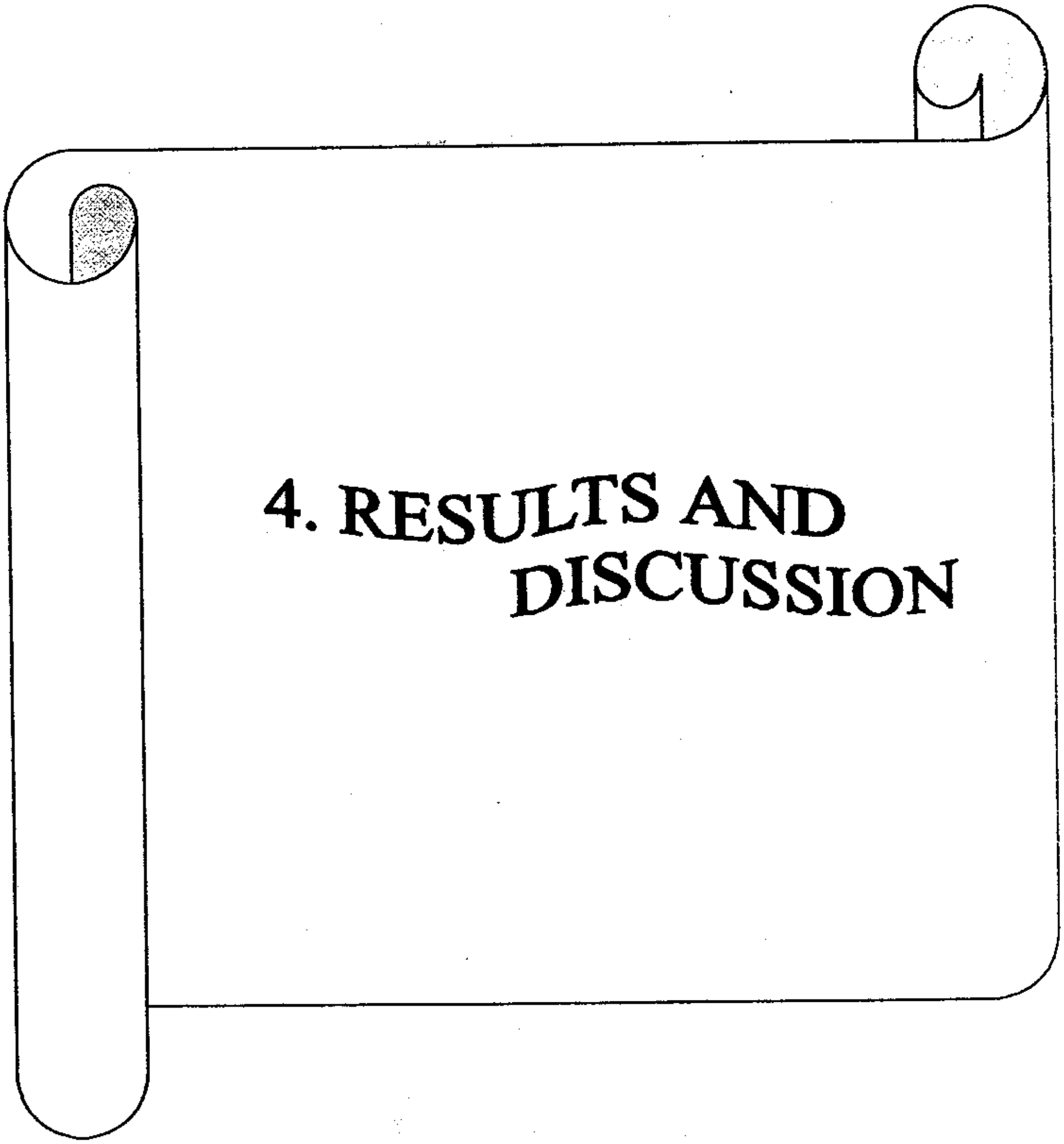


4. RESULTS AND DISCUSSION

4. Results and Discussion

4.1. Physical and chemical properties of the investigated soils:

Date presented in Table (1) reveal that the soil sample representing the calcareous soils of Borg-El-Arab is of a clay loam texture. It has clay content of about 37.1% while the soil sample representing the Nile alluvial non-calcareous soils of Moshtohor is of clay texture where its clay content attained about 56%.

The $CaCO_3$ content of Borg El-Arab is relatively high (35.5%) whereas that of Moshtohor was less than 3%. On the other hand, the alluvial soil of Moshtohor revealed slightly more organic matter content than that of Borg El-Arab.

Value of pH of the calcareous soil of Borg El-Arab soil was higher than that of Moshtohor one where it was 8.2 in the former soil and only 7.7 in the latter one. Hydrolysis of $CaCO_3$ in the calcareous soil may account for its high pH value.

Regarding the soils content of soluble cations, data in Table (2) reveal that it was dominated by Ca^{2+} followed by Mg^{2-} ions then Na^+ ones whereas K^+ ions were of the least abundance.

SO_4^{2-} anions dominated the anionic composition of the calcareous soil whereas Cl^- anions prevailed in the Nile alluvial noncalcareous one. In both the studied soils, concentration of HCO_3^- anions was the least whereas CO_3^{2-} anions were not detected.

Table (1): Particle size distribution, calcium carbonate and organic matter contents of the studied soil samples.

Location of the soil sample	Particle size distribution %				Textural class	$CaCO_3$ %	Organic matter %
	C. Sand	F. Sand	Silt	Clay			
Borg El-Arab (The calcareous soil sample)	4.50	35.40	24.30	35.80	Clay loam	35.50	0.85
Moshtohor (the Nile alluvial noncalcarewous soil sample)	5.50	20.30	17.90	56.30	Clay	2.70	1.20

Table (2): Some chemical characteristics of the studied soil samples.

Location of the soil sample		**EC**	**Soluble cations and anions m mol$_c$ L^{-1}**							**CEC**	**Exchangeable cations c mol$_c$ kg^{-1}**			
	pH	**dS/m**	**Ca^{++}**	**Mg^{++}**	**Na^{+}**	**K^{+}**	**HCO_3^{-}**	**Cl^{-}**	**$SO_4^{=}$**	**c mol$_c$ kg^{-1}**	**Ca^{++}**	**Mg^{++}**	**Na^{+}**	**K^{+}**
Borg El-Arab (The calcareous soil sample)	8.2	3.4	18.5	10.1	4.97	0.43	2.5	13.4	18.1	22.0	14.0	5.5	0.85	1.3
Moshtohor (the Nile alluvial noncalcarewous soil sample	7.7	2.1	9.5	7.3	3.55	0.65	1.9	12.7	6.4	43.6	21.7	18.2	3.00	1.1

Cation exchange capacity (CEC) of the calcareous soil was 22.0 $cmole_c/kg$ soil whereas that of the Nile alluvial noncalcareous one was as high as a bout 44 $cmole_c\,kg^{-1}$.

The higher content of clay in the Nile alluvial non-calcareous soil as well as its higher content of the organic matter account for such a finding.

Exchangeable cations followed the ascending order: $Na^+ < K^+ < Mg^{2+} < Ca^{2+}$ in the calcareous soil whereas they were arranged descendingly in the following order: $K^+ < Na^+ < Mg^{2+} < Ca^{2+}$ in the Nile alluvial noncalcareous soil. Such patterns of order seemed to be coinciding with the soluble contents of these cations in soils under study.

4.2. Mineralogical composition of the studied exchange materials:-

4.2.1. Mineralogical composition of the commercial clay minerals used:

The powder clay minerals used were subjected to X-ray diffraction beam from 2 to 27 θ to identify and recognize the mineralogical composition of the commercial clay minerals used.

4.2.1.1. XRD of the commercial attapulgite clay mineral:

X-ray diffraction pattern of the commercial attapulgite clay mineral is shown in Fig. (1). The patterns reveal that attapulgite is the dominant clay mineral as noticed from clear diffraction patterns at 10.5, 6.44 and 3.69 A°. Kaolonite and quartz are also detected in the sample as pointed out from diffraction patterns at 7.2, 3.57 A° and 4.26 A°, respectively.

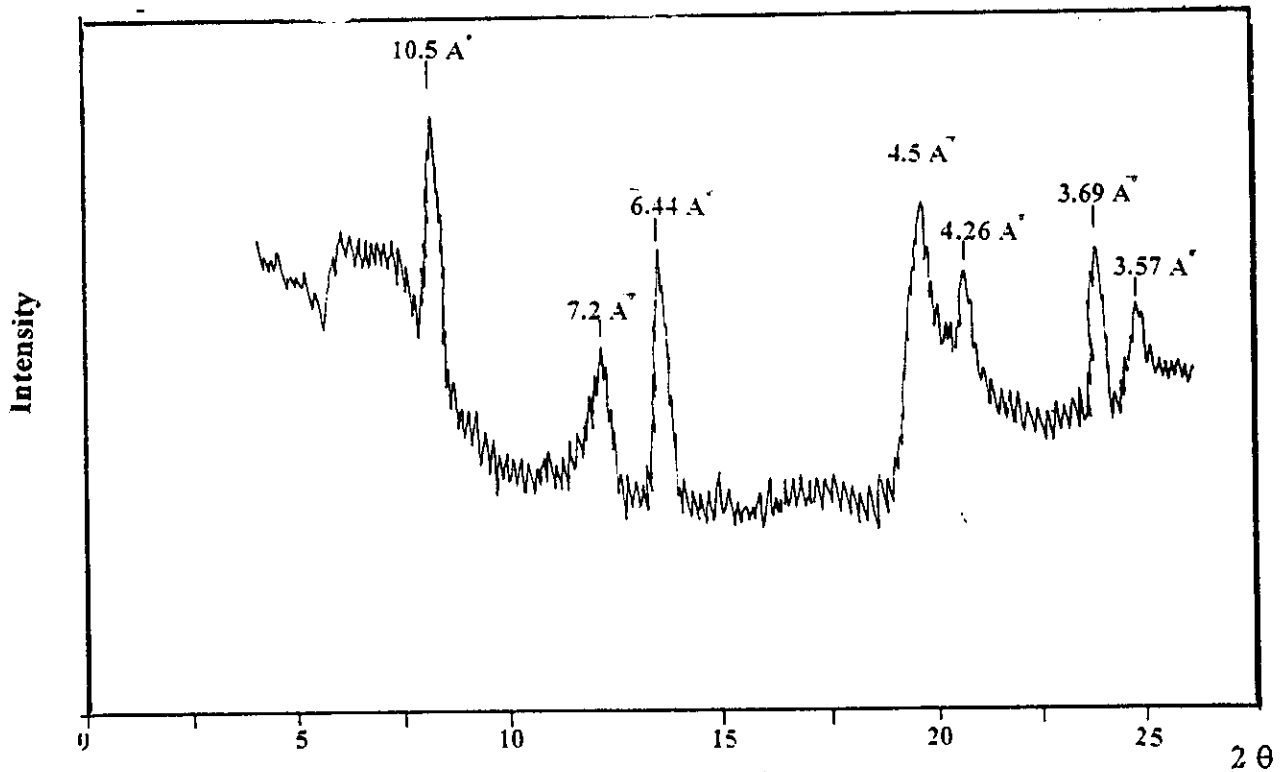


Fig. (1): X- ray diffraction pattern of Palygorskite used.

4.2.1.2. XRD of the commercial bentonite clay mineral:

Obtained pattern in Fig. (2) indicates the dominancy of montmorillonite mineral in the bentonite sample as detected from clear basal spacing at 14.24 A° (as first order) and 4.51 A° (as third order). Besides, some kaolinite and quartz were nominated.

