH 8.95 and then analyzing the extract by using flame photometer(Table 2).

In order to study the effect of pH of the irrigation water on the cation exchange capacity of the soil, 2.5 gm of the samples was added to 100ml water at pH 7.5 , shaken well for one hour and kept for one day. It was filtered and washed with distilled water to remove the soluble salts, and cation in the exchangeable complex was determined after extraction with ammonium acetate solution at pH 7.5 and using flame photometer. The same experiments were carried out with effluent water at pH 5.5 and 4.5. The extractions were also carried out at the same experimental pH. The results are presented in Table 2.

The effect of different salt concentration in the effluent on the exchange capacity of soil at varying pH values have also been investigated. After one hour of vigorous shaking of the effluent with soil, it was kept for one day, filtered and the soluble salts were removed. Then the exchangeable ions were extracted with ammonium acetate and analyzed flame photometrically (Table 3).

The extent of sodium exchange to the exchange complex can be restricted by adding the salts of calcium to the soil or to the irrigation water [2,11,19- 22]. This effect was investigated by the addition of calcium as $CaCO_3$ (0.5% to the soil), 200 mg/L of calcium as Calcium acetate and 500 mg/L of potassium as potassium chloride to the effluent respectively. The results are presented in table 4 , 5 and 6.

RESULTS AND DISCUSSION

At nearly 87me/100gm, the cation exchange capacity of the Mehsana soil is well above the average for sandy soils, even though the texture classification of these soil is sandy. The sodium percentage of the exchangeable cation is also low at about 6%.

Table 1. Soluble cations present in the soil of Mehsana region in meq/100gm soil

pH	Na	K	Ca
8.95	2.41	0.12	1.30

Table 2. Effect of pH of irrigation water (control) on the cationic exchange of Mehsana soil

pH	Exchangeable ions (meq/100gm soil)		
	Na	Ca	K
8.95	6.1	81.0	0.50
8.50	6.2	87.5	0.54
7.50	6.2	98.0	0.23
5.50	6.3	9.80	0.33
4.50	5.7	185.0	0.55

Table 3. Effect of pH and concentration of effluent on cation exchange capacity of soil of Mehsana region

		Na			Ca			K		
		pH			pH			pH		
		7.5	5.5	4.5	7.5	5.5	4.5	7.5	5.5	4.5
Control (600 mg/L TDS)		6.16	6.26	5.7	98	98	185	0.23	0.35	0.55
Effluent concentration in mg/L	1500	4.3	7.2	8.8	120	240	255	0.35	0.84	0.95
	3000	5.3	7.2	9.0	110	225	252.5	0.33	0.83	0.93
	5000	7.4	8.4	10.6	100	205.5	232.5	0.39	0.84	0.95
	9000	7.6	11.0	11.2	105	202.5	232.5	0.35	0.85	1.01

	F_{Na}	F_{Ca}	F_{K}
pH	9.15*	32.87*	46.59*
TDS	5.34**	4.38**	7.95**

* required F value at 0.01 = 8.65
** required F value at 0.01 = 7.01 and at 0.05 = 3.84

Table 4. Percentage of Sodium in the exchange complex of soil during the application of irrigation water with different TDS content at different pH values

pH	Effluent TDS concentration in mg/L				
	Control (600 mg/L TDS)	1500	3000	5000	9000
7.5	5.9	3.5	4.6	6.9	6.7
5.5	6.0	2.9	3.1	3.9	5.1
4.5	3.0	3.3	3.4	4.3	4.6

Table 5. $CaCO_3$ addition to the soil before effluent treatment

		Na			Ca			K		
		pH			pH			pH		
		7.5	5.5	4.5	7.5	5.5	4.5	7.5	5.5	4.5
Control (600 mg/L TDS)		6.16	6.26	5.7	98	98	185	0.23	0.35	0.55
Effluent concentration in mg/L	1500	4.39	6.28	8.77	117.5	250	295	0.28	0.74	0.82
	3000	6.18	7.1	9.0	107.5	230	270	0.28	0.70	0.87
	5000	7.24	9.3	10.58	112.5	225	265	0.37	0.77	0.86
	9000	10.23	12.27	11.2	105	225	247.5	0.36	0.79	0.87