4.2.2. Mineralogical composition of the clay fraction of studied soil samples:-

4.2.2.1. The calcareous soil sample of Borg El-Arab:-

Fig. (3) shows X-ray diffraction patterns of clay fraction (< 2 μm) separated from the surface layer of the calcareous soil sample. The figure reveals that feldspars and calcite dominated in the clay fractions as indicated from clear stable diffraction patterns at 2.8, 3.25, 3.8 A° and 3.03 A°, 2.29 A°, respectively.

The stable diffraction pattern at 10.4 A° in all treatments confirmed the presence of attapulgite which dominates in the calcareous sediments. The presence of quartz was indicated by diffraction pattern at 3.33 A°, which remained stable in all treatments.

The figure denotes also that kaolinite is present in small quantities (relative to other minerals) as indicated by the stable diffraction patterns at 7.2 and 3.57 A° in Mg- air dried, Mg-glycolated and K- air dried, which disappeared in the treatment of K heated at 550 °C because of the destruction of kaolinite structure. Beside kaolinite, some illite mineral exists, as shown from the figure indicated by diffraction patterns at ~ 10 A° in all treatments and confirmed by clear diffraction pattern at 4.5 A° as the second order.

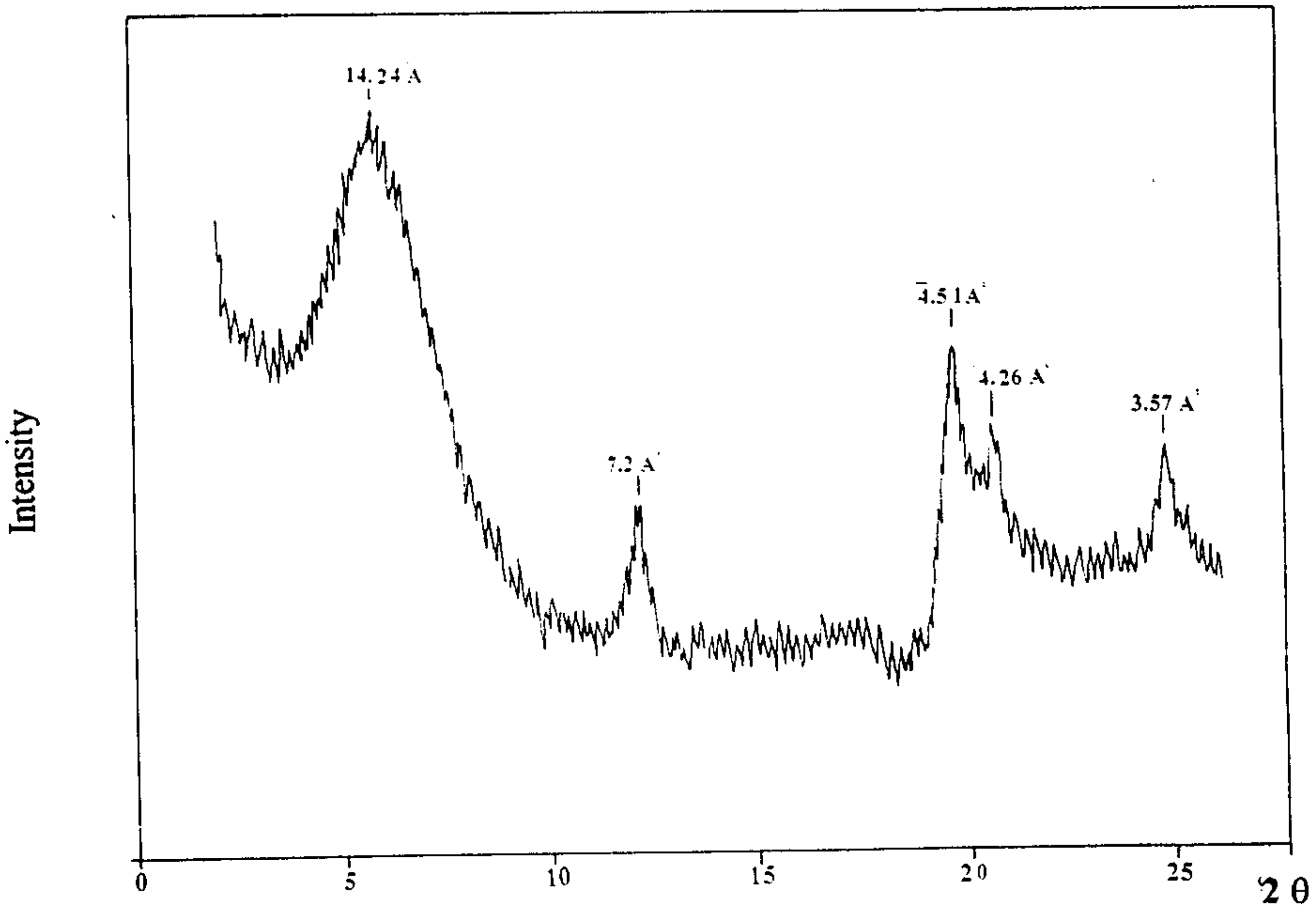


Fig. (2): X- ray diffraction pattern of Bentonite used.

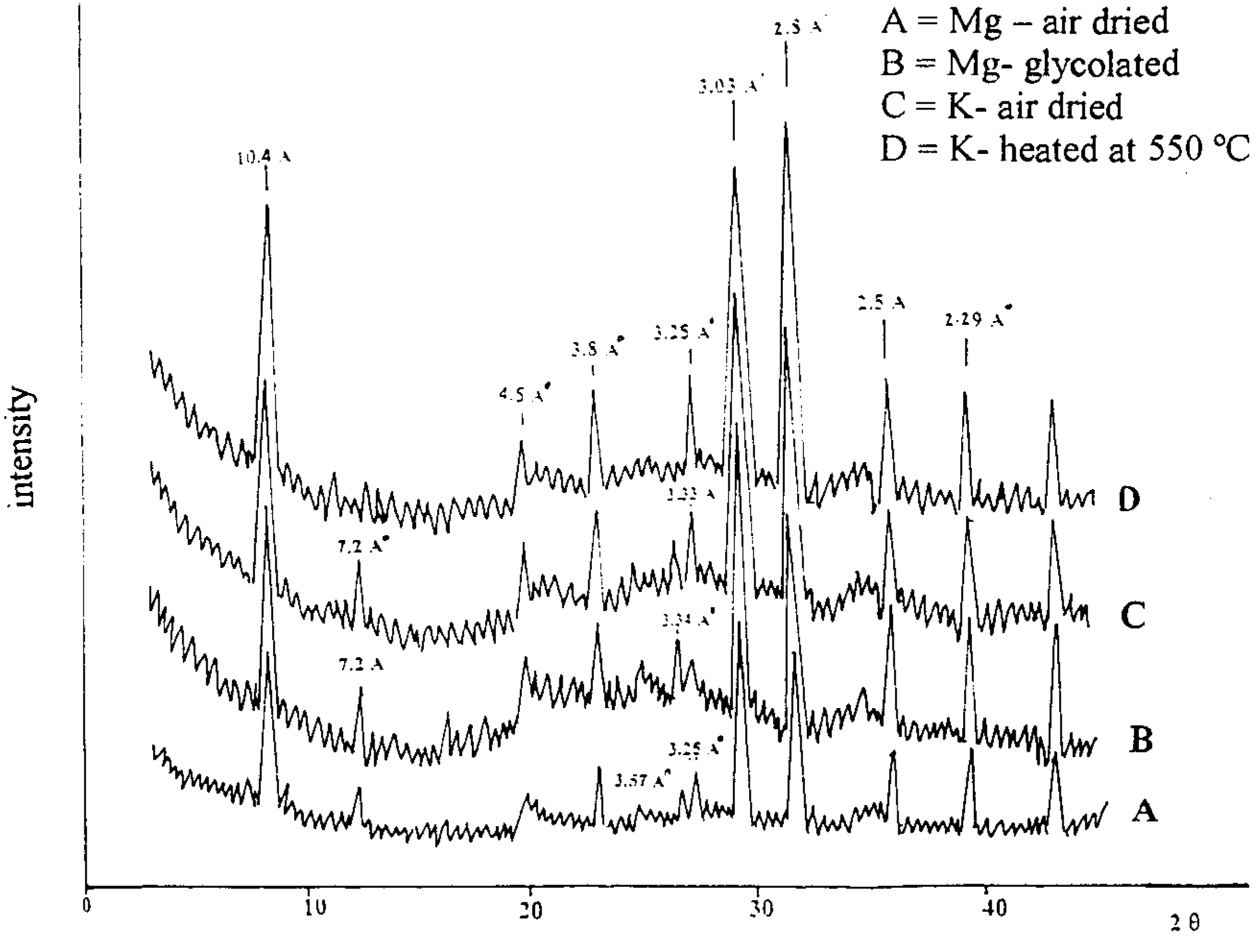


Fig. (3): X- ray diffraction pattern of the clay fraction separated from surface layer of Borg El-arab soil.

4.2.2.2. The Nile alluvial- noncalcareous soil sample of Moshtohor:-

The X-ray diffraction patterns of the clay fraction separated from the surface layer of Moshtohor soil sample are shown in Fig. (4). It is clear from the figure that the clay fraction is generally composed of the following minerals:

Montmorillonite: as indicated by diffraction patterns at 14.7 A° in Mg- air dried which expands to 17.45 A° in Mg- glycolated, contracted to about 10 A° in both K- air dried and K- heated at 550°C.

Kaolinite: as indicated by the stable diffraction patterns at 7.3 A°, in Mg- air dried, Mg- glycolated and K- air dried treatment which disappeared in K heated at 550 °C treatment.

Hydrous mica: as denoted from stable diffraction patterns in all treatments at 10 ~ 4.5 and 3.6 A°

Dolomite: is found in clay fraction as indicated from diffraction pattern at 3.2 A° which is still stable in all treatments.

The presence of **quartz and plagyoclase** is recommended from stable diffraction patterns in all treatments at 3.34 A° and 3.2 A°, respectively.

Due to the variation of soil formations and genesis in each location the clay mineralogical composition showed some differences.

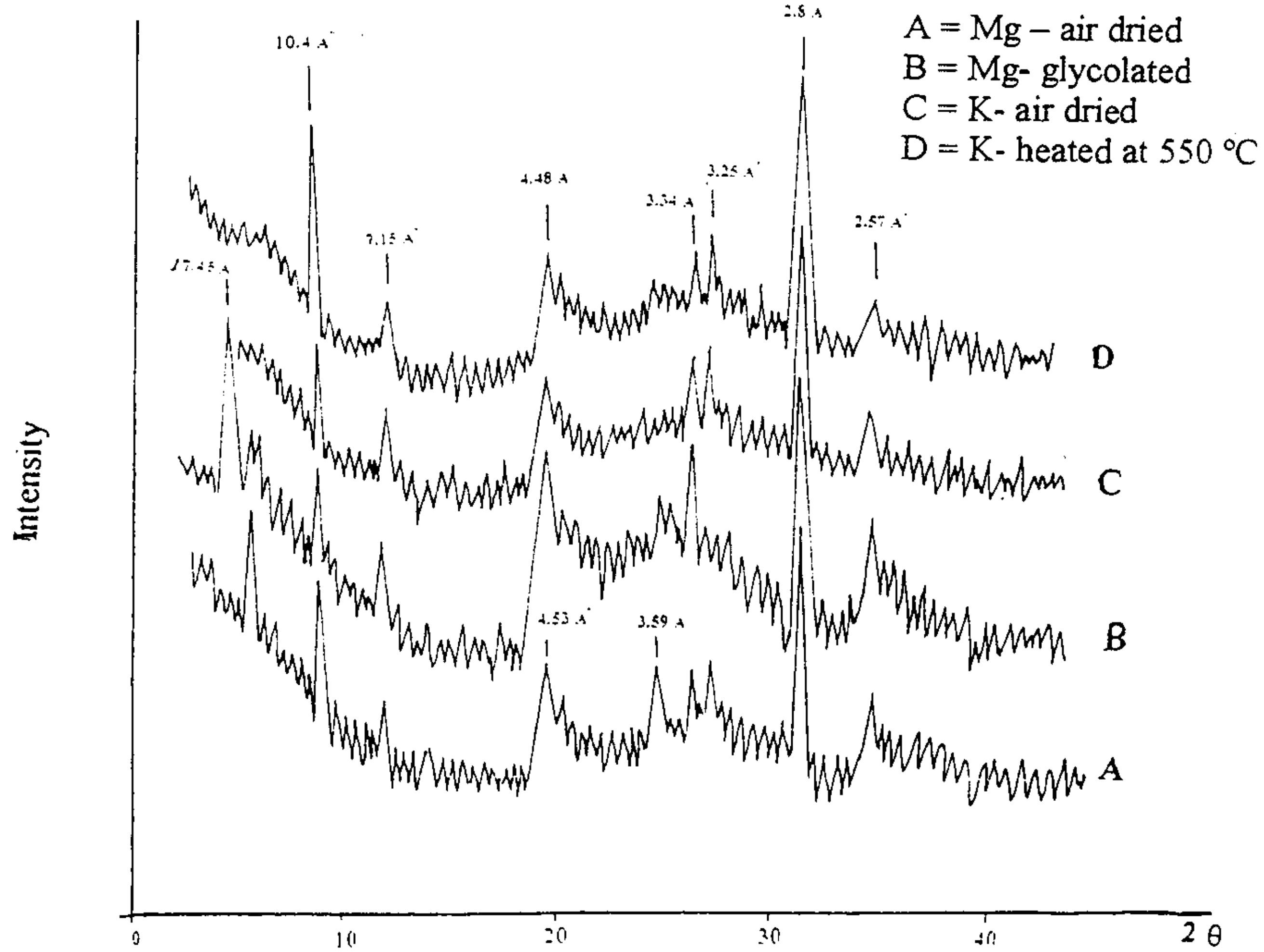


Fig. (4): X- ray diffraction pattern of the clay fraction separated from surface layer of Moshtohor soil.

4.3. Na - Ca exchange isotherms:

4.3.1. Na - Ca exchange on the studied calcareous and Nile alluvial noncalcareous soils:

The data from the Na-Ca exchange experiment conducted on the investigated soils are given in Table (3) and illustrated graphically in Figs. (5 and 6).

It is obvious from these Tables and Figure that increasing Na/Ca ratio in equilibrium solution resulted in increase in exchangeable Na on soils and consequently increased equivalent exchangeable Na fraction, i.e. E_{Na}. This result stands in well agreement with that of **Abbas (1985)** who stated that the effect of Na concentration on the displacement of Ca is attributed to the law of mass - action, since exchange reaction is considered to be stoichiometric in nature involving quantitative relationships. Therefore, as concentration of Na increased in the surrounding solution, it leads to a greater cationic replacement of Ca .

Thus, our results imply that the studied soils could accumulate quite different amounts of exchangeable Na when irrigated with a given water and consequently an assessment of sodicity hazard that is based solely on SAR ($Na/\sqrt{Ca + Mg}$ in $mmol\ L^{-1}$) may not be totally reliable.

However, the increase in exchangeable Na and its equivalent fractions were shown to be higher in the Nile alluvial noncalcareous soil than the calcareous one.

Such a finding might be due to more release of Ca in equilibrium solution of the calcareous soil. This Ca can preclude attainment of thermodynamic equilibrium **(Jurinak et al, 1984)**.

Table (3): Concentrations and activities of soluble Na and Ca, exchangeable Na and Ca, equlvalent and mole fractions of exchangeable Na, selectivity coefficients, SAR, SAR* and ESR for Na-Ca equilibria of the studied calcareous and Nile alluvial noncalcareous soils.

Type of the exchange material	Na/Ca ratio in equilibrium solution	C_{Na}	a_{Na}	C_{Ca}	a_{Ca}	Ex. $_{Na}$	Ex. $_{Ca}$	E Na	*N* Na	K_G^*	K_{GT}^*	K_V^*	SAR_C	SAR*	ESR
		mol L^{-1}				c mol_c kg^{-1}									
The calcareous soil (Borg El- Arab)	10:90	0.002	0.0017	0.009	0.005	2.44	22.10	0.10	0.18	4.41	17.54	63.81	0.021	0.025	0.110
	25:75	0.006	0.0051	0.007	0.004	3.70	20.00	0.16	0.27	2.19	4.03	13.96	0.072	0.085	0.185
	50:50	0.010	0.0085	0.005	0.003	4.80	17.90	0.21	0.35	1.62	2.06	6.80	0.141	0.166	0.268
	75:25	0.014	0.0120	0.003	0.002	6.96	17.30	0.29	0.45	1.35	1.30	4.03	0.256	0.298	0.402
	90:10	0.018	0.0155	0.001	0.001	7.75	16.90	0.31	0.48	0.69	0.33	1.01	0.570	0.660	0.459
The Nile alluvial noncalcareous soil (Moshtohor)	10:90	0.002	0.0017	0.009	0.005	5.00	39.40	0.11	0.20	5.07	22.83	82.09	0.021	0.025	0.127
	25:75	0.006	0.0051	0.007	0.004	10.00	34.80	0.22	0.36	3.40	8.96	29.30	0.072	0.085	0.287
	50:50	0.010	0.0085	0.005	0.003	15.10	26.70	0.36	0.53	3.41	7.42	21.80	0.141	0.166	0.566
	75:25	0.014	0.0120	0.003	0.002	22.70	23.10	0.50	0.66	3.29	5.47	14.64	0.256	0.298	0.983
	90:10	0.018	0.0155	0.001	0.001	28.60	16.10	0.64	0.78	2.69	2.61	6.36	0.570	0.660	1.776

C_{Na}, C_{Ca} are concentrations of Na and Ca respectively in equilibrium solution.

a_{Na}, a_{Ca} are activities of Na and Ca respectively in equilibrium solution.

Ex $_{Na}$, Ex $_{Ca}$ are exchangeable Na and Ca respectively on the exchange complex (solid phase).

E $_{Na}$ is the equivalent fraction of exchangeable Na on the exchange complex .

K_G^*: Gapon's selectivity coefficient.

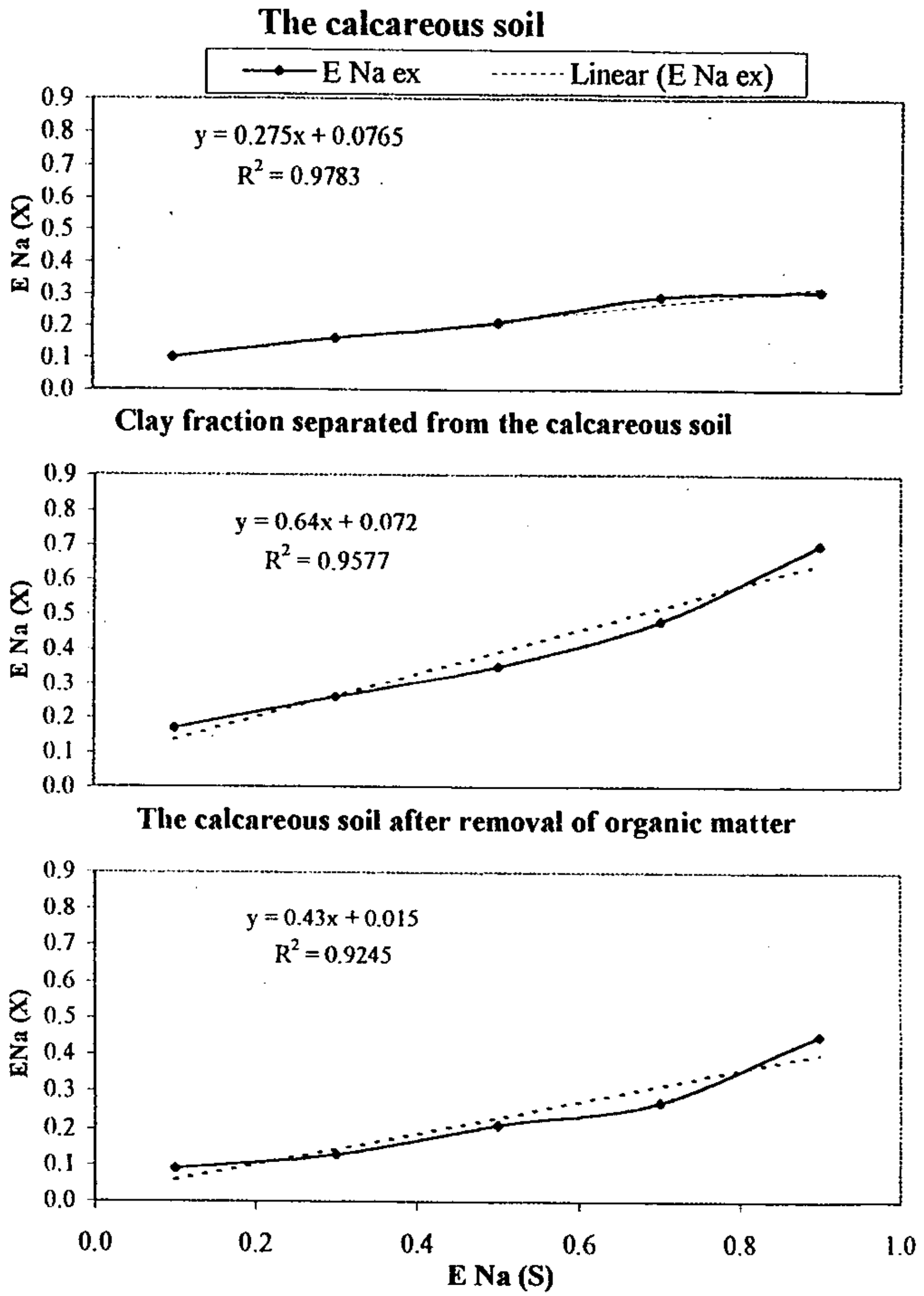
K_{GT}^*: Gaines- Thomas selectivity coefficient.

K_V^*: Vanselow's selectivity coefficient

SAR_c : Sodium adsorption ratio calculated on concentration basis.

SAR*: Sodium adsorption ratio calculated on activity basis.

ESR: Determined exchangeable Na ratio.