	F_{Na}	F_{Ca}	F_K
pH	5.46*	36.38*	66.0*
TDS	11.74**	4.81**	9.0**

* required F value at 0.01 = 8.65 and at 0.05 = 4.46
** required F value at 0.01 = 7.01 and at 0.05 = 3.84

Table 6. Na/(Ca + K)% during the $CaCO_3$ addition to the soil prior to the application of irrigation water containing different amount of TDS at varying pH levels

pH	TDS content in irrigation water (mg/L)				
	Control (600 mg/L TDS)	1500	3000	5000	9000
7.5	6.3	3.7	5.7	6.4	9.7
5.5	6.4	2.5	3.1	4.1	5.4
4.5	3.1	3.0	3.3	4.0	4.5

Table 7. Effect of $Ca(CH_3COO)_2$ to the effluent on the cation exchange

		Na			Ca			K		
		pH			pH			pH		
		7.5	5.5	4.5	7.5	5.5	4.5	7.5	5.5	4.5
Control (600 mg/L TDS)		6.16	6.26	5.7	98	98	185	0.23	0.35	0.55
Effluent concentration in mg/L	1500	2.28	7.45	5.14	100	315	260	0.24	0.66	0.73
	3000	2.83	7.85	5.81	90	285	235	0.27	0.72	0.57
	5000	2.96	8.8	8.26	85	335	235	0.24	0.66	0.69
	9000	4.18	8.62	10.16	100	350	240	0.27	0.60	0.69

	F_{Na}	F_{Ca}	F_K
pH	10.12*	15.01*	33.95*
TDS	1.43**	1.81**	2.06**

* required F value at 0.01 = 8.65
** required F value at 0.05 = 3.84

Table 8. Na/(Ca+K)% when $Ca(CH3COO)2$ was added to the irrigation water

pH	TDS concentration in irrigation water (mg/L)				
	Control (600 mg/L TDS)	1500	3000	5000	9000
7.5	6.3	2.3	3.1	3.5	4.2
5.5	6.4	2.4	2.7	2.6	2.5
4.5	3.1	2.0	2.5	3.5	4.2

Table 9. Effect of KCl in the effluent on exchange capacity

		Na			Ca			K		
		pH			pH			pH		
		7.5	5.5	4.5	7.5	5.5	4.5	7.5	5.5	4.5
Control (600 mg/L TDS)		6.16	6.26	5.7	98	98	185	0.23	0.35	0.55
Effluent concentration in mg/L	1500	3.02	5.39	6.73	72.5	255	262.5	1.05	1.11	1.53
	3000	3.21	5.96	7.28	87.5	252.5	247.5	0.78	1.18	1.51
	5000	5.13	7.3	7.83	105	270	242.5	0.78	1.12	1.26
	9000	8.26	7.23	9.28	90	260	242.5	0.75	1.14	1.32

	F_{Na}	F_{Ca}	F_K
pH	5.02*	21.23*	31.44*
TDS	3.97**	2.017**	33.44**

* required F values at 0.01 = 8.65 and 0.05 = 4.46
** required F values at 0.01 = 7.01 and 0.05 = 3.84

Table 10. Na/(Ca+K)% when 50 mg/L KCl was added to the irrigation water containing different TDS concentrations

pH	TDS concentration in irrigation water (mg/L)				
	Control (600 mg/L TDS)	1500	3000	5000	9000
7.5	6.3	4.1	3.6	4.8	9.1
5.5	6.4	2.1	2.3	2.7	2.8
4.5	3.1	2.5	2.9	3.2	3.8

Fig. 1. Effect of pH of irrigation (control) water on Na/(Ca + K) percentage of soil

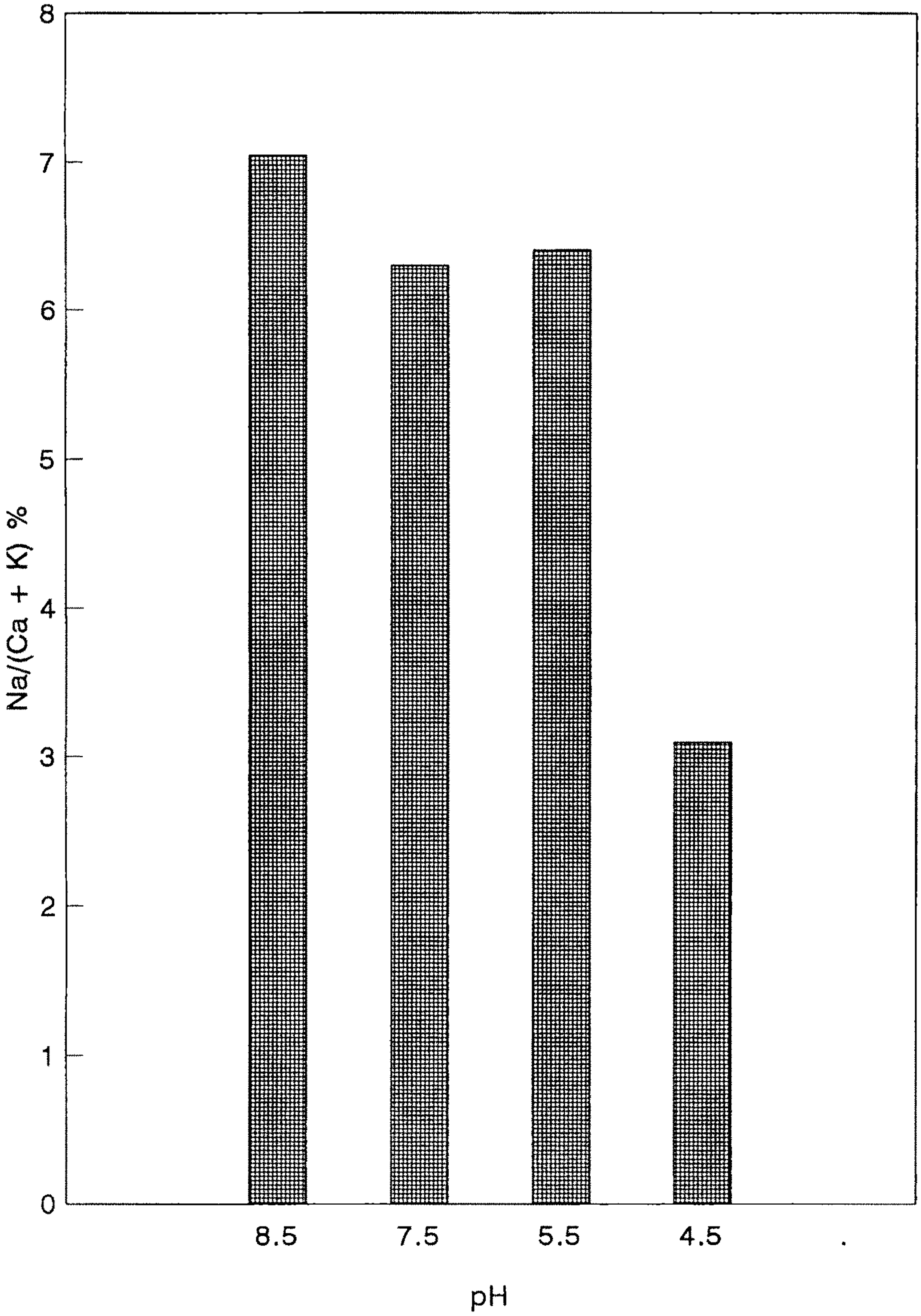


Fig. 2. Na/(Ca + K) percentage in soil after various treatments at pH 7.5

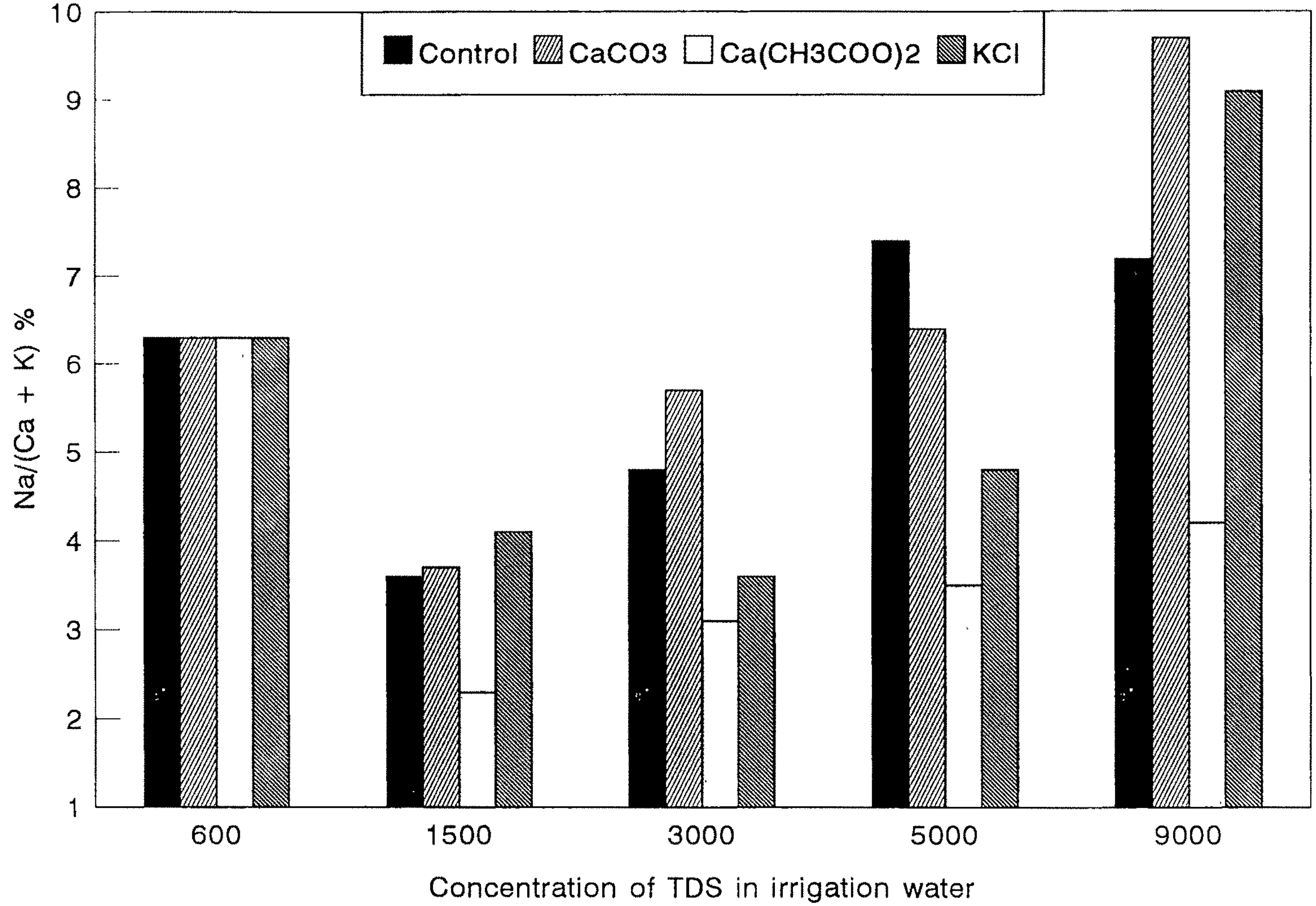


Fig. 3. Na/(Ca + K) percentage in soil after various treatments at pH 5.5

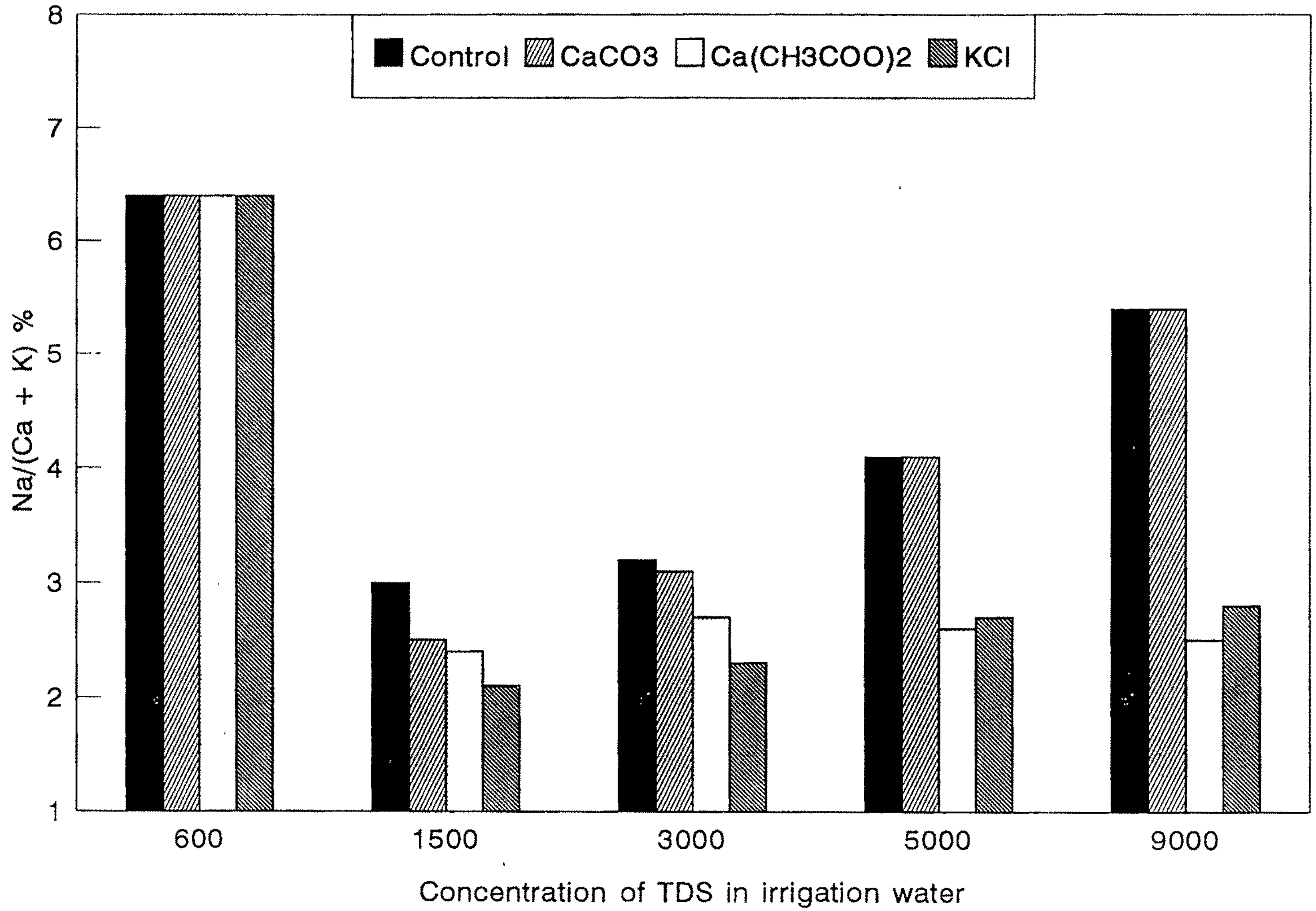
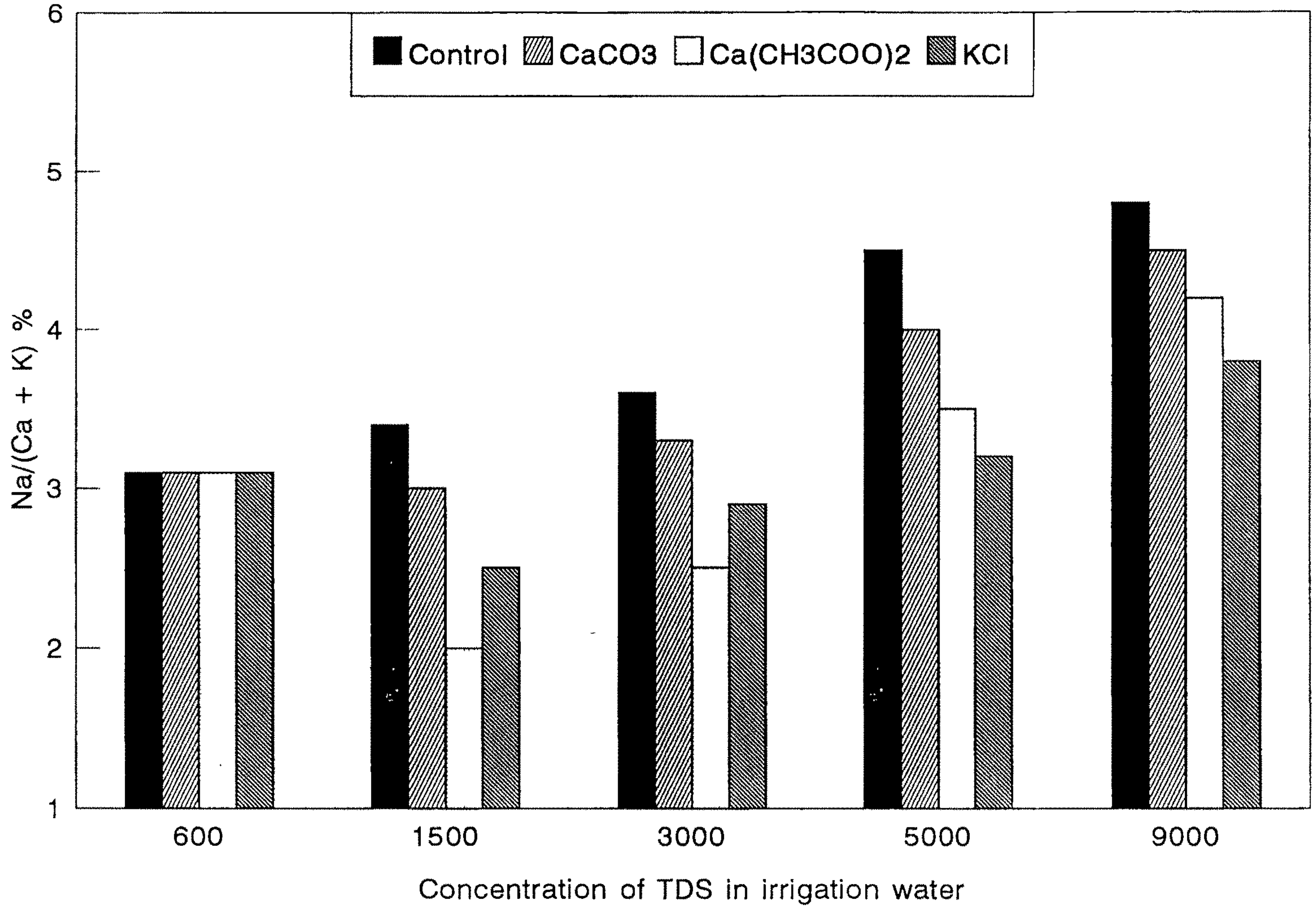


Fig. 4. Na/(Ca + K) percentage in soil after various treatments at pH 4.5



This is probably the reason why this region has been able to grow crops for a sustained period with high TDS irrigation water. It was observed that the pH has high influence on the exchange capacity and the exchangeable calcium increased with decreasing pH (Table 2). But the exchangeable sodium was not much effected by the change in pH. The exchangeable sodium remained nearly the same even though there was a small trend of reduction. However, the exchangeable calcium and total CEC increased significantly while potassium remained stationary. Thus Na/Ca+K ratio was more favourble (Fig.1)

These results can be interpreted in two ways. First one is that of the opening of the clay lattice and the second one being the opening of the peripheral charges on the clay surfaces to accommodate additional calcium on the particle surface. Even though the soils have less than 1% $CaCO_3$, there is sufficient calcium in soil to account for this phenomenon. The sodium content in the irrigation water is not strong enough to induce clay dispersion in the soil.

The concentrated effluent treatment(9000 mg/L) didnot change the exchangeable sodium level at pH 7.5(Table 3). Similarly the 600mg/L irrigation water did not change the sodium content level even when the pH was dropped to 4.5. But the treatment with higher salt content aining water increased both the exchangeable sodium and calcium level of the exchange complex as the pH of the irrigation water was dropped. In case of calcium and potassium, the increase was prominent when the water with 1500 mg/L NaCl was used. Later when the water with high TDS was applied, there was a small change in the exchangeable calcium, but not much difference in exchangeable potassium was observed. This can be attributed to the increase in exchangeable sodium in the exchange complex as the TDS in the irrigation water increased. Yet the

Na/Na+Ca+K% was much less than the maximum limit of Na% in the soil and this kept the soil more permeable [10] (Table-4). In all these treatment the effect of pH was significant beyond 0.01 level and the effect of salt concentration was significant beyond 0.05 level.

When 0.05% $CaCO_3$ was added to the soil before the treatments were imposed not much change in the sodium content was noticed even at lower pH compared to the experiment without the addition of $CaCO_3$. But an Increase in the Calcium content in the exchange complex was noticed(Table 5). This was higher at lower pH. This may be due to the opening of the peripheral charges on the clay surfaces to accommodate additional calcium on the particle . surface. Here also like the earlier experiments, a sudden hike in the calcium and potassium is found when water containing 1500 mg/L TDS was applied to the soil. Later with higher TDS content calcium was found to be decreasing slightly and potassium remained almost constant. The Na/Ca+K% was very less showing the higher percentage of calcium in the soil, which keeps the soil more permeable (Table 6).

The addition of 200 mg/L calcium acetate to the irrigation water increased the calcium content in the exchange complex abnormally (Table 7). The calcium intake at the exchange site was higher at pH 5.5 than at pH 4.5 compared to the $CaCO_3$ addition. Thus allowing Na/Ca+K ratio to lower down. This must be due to the higher solubility of calcium acetate at higher pH than calcium carbonate. In this case Na/Ca+K ratio remained practically constant (Table 8). Effect of pH was significant beyond 0.01 level while TDS content effect was significant beyond 0.1 level during these treatments.

The addition of 50 mg/L potassium chloride to the irrigation water increased the amount of potassium as well as calcium in the exchangeable complex compared to the increase in the sodium content. Increase in the calcium content was significant beyond 0.05 level and that of potassium was beyond 0.01 level (Table 9). Here also Na/Ca+K ratio was found to be very low as in the case of calcium acetate treatment and practically constant during the application of water with high TDS (Table 10).

Thus at pH 7.5 addition of calcium acetate and potassium chloride to the irrigation water reduce the sodium uptake to the exchange site more than that when calcium carbonate was added to the soil during the treatment. Thus allowing the Na/Ca+K % to a lower value. But as the pH was lowered to 5.5 and 4.5 the Na/Ca+K ratio remained almost constant in all the experiment. Yet calcium acetate and potassium chloride addition made the ratio still smaller than the other experiments, thus allowing the exchangeable sodium to a lower value and increasing the permeability of the soil (Fig 2, 3 and 4). Indications are that Mehsana soils have additional buffering capacity in terms of exchange and it is this capacity which is able to resist the ill effect of high TDS irrigation. There are reports that adsorption of sodium on the exchange site is blocked by the strong electrolyte. The present studies also suggest that even when strong sodium chloride based effluent is used there is no appreciable uptake of sodium in the exchange complex. Only at the highest level of 9000 mg/L, there is an appreciable sodium adsorption and it is not clear whether sodium has been adsorbed in the lattice or on the periphery.

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