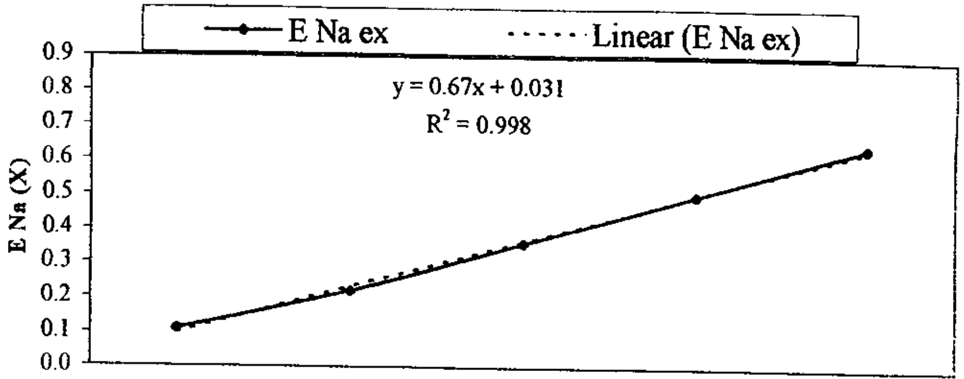
The calcareous soil

Clay fraction separated from the calcareous soil

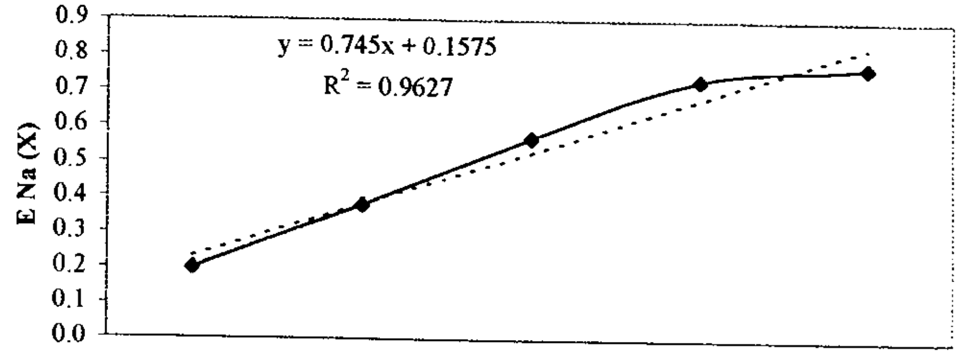
The calcareous soil after removal of organic matter

Fig. (5): Relationship between equivalent fractions of soluble Na in equilibrium solution and equivalent fractions of exchangeable Na on the calcareous soil, clay fraction separated from this soil and O.M free- calcareous soil (Na-Ca exchange equilibria).

The Nile alluvial noncalcareous soil



Clay fraction separated from Nile alluvial noncalcareous soil



The Nile alluvial noncalcareous soil after removal of organic matter

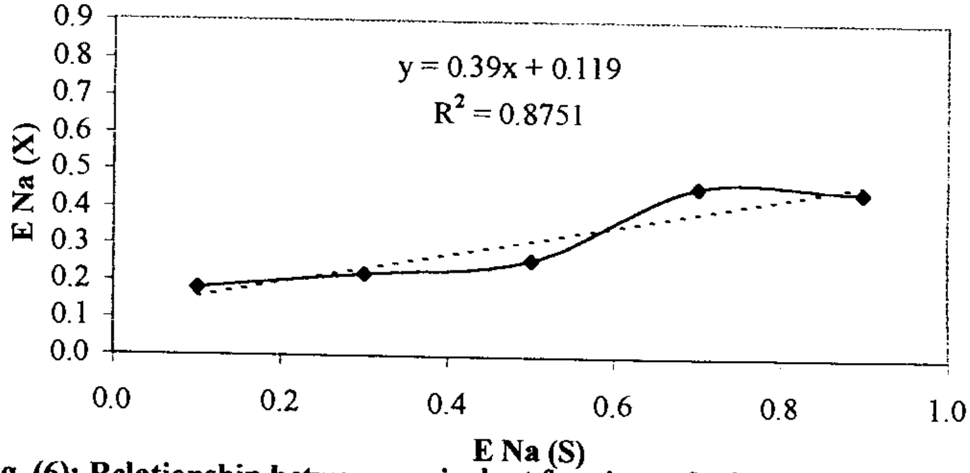


Fig. (6): Relationship between equivalent fractions of soluble Na in equilibrium solution and equivalent fractions of exchangeable Na on the Nile alluvial noncalcareous soil, clay fraction separated from this soil and O.M free- Nile noncalcareous soil (Na-Ca exchange equilibria).

A non-constancy of the calculated selectivity coefficients is apparent. All the selectivity coefficient values i.e. K_G, K_{GT} and K_V^a tended to decrease with increasing exchangeable Na and consequently E_{Na}.

These results mean that, in general, both the studied soils exhibited some preference for Na over Ca at low E_{Na} values and some preference for Ca at high E_{Na} values.

The decreased preference of Ca at the high E_{Ca} i.e. low E_{Na} is ascribed as mentioned before to the adsorption of monovalent complexes of Ca ions, such as $CaCl^+$ from an aqueous phase containing chloride.

4.3.2. Na- Ca exchange on the clay fractions separated from the calcareous and Nile alluvial noncalcareous soils:-

Data of Na and Ca concentrations, their Na/Ca ratios in equilibrium solutions as well as equivalent and mole fractions of exchangeable Na are presented in Table (4) and illustrated graphically in Figs. (5 and 6).

Increasing Na concentration and consequently Na/Ca ratio in equilibrium solution was associated with a gradual increase in exchangeable Na content corresponding to gradual decrease in exchangeable Ca content. In other words, increasing Na/Ca ratio in equilibrium solution resulted in equivalent fraction of exchangeable Na to increase and equivalent fraction of exchangeable Ca to decrease.

It follows from the forgoing that if the situation in the soil solution changes as a result of external factors, the equilibrium between complex and solution is disturbed. A new equilibrium

Table (4): Concentrations and activities of soluble Na and Ca, exchangeable Na and Ca, equivalent and mole fractions of exchangeable Na, selectivity coefficients, SAR, SAR* and ESR for Na-Ca equilibria of the clay fraction separated from the studied calcareous and Nile alluvial noncalcareous soils.

Type of the exchange material	Na/Ca ratio in equilibrium solution	C_{Na}	a_{Na}	C_{Ca}	a_{Ca}	$Ex._{Na}$	$Ex._{Ca}$	E Na	*N* Na	K_G^*	K_{GT}^*	K_V^*	SAR_C	SAR*	ESR
		mol L^{-1}				c mol_c kg^{-1}									
The clay fraction separated from the calcareous soil (CFC)	10:90	0.002	0.0017	0.009	0.005	4.19	19.80	0.17	0.30	8.46	59.05	201.09	0.021	0.025	0.212
	25:75	0.006	0.0051	0.007	0.004	6.31	17.74	0.26	0.42	4.20	13.04	41.31	0.072	0.085	0.356
	50:50	0.010	0.0085	0.005	0.003	8.37	15.71	0.35	0.52	3.21	6.72	19.96	0.141	0.166	0.533
	75:25	0.014	0.0120	0.003	0.002	11.52	12.50	0.48	0.65	3.09	4.97	13.43	0.256	0.298	0.922
	90:10	0.018	0.0155	0.001	0.001	16.95	7.10	0.70	0.83	3.62	3.86	9.06	0.570	0.660	2.387
The clay fraction separated from the noncalcareous soil (CFN)	10:90	0.002	0.0017	0.009	0.005	9.02	35.40	0.20	0.34	10.18	82.67	274.86	0.021	0.025	0.255
	25:75	0.006	0.0051	0.007	0.004	16.90	27.00	0.38	0.56	7.40	33.66	97.21	0.072	0.085	0.626
	50:50	0.010	0.0085	0.005	0.003	25.30	19.00	0.57	0.73	8.02	27.61	70.30	0.141	0.166	1.332
	75:25	0.014	0.0120	0.003	0.002	32.40	12.20	0.73	0.84	8.90	21.69	50.24	0.256	0.298	2.656
	90:10	0.018	0.0155	0.001	0.001	34.30	10.20	0.77	0.87	5.09	5.95	13.43	0.570	0.660	3.363

See footnote Table (3).

will then be established in which complex- composition and solution- composition undergo mutual adjustment. These adjustments are effectuated by equivalent exchange between both solution phase and the exchange complex.

A comparison between equivalent fractions of exchangeable Na and exchangeable Ca on the studied soils on one side and their corresponding values on the clay fractions of these soils on the other one, indicates that the increase in the exchangeable Na fraction is at the expense of exchangeable Ca one on clay fractions. This might presumably indicate to the higher affinity for Na on the clay separate than on soil whereas the opposite was true for Ca.

Values of the selectivity coefficients K_G^a, K_{GT}^a and K_v^a were generally lower for the clay fraction separted from the calcareous soil (CFC) than for the clay fraction separated from the Nile alluvial non calcareous soil (CFN) except at the lowest ratio of Na in the equilibrium solutions where an opposite trend was obtained. Noteworthy to indicate that increasing E_{Na} was associated with a gradual decrease in selectivity coefficients indicating once again to the high preferential of the clay fractions of both the studied soils for Na at the low Na/Ca ratios in the equilibrium solution and vice versa. This finding is in well agreement with those of **Levy et al., (1988)** and **Rhue and Mansell (1988)** who stated that selectivity for Na by Cecil soil increased sharply at low Na mole fractions.

The values of all the investigated selectivity coefficients recorded for the clay fraction separated from the studied soils are higher than the corresponding ones recorded for the soils as awhole. This might be an indication to the higher affinity of the clay fraction for exchangeable cations (Na at low Na/Ca ratio and Ca at high Na/Ca ratio) than the soil themselves. The higher cation exchange capacity of the clay fraction than the coarser ones may account for such a finding.

4.3.3. Na- Ca exchange on the calcareous and Nile alluvial noncalcareous soils after removal of organic matter:-

Organic matter has a relatively high affinity for divalent cations and studies have confirmed that when soils were reacted with sodic solutions (**Pratt and Grover, 1964**; **Haghnia and Pratt, 1988**; **Curtin et al., 1995**). The results of the current study presented in Table (5) and illustrated in Figs. (5 and 6), however, reveal that removal of the organic matter although resulted in contradictory effects on equivalent exchangeable Ca fraction on the calcareous soil, yet it resulted in a general increase in this exchangeable equivalent fraction on the Nile alluvial noncalcareous one. **Bolt et al., (1978)** reported that for organic adsorbers (soil organic matter) the situation with respect to divalent ions may be quite different due to chelate formation.

The effect of increasing Na/Ca ratio in the equilibrium solution on increasing equivalent fraction of the exchangeable Na on organic matter free- soils is similar to that previously attained with Na-Ca system of soils and their separated clay fractions.

Relatively lower selectivity coefficients were obtained herein compared with those obtained for the soils or their separated clay fractions. Such a finding assures that the organic matter content is of special concern in increasing preference of soils for Na with special concern at high Na/Ca ratios in the equilibrium solution. **Van Dijk (1971)** reported that soil organic

Table (5): Concentrations and activities of soluble Na and Ca, exchangeable Na and Ca, equivalent and mole fractions of exchangeable Na, selectivity coefficients, SAR, SAR* and ESR for Na-Ca equilibria of the studied calcareous and Nile alluvial noncalcareous soils after removal of organic matter.

Type of the exchange material	Na/Ca ratio in equilibrium solution	C_{Na}	a_{Na}	C_{Ca}	a_{Ca}	$Ex._{Na}$	$Ex._{Ca}$	E Na	*N* Na	$K_G{}^a$	$K_{GT}{}^a$	$K_V{}^a$	SAR_C	SAR*	ESR
		mol L^{-1}				c mol_c kg^{-1}									
The calcareous after removal of the organic matter	10:90	0.002	0.0017	0.009	0.005	2.50	25.60	0.09	0.16	3.90	13.88	50.99	0.021	0.025	0.098
	25:75	0.006	0.0051	0.007	0.004	3.55	23.90	0.13	0.23	1.76	2.68	9.50	0.072	0.085	0.149
	50:50	0.010	0.0085	0.005	0.003	5.85	22.50	0.21	0.34	1.57	1.95	6.46	0.141	0.166	0.260
	75:25	0.014	0.0120	0.003	0.002	7.80	20.70	0.27	0.43	1.26	1.16	3.64	0.256	0.298	0.377
	90:10	0.018	0.0155	0.001	0.001	12.90	15.60	0.45	0.62	1.25	0.86	2.36	0.570	0.660	0.827
The noncalcareous soil after removal of the organic matter	10:90	0.002	0.0017	0.009	0.005	8.80	40.50	0.18	0.30	8.69	61.97	210.33	0.021	0.025	0.217
	25:75	0.006	0.0051	0.007	0.004	10.90	37.80	0.22	0.37	3.41	9.02	29.47	0.072	0.085	0.288
	50:50	0.010	0.0085	0.005	0.003	12.56	36.30	0.26	0.41	2.08	3.23	10.28	0.141	0.166	0.346
	75:25	0.014	0.0120	0.003	0.002	17.90	20.90	0.46	0.63	2.87	4.44	12.16	0.256	0.298	0.856
	90:10	0.018	0.0155	0.001	0.001	22.00	27.00	0.45	0.62	1.23	0.84	2.32	0.570	0.660	0.815

See footnote Table (3).

matter in general acts like a weak field exchanger, showing preference for ions of lower hydrogen energies.

4.3.4. Na-Ca exchange on the commercial used clay minerals:-

Data presented in Tables (6 &7) and graphically illustrated, in Fig. (7) reveal that lower Na was exchangeable on attapulgite clay mineral than bentonite at all the studied Na/Ca ratios in the equilibrium solution. This was reflected on values of equivalent fractions of exchangeable Na on both the clay minerals, which were lower on the former than the latter. However, it was found generally that increasing Na/Ca ratio in equilibrium solution resulted in higher equivalent fraction of exchangeable Na and vice versa. On the other hand, the equivalent exchangeable Ca fraction tended to decrease gradually by increasing Na/Ca ratio in the equilibrium solution. **Thellier and Sposito (1988)**, on the other hand, reported that total adsorbed Na or Ca was independent of exchanger composition.

Values of all the selectivity coefficients i.e. K_G^a, K_{GT}^a and K_v^a were inversely related to values of the equivalent exchangeable Na fraction E_{Na}. This occurred with both the studied clay minerals. However, the inverse relation was more obvious in case of bentonite. Such a finding is an indication to the decrease in Na preference and on the other hand increase in Ca preference by increasing concentration of Na relative to Ca in the equilibrium solution. **Abbas (1985)** went almost to a similar conclusion. **Levy et al., (1988)** also attained almost the same finding.

Table (6): Concentrations and activities of soluble Na and Ca, exchangeable Na and Ca, equivalent and mole fractions of exchangeable Na, selectivity coefficients, SAR, SAR* and ESR for Na-Ca equilibria of commercial attapulgite clay mineral.

Type of the exchange material	Na/Ca ratio in equilibrium solution	C_{Na}	a_{Na}	C_{Ca}	a_{Ca}	$Ex._{Na}$	$Ex._{Ca}$	E Na	*N* Na	$K_G{}^a$	$K_{GT}{}^a$	$K_V{}^a$	SAR_C	SAR*	ESR
		mol L^{-1}				c mol_c kg^{-1}									
Attapulgite	10:90	0.002	0.0017	0.009	0.005	17.00	89.00	0.16	0.28	7.64	48.94	168.72	0.021	0.025	0.191
	25:75	0.006	0.0051	0.007	0.004	18.60	87.40	0.18	0.30	2.52	5.22	17.75	0.072	0.085	0.213
	50:50	0.010	0.0085	0.005	0.003	21.60	84.00	0.20	0.34	1.55	1.91	6.34	0.141	0.166	0.257
	75:25	0.014	0.0120	0.003	0.002	27.60	79.00	0.26	0.41	1.17	1.02	3.23	0.256	0.298	0.349
	90:10	0.018	0.0155	0.001	0.001	35.64	70.20	0.34	0.50	0.77	0.39	1.17	0.570	0.660	0.508

See footnote Table (3).

Table (7): **Concentrations and activities of soluble Na and Ca, exchangeable Na and Ca, equivalent and mole fractions of exchangeable Na, selectivity coefficients, SAR, SAR* and ESR for Na-Ca equilibria of commercial bentonite clay mineral.**

Type of the exchange material	Na/Ca ratio in equilibrium solution	C_{Na}	a_{Na}	C_{Ca}	a_{Ca}	Ex. $_{Na}$	Ex. $_{Ca}$	E Na	*N* Na	K_G^*	K_{GT}^*	K_V^*	SAR_C	SAR*	ESR
		mol L^{-1}				c mol_c kg^{-1}									
Bentonite	10:90	0.002	0.0017	0.009	0.005	4.80	21.60	0.18	0.31	8.88	64.55	218.49	0.021	0.025	0.222
	25:75	0.006	0.0051	0.007	0.004	8.30	18.40	0.31	0.47	5.33	19.59	59.77	0.072	0.085	0.451
	50:50	0.010	0.0085	0.005	0.003	15.40	11.10	0.58	0.74	8.36	29.27	74.06	0.141	0.166	1.387
	75:25	0.014	0.0120	0.003	0.002	16.60	10.30	0.62	0.76	5.40	11.18	27.65	0.256	0.298	1.612
	90:10	0.018	0.0155	0.001	0.001	17.50	9.10	0.66	0.79	2.91	2.90	7.00	0.570	0.660	1.923

See footnote Table (3).

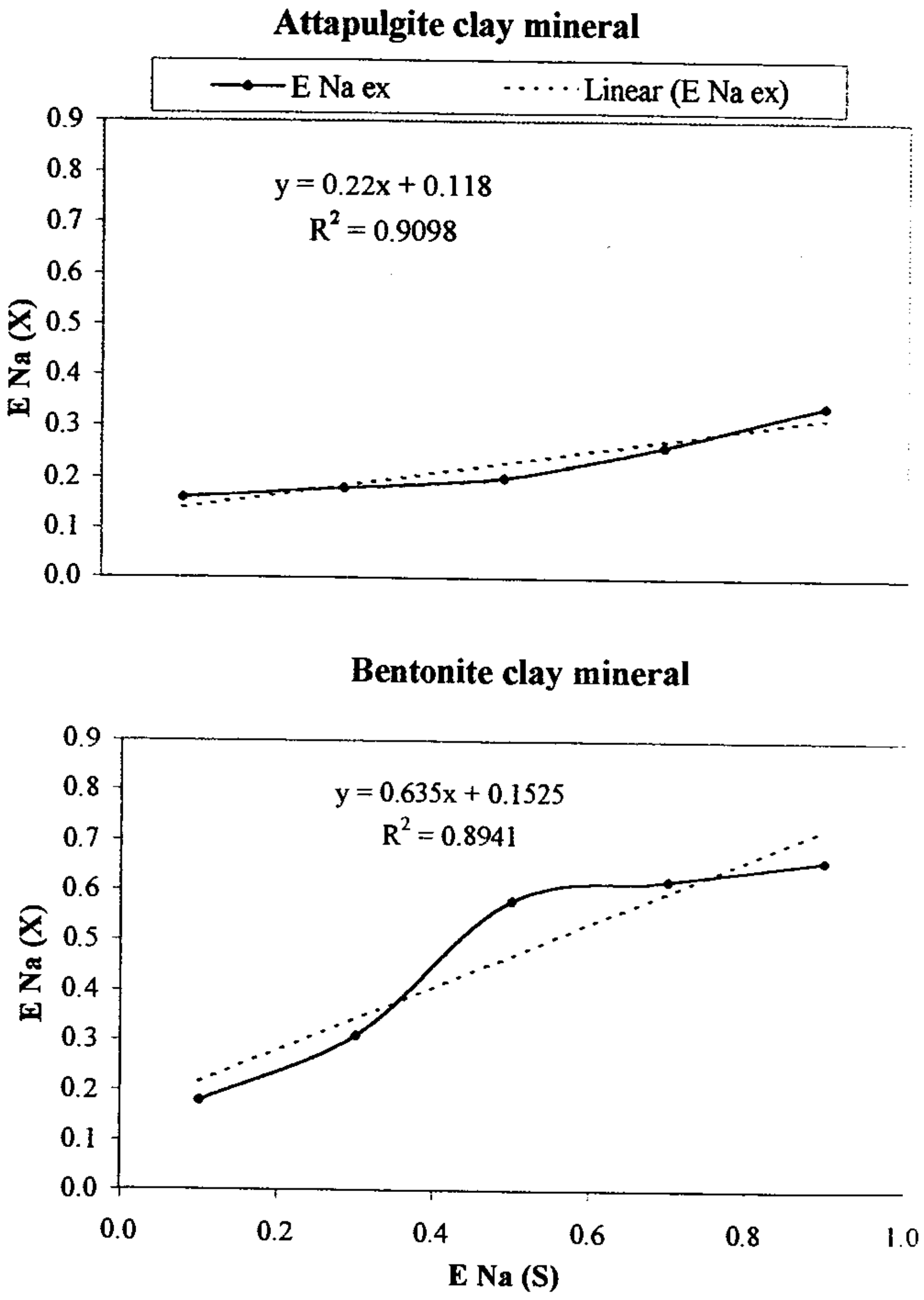


Fig. (7): Relationship between equivalent fractions of soluble Na in equilibrium solution and equivalent fractions of exchangeable Na on the used commercial clay minerals (Na-Ca exchange equilibria).

Unlike the results obtained herein, **Amrheim and Suarez (1991)** reported that there is no indication that mineralogy affected Na-Ca selectivity.

4.4. Sodium adsorption ratio (SAR) as related to exchangeable sodium ratio (ESR):-

Data of ion concentration and ion activity obtained from all Na-Ca exchange equilibria were used for calculating sodium adsorption ratio on basis of concentration (SAR= $\frac{\text{Na (mmol } L^{-1})}{\sqrt{\text{Ca (mmol } L^{-1})}}$) and on basis of activity (SAR*= $\frac{a_{\text{Na}} (\text{m mol } L^{-1})}{a_{\text{Ca}} (\text{m mol } L^{-1})}$). Exchangeable sodium ratios (ESR=$\frac{Na_{ex}}{Ca_{ex}}$ i.e. $\frac{Na_{ex}}{CEC - Na_{ex}}$) were also calculated for all exchange equilibria of Na-Ca. The calculated SAR and ESR values are presented in Tables (3-7).

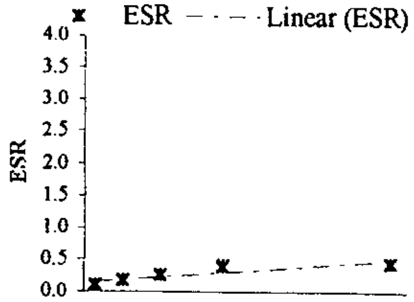
Values of ESR of the investigated exchange materials as function of SAR or SAR* of the applied NaCl and $CaCl_2$ solutions are presented in Table (8) and illustrated graphically in Figs. (8 and 9), respectively. Highly significant correlations were attained between the two parameters for all the exchange equilibria indicating that a close relationship exists between ions in equilibria solutions and the corresponding ones on the exchange materials. The correlation with ESR increased slightly when SAR* was used instead of SAR. This is a practical demonstration that ion activity is certainly a more representative parameter than ion concentration. **Abbas (1985)** went to a

Table (8): Regression equations, linear correlation coefficient (r) for the relationship between the exchangeable sodium ratios (ESR) and sodium adsorption (SAR) ratios in terms of concentration (SARC) and corrected for solution phase activities (SAR)*.

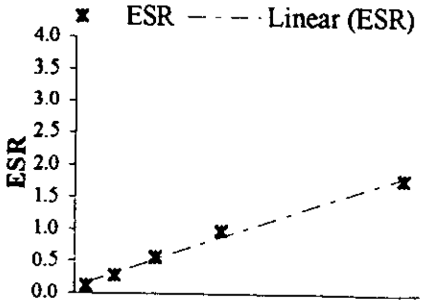
Type of exchange material	Correlation coefficient (r)		Regrassion equation	
	ESR:SARc	ESR:SAR*	ESR:SAR*	ESR:SAR_C
The calcareous soil (Borg El-Arab)	0.911**	0.962**	ESR= 1.3675 SAR* - 0.1776	ESR= 0.24535 SAR_C. 0.0247
The Nile alluvial noncalcareous soil (Moshtohor)	0.955**	0.997**	ESR= 0.3292 SAR* - 0.0342	ESR= 0.05604 SAR_C + 0.00327
Separated clay from Cal. Soil	0.994**	0.965**	ESR= 0.24599 SAR* - 0.0049	ESR= 0.04056 SAR_C + 0.00941
Separated clay from alluvial Soil	0.939**	0.976**	ESR= 0.15467 SAR* - 0.0426	ESR= 0.2728 SAR_C + 0.00026
Calcareous soil after removal of O.M	0.999**	0.982**	ESR= 0.74808 SAR* - 0.0439	ESR= 0.12488 SAR_C + 0.00247
Nile alluvial noncalcareous soil after removal of O.M	0.833**	0.884**	ESR= 0.59483 SAR* - 0.0882	ESR= 0.10717 SAR_C. 0.0089
Bentonite commercial clay mineral	0.996**	0.992**	ESR= 1.68352 SAR* - 0.2992	ESR= 0.28483 SAR_C - 0.0413
Attapulgyte commercial clay mineral	0.854**	0.918**	ESR= 0.25101 SAR* - 0.0689	ESR= 0.04578 SAR_C. 0.0061

** Significant at 1% level.

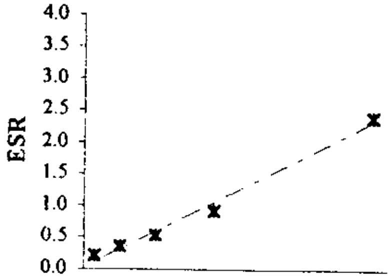
The calcareous soil



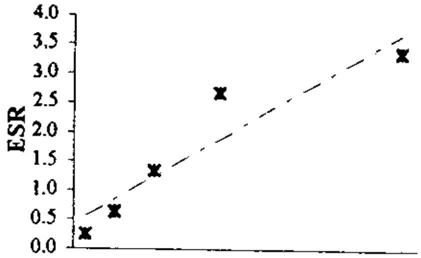
Nile alluvial noncalcareous soil



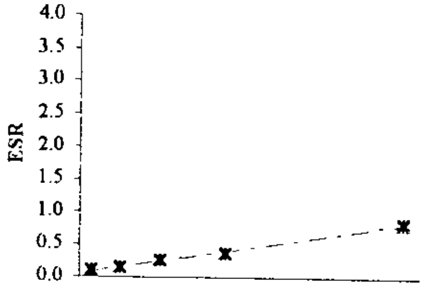
The clay fraction separated from the clacareous soil



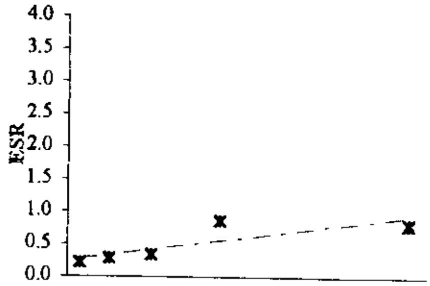
The clay fraction separated from the Nile alluvial nonclacareous soil



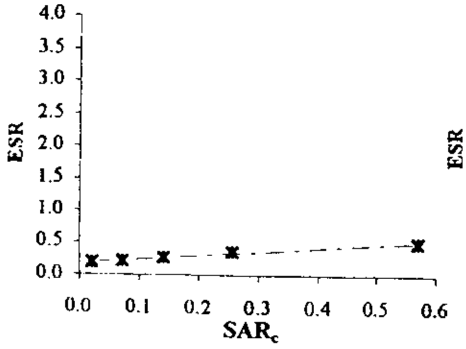
The calcareous soil after removal of the organic matter



The Nile alluvial noncalcareous soil after removal of the organic matter



Commercial attapulgite clay mineral



Commercial bentonite clay mineral

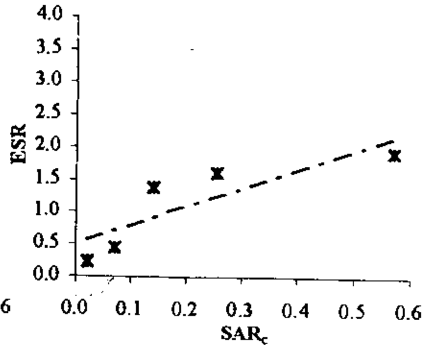


Fig. (8): Exchangeable sodium ratio (ESR) as related to sodium adsorptio ratio calculated on basis of concentration (SAR$_C$) in solution

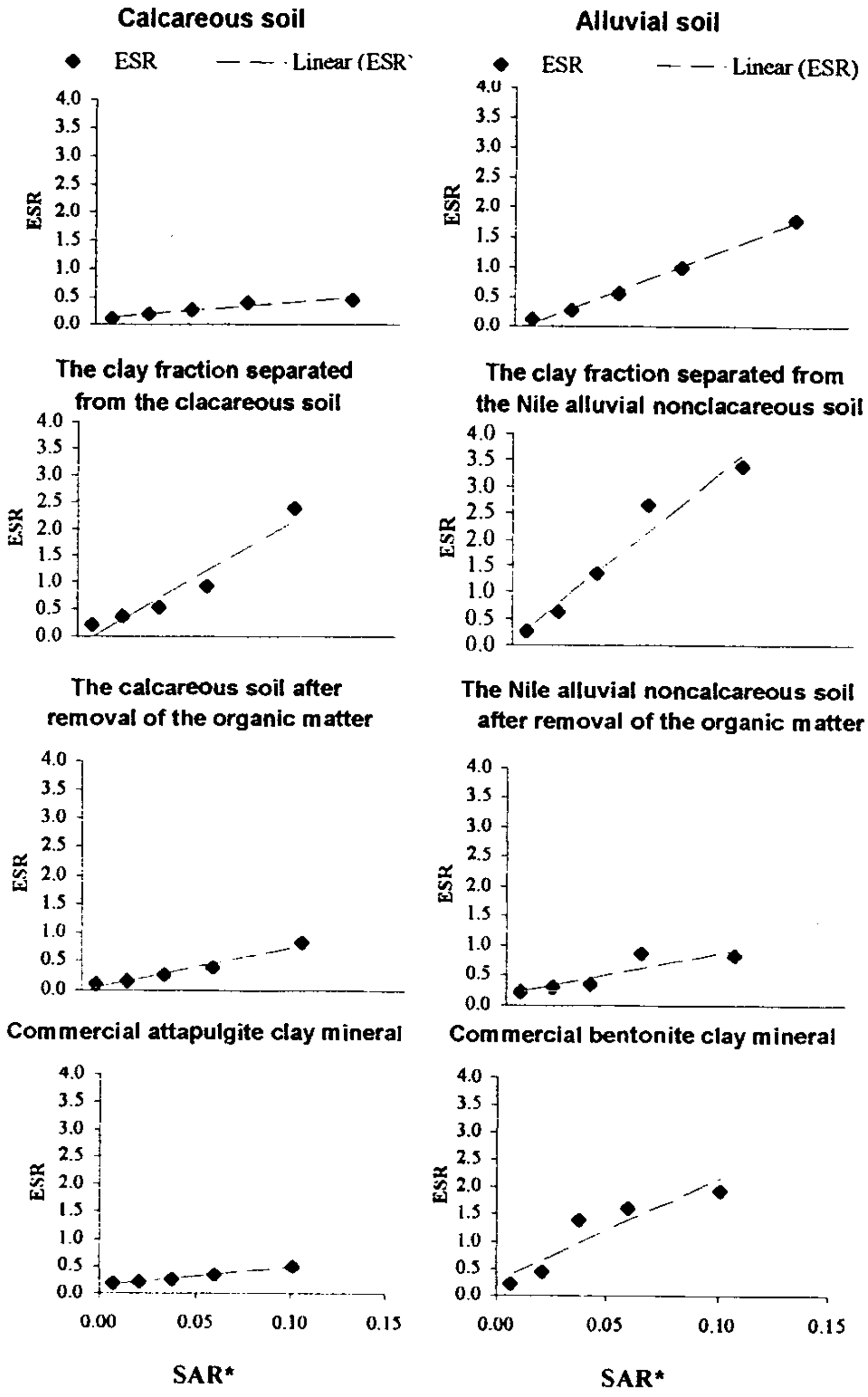


Fig. (9): Exchangeable sodium ratio (ESR) as related to sodium adsorption ratio calculated on basis of activity (SAR*) in solution phase of Na-Ca.

milar finding. This finding adds further evidence that SAR value would be a reliable parameter for estimating exchangeable Na on soil complex. However, the results obtained herein and represented by Figs. (8 & 9) imply that the investigated exchange materials could accumulate quite different amounts of exchangeable Na when irrigated with a given water. Thus, assessment of sodicity hazard that is based solely on the SAR of the water may not totally reliable. The selectivity coefficients of the exchange materials in question which are measures of the preferential adsorption of these materials for certain ion at the expense of another might account for such aforementioned differences in amount of exchangeable Na (**Curtin et al., 1995**). Also, differences in cation release due to extensive leaching with NaCl – $CaCl_2$ solutions appear to be responsible for differences in ESR-SAR relationship since the washed exchange materials still contained considerable amounts of exchangeable K (i.e. K extractable in NH_4OAc) caused apparently by release of K from nonexchangeable forms. Addition of K to a Na-Ca system has been shown to displace more exchangeable Na than Ca resulting in an apparent increase in selectivity for Ca compared to Na (**Rhue and Mansell, 1988**). Figs. (8&9) reveal that the removal of the organic matter very slightly influenced Na-Ca selectivity where the values of ESR at the different SAR or SAR* values showed small differences between soils before and after removal of the organic matter.

At any SAR value, the corresponding ESR one of soil before removal of organic matter seemed relatively higher than that of soil after removal of the organic matter. The difference seemed more obvious in the Nile alluvial noncalcareous soil (the higher in its O.M content) than the calcareous one (the lower in its O.M. content). Such a finding might indicate to higher affinity of the organic sites for Na relative to Ca. On the other hand, **Haghnia and Pratt (1988)** attained an adverse conclusion and reported that organic sites have strong affinity for Ca relative to Na.

Figs. (8 and 9) reveal also that at any SAR value the Nile alluvial noncalcareous soil showed higher affinity for Na than the calcareous one. The differences in mineralogical composition between the two soils may account for such a difference. This is evident by the same figures upon comparison between ESR_S of bentonite with those of attapulgite at the SAR_s or SAR_s^* where it was found that values of the former were relatively higher than the corresponding ones of the latter. These results may lead us to conclude that both the Nile alluvial noncalcareous soil and bentonite clay mineral are of higher affinity for Na than the calcareous soil and attapulgite. **Gupta et al., (1984)** observed an increase in Ca selectivity in presence of $CaCO_3$ (as the case in calcareous soil) during the CEC determination. This is in consistent with the problem of incomplete Na saturation during the CEC determination resulting in lower apparent ESR values. **Amrhein and Suarez (1990 and 1991)** reported that determination of Na-Ca selectivity presents problems in calcareous soils because of the release of Ca and Mg by weathering of silicate minerals.

4.5. K-Ca exchange isotherms:

4.5.1. K-Ca exchange on the studied calcareous and Nile alluvial noncalcareous soils:

Data presented in Table (9) reveal concentrations of soluble cations i.e. K^+ and Ca^{2+} and their corresponding activity values expressed in mol L^{-1}. The table reveals also, values of adsorbed K^+ and Ca^{2+} expressed in $cmol_c\ kg^{-1}$ as well as the mole and equivalent fractions of K^+ in both the studied calcareous (Borg El-Arab) and Nile alluvial non-calcareous (Moshtohor) soils.

It can be easily noticed that increasing K^+ concentration in equilibrium solution resulted in a gradual increase in its exchangeable amounts on exchange complexes of both the investigated soils. However, it is of importance to indicate that at any K/Ca ratio in equilibrium solution, K^+ adsorbed by the calcareous soil seemed far less than that adsorbed by the Nile alluvial noncalcareous one (Figs. 10 and 11). This means more preferential adsorption for K^+ on the Nile alluvial noncalcareous soil than the calcareous one. Such a finding might be attributed to the phenomenon of the preferential adsorption and fixation of K^+ by hydrous mica (illite) and montmorillonite, which are found in appreciable higher quantities in the Nile alluvial noncalcareous soil than the calcareous one. Preference for K^+ by kaolinite was reported also in a number of studies (**Hoover 1944, Raney and Hoover 1946, Shwartmann 1962; Marques 1964; Jensen 1973; Udo 1978; and Levy et al., 1988**). As K/Ca ratio in equilibrium solution was raised from 10:90 to 90:10, the equivalent K^+ fraction on the exchange complex increased from

Table (9): Concentrations and activities of soluble K and Ca, exchangeable K and Ca, equivalent and mole fractions of exchangeable K, selectivity coefficients, for K-Ca equilibria of the studied calcareous and Nile alluvial noncalcareous soils.

Type of the exchange material	K/Ca ratio in equilibrium solution	C_K	a_K	C_{Ca}	a_{Ca}	Ex_K	Ex_{Ca}	E K	*N*K	K_G^a	K_{GT}^a	K_V^a
		mol L^{-1}				c mol_c kg^{-1}						
The calcareous soil (Borg El- Arab)	10:90	0.002	0.0017	0.009	0.0045	1.86	22.64	0.08	0.14	3.28	9.97	37.05
	25:75	0.006	0.0051	0.007	0.0036	3.33	21.28	0.14	0.24	1.85	2.96	10.42
	50:50	0.010	0.0085	0.005	0.0026	4.76	19.80	0.19	0.32	1.45	1.69	5.67
	75:25	0.014	0.0120	0.003	0.0016	7.18	17.53	0.29	0.45	1.37	1.34	4.15
	90:10	0.018	0.0155	0.001	0.0006	9.80	14.70	0.40	0.57	1.01	0.61	1.75
The Nile alluvial noncalcareous soil (Moshtohor)	10:90	0.002	0.0017	0.009	0.0045	7.16	38.20	0.16	0.27	7.49	47.27	163.31
	25:75	0.006	0.0051	0.007	0.0036	10.80	34.20	0.24	0.39	3.73	10.59	34.15
	50:50	0.010	0.0085	0.005	0.0026	13.50	30.96	0.30	0.47	2.63	4.81	14.75
	75:25	0.014	0.0120	0.003	0.0016	26.40	19.30	0.58	0.73	4.59	8.88	22.52
	90:10	0.018	0.0155	0.001	0.0006	30.00	15.80	0.66	0.79	2.88	2.85	6.90

C_K, C_{Ca} are concentrations of K and Ca respectively in equilibrium solution.

a_K, a_{Ca} are activities of K and Ca respectively in equilibrium solution.

Ex_K, Ex_{Ca} are exchangeable K and Ca respectively on the exchange complex (solid phase).

E_K is the equivalent fraction of exchangeable K on the exchange complex .

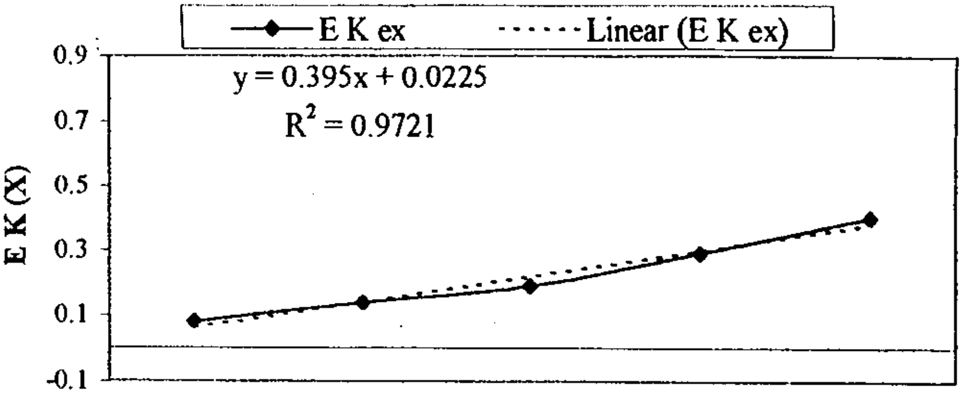
N K is the mole fraction of exchangeable K on the exchange complex.

K_G^a: Gapon's selectivity coefficient.

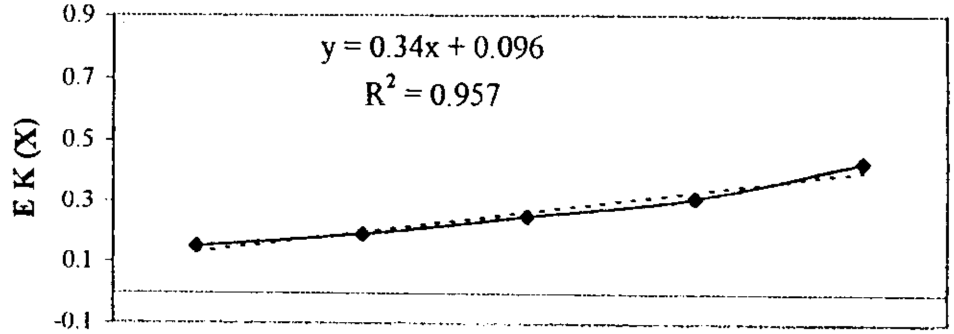
K_{GT}^a: Gaines - Thomas selectivity coefficient.

K_V^a: Vanselow's selectivity coefficient

Calcareous soil



Clay fraction separated from the calcareous soil



The calcareous soil after removal of organic matter

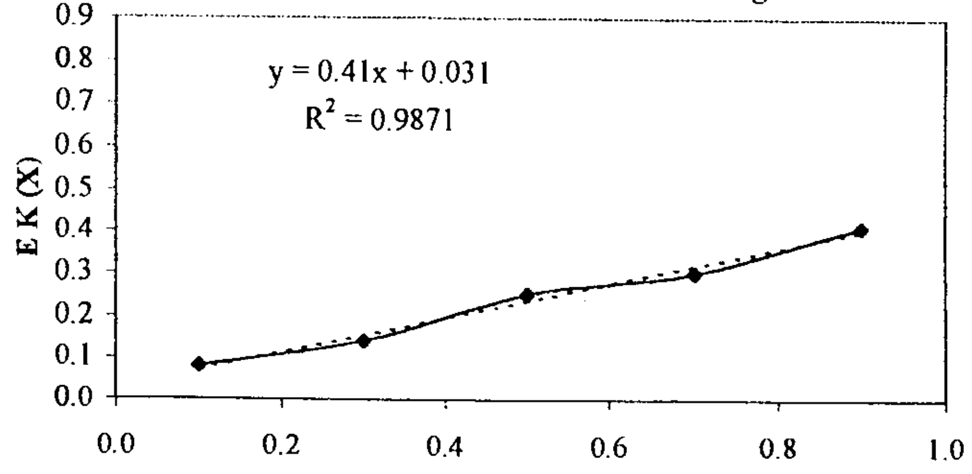
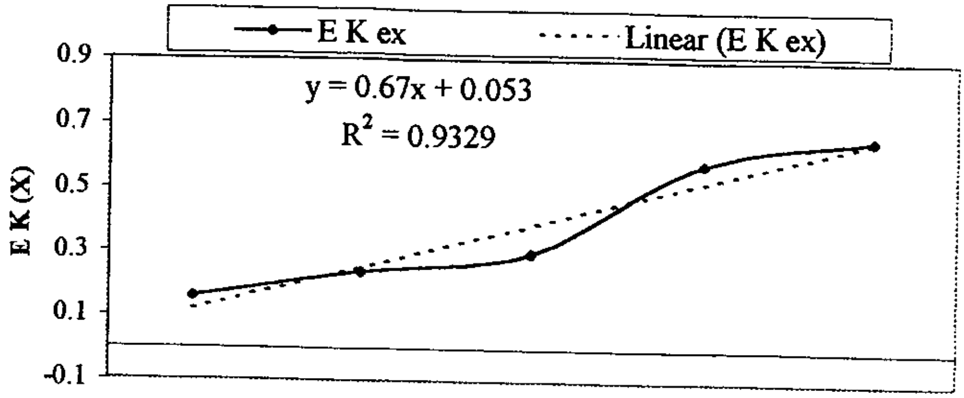
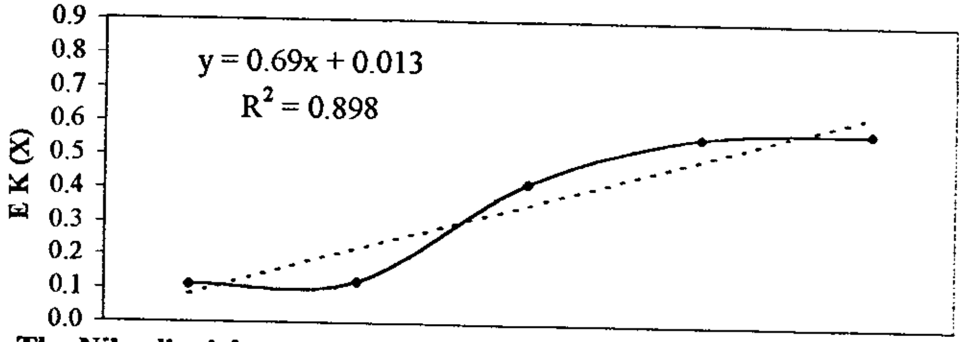


Fig. (10): Relationship between equivalent fractions of soluble K in equilibrium solution and equivalent fractions of exchangeable K on the calcareous soil, clay fraction separated from this soil and O.M free- calcareous soil (K-Ca exchange equilibria).

Alluvial soil



Clay fraction separated from the Nile alluvial noncalcareous soil



The Nile alluvial noncalcareous soil after removal of organic matter

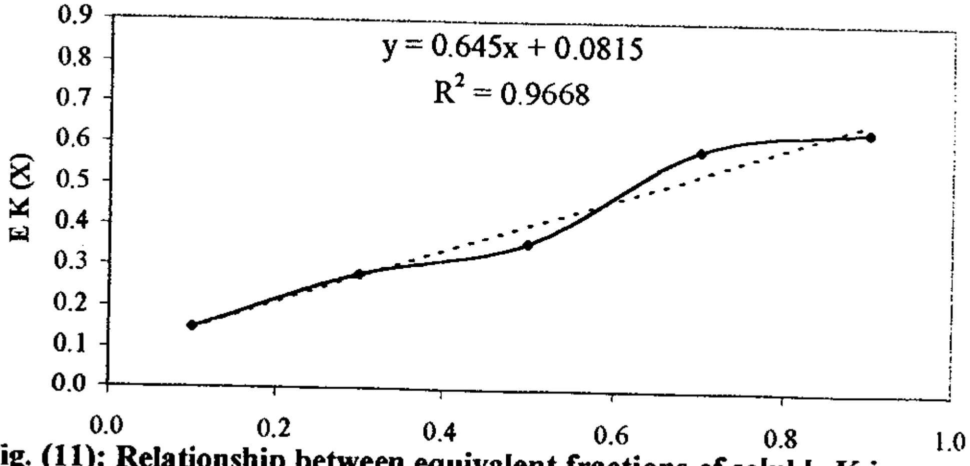


Fig. (11): Relationship between equivalent fractions of soluble K in equilibrium solution and equivalent fractions of exchangeable K on the Nile alluvial noncalcareous soil, clay fraction separated from this soil and O.M free- Nile noncalcareous soil (K-Ca exchange equilibria).

0.076 to 0.400 and from 0.158 to 0.655 in the calcareous and non-calcareous soils, respectively. Thus, it could be concluded that K/Ca adsorption ratio is dependent on K/Ca solution ratio. This finding stands in well agreement with those of **Levy et al., (1988)** and **Khider (1995)** who reported that as the K/Ca solution ratio increased, the K adsorption increased whereas the Ca^{2+} adsorption decreased and that led to a subsequent increase in K/Ca adsorbed equivalent ratios.

Selectivity coefficients were calculated from the Vanselow's equation **(Vanselow, 1932)**; Gapon's equation **(Gapon, 1933)** and Gaines and Thomas equation (**Gaines and Thomas, 1953**). The results obtained were presented in Table (9).

Gapon's selectivity coefficient (K_G^a):--

The data reveal that values of Gapon's coefficient calculated on activity basis were not constant as they were dependent on K/Ca ratio in equilibrium soil solution as well as nature of the equilibrating soil itself.

K_G^a values of the calcareous soil tended to decrease gradually as K/Ca ratio in equilibrium solution increased. This indicates to the preference for K adsorption at the lower K concentrations in solution.

On the other hand, K_G^a values of Gapon's coefficient of the Nile alluvial noncalcareous soil although seemed to decrease as K/Ca ratio in equilibrium solution was raised from 25:75 up to 50:50, yet they showed a pronounced increase when ratio was further raised up to 75:25 thereafter decreased once again. This means that increasing exchangeable K percentage from 16.43 to

30.96% of the CEC of the noncalcareous soil was associated with a corresponding decrease in values of Gapon's selectivity coefficient from 7.49 to 2.63 $(\text{mol L}^{-1})^{-0.5}$. This finding agrees to some extent with those of **Bolt et al., (1963), Carson and Dixon (1972) and Shaviv et al. (1985)** who found a sharp decrease in the selectivity coefficient K_G as exchangeable K^+ increased from 5 to 15% of the cation exchange capacity.

The aforementioned relationship confirms the general behavior reported by the **U.S. Sal. Lab. Staff report (1954)** in which a correlation was found for a number of soils between E_P and the potassium adsorption ratio (PAR) where E_P was defined:

$$E_P = K_{ex} / (CEC - K_{ex})$$

K_{ex} being exchangeable K^+ in $\text{mmol}_c\ \text{K}_g^{-1}$ and $PAR = [K^+]/([Ca^{2+}]+[Mg^{2-}])^{0.5}$

where brackets denote concentration in mmol L^{-1}.

This relationship was expressed in the **U.S. Sal. Lab. Staff report (1954)** by the linear regression

$$E_p = 0.0360 + 0.1051 \,.\, PAR, \quad r = 0.972$$

Thus, for a given pair of exchanging ions in K -Ca system we get an expression for the selectivity coefficient

$$K_G = E_P / PAR = K_{ex} \,.\, [Ca^{2+}]^{0.5} / Ca_{ex} \,.\, [K^+].$$

Using the relationship from the last two equations to calculate K_G vs E_P leads to the conclusions that K_G rapidly declines with increasing E_P which coincides with the results obtained herein.

Gaines - Thomas selectivity coefficient (K_{GT}^{a}):

Values of K^{a}_{GT} decreased as K/Ca ratio increased in the equilibrium solution and consequently the K equivalent exchangeable fraction increased. This occurred in both the investigated soils at all the K/Ca solution ratios except for the Nile alluvial noncalcareous soil at a K/Ca ratio of 75:25 where an increase in K^{a}_{GT} occurred .

The values K^{a}_{GT} of the calcareous soil ranged from 0.67 to 10.83 whereas the corresponding values of the Nile alluvial non-calcareous one ranged from 3.86 to 50.0.

K^{a}_{GT} Values were generally lower for the calcareous soil than the Nile alluvial noncalcareous one. This means that the calcareous soil is of a lower preference for K than the Nile alluvial noncalcareous soil since the exchangeable K fraction E_K at any K/Ca ratio in the equilibrium solution was higher in the non-calcareous soil than in the calcareous one. This finding might indicate that K^{a}_{GT} value can be used as an indicator for evaluating to what extent K is retained in an exchangeable form within a soil, therefore, it is a suitable parameter for comparing the retentively of Ex K by a soil with that of another. This may lead us to a general conclusion that K^{a}_{GT} differs from a soil to another not only due to the cations ratio in soil solution but also due to type of the clay mineral dominating in soil and its content of organic matter. It could be concluded also from the abovementined discussion that when soils are fertilized with K, K undergoes exchange and fixation reactions through which an appreciable part of it changes into the exchangeable or fixed form as it is shown by the equation:

$$\text{Soluble } K \rightleftharpoons \text{Exchangeable } K \rightleftharpoons \text{Fixed } K.$$

Such a convention in soluble K form to the other forms protects K against loss by leaching .

Vanselow's selectivity coefficient:

Values of Vanselow's coefficient seemed to be inversely proportional to values of equivalent fraction of K on the soil complex (E_K values), which are themselves dependent on K/Ca ratio in soil equilibrium solution. Such findings indicate some preference for K at the low K/Ca solution ratios. These results are in agreement with those of Marques (1964) whose results showed preferential adsorption for K in relation to other cations which could be explained by postulating the presence of sites with high affinity as well as sites of low affinity for K. **Jensen (1973)** suggested that exchange sites with a non-uniform affinity for K ions relative to Ca ions could explain similar findings. Elsewhere, **Jensen (1972)** attributed the stronger binding of K compared to Ca partly to the presence of specific K adsorption sites on clay and partly to the smaller hydration volume of K ions. Some explanations have been offered for decreased preference of Ca in a heterovalent exchange reaction. This is ascribed to the adsorption of monovalent complexes of divalent ions, such as $CaCl^+$, from an aqueous phase containing chloride and in which E_{Ca} is large (**Sposito et al, 1983a**). This results in a apparent decrease in divalent ions preference at large E_{Ca} values because monovalent cations will compete more effectively for exchange sites with the divalent cations, since a fraction of the latter now occurs as monovalent complexes.

4.5.2. K-Ca exchange on the clay fractions separated from thecalcareous and Nile alluvial non-calcareous soils :

Data presented in Table (10) and illustrated graphically in Figs. (10 and 11) reveal that increasing K/Ca ratio in equilibrium solution was associated with a gradual increase in E_K values on exchange sites of both the clay fraction samples separated from the calcareous (CFC) and Nile alluvial noncalcareous alluvial (CFN) soils, respectively. Exchangeable Ca fraction, on the other hand, took an opposite trend to the aforementioned one.

These results coincide with those of **Sposito and Le Vesque (1985), Ogwada and Sparks (1986), Shainberg et al. (1987), Levy et al. (1988) and Khider (1995)**.

There are two explanations for a decreased preference for Ca at high E_{Ca} values. Firstly, the negative potential in the double layer is decreased by increasing the fraction of adsorbed Ca, this decreasing the exchanger's affinity for Ca relative to K. Secondly; exchange sites differing in their affinity for Ca exist. Thus the sites with the low affinity for Ca are the last to be occupied with Ca and the affinity for Ca decreases as E_{Ca} increases .

A comparison between E_K values of the investigated soils (Figs. 10 and 11) shows that E_K values of the clay fraction separated from the calcareous soil (CFC) were somewhat higher than the corresponding ones of the clay fraction separated from the Nile alluvial noncalcareous (CFN) soil when K/Ca ratio in equilibrium solution did not exceed 25:75 (i.e. 1:3) thereafter the values of E_K of the CFC tended to be lower than those of the CFN. Such a finding means that preference for K on the exchange sites of the CFC is higher than that of the CFN at low

Table (10): Concentrations and activities of soluble K and Ca, exchangeable K and Ca, equivalent and mole fractions of exchangeable K, selectivity coefficients, for K-Ca equilibria of the clay fraction separated from calcareous and Nile alluvial noncalcareous soils.

Type of the exchange material	K/Ca ratio in equilibrium solution	C_K	a_K	C_{Ca}	a_{Ca}	Ex_K	Ex_{Ca}	E K	*N*K	K_G^a	K_{GT}^a	K_V^a
		mol L^{-1}				c mol_c kg^{-1}						
The clay fraction separated from the calcareous (CFC) soil	10:90	0.002	0.0017	0.009	0.0045	3.50	20.30	0.15	0.26	6.89	40.51	141.27
	25:75	0.006	0.0051	0.007	0.0036	4.50	19.40	0.19	0.32	2.74	6.10	20.54
	50:50	0.010	0.0085	0.005	0.0026	5.88	18.00	0.25	0.40	1.97	2.92	9.37
	75:25	0.014	0.0120	0.003	0.0016	7.40	16.40	0.31	0.47	1.51	1.58	4.81
	90:10	0.018	0.0155	0.001	0.0006	10.30	13.70	0.43	0.60	1.14	0.74	2.07
The clay fraction separated from the noncalcareous soils	10:90	0.002	0.0017	0.009	0.0045	4.98	39.50	0.11	0.20	5.04	22.55	81.13
	25:75	0.006	0.0051	0.007	0.0036	5.34	38.90	0.12	0.22	1.62	2.31	8.26
	50:50	0.010	0.0085	0.005	0.0026	18.80	25.60	0.42	0.59	4.43	11.29	31.73
	75:25	0.014	0.0120	0.003	0.0016	24.64	19.70	0.56	0.71	4.19	7.81	20.09
	90:10	0.018	0.0155	0.001	0.0006	26.10	18.75	0.58	0.74	2.11	1.86	4.70

See footnote Table (9).

K/Ca ratio in equilibrium solution and the opposite is true at the higher K/Ca ratios in the equilibrium solution. These results agree partly with those obtained by **Khider (1995)** who found a general increase in the adsorbed K relative to Ca as the K/Ca ratio in the equilibrium solution increased but added that CFC attained relatively higher E_K values relative to the CFN under all the K/Ca solution ratios.

<u>Gapon's selectivity coefficient</u> :

Data presented in Table (10) reveal that the general trend of Gapon's selectivity coefficient for K-Ca exchange on both CFC and CFN was to decrease with increase in E_K. In lowest range of E_K values, the K_G selectivity coefficient values for K-Ca of both CFC and CFN were large. The results presented herein are in agreement with the findings of **Marques (1964); Levy et al., (1988),** and **Karmarkar et al., (1991)** who reported that the competition between K^+ and $CaCl^+$ on external exchange sites accounts for such a result.

<u>Gaines - Thomas selectivity coefficient</u> :

Data in Table (10) show that values of Gaines-Thomas selectivity coefficient were generally inversely related to the K/Ca ratio in the equilibrium solution. Increasing K/Ca ratio in equilibrium solution resulted in higher E_K but lower $K_{GT}{}^a$ in most cases. This finding indicates to the existence of the preference adsorption of K at the lower K-saturation percentage as previously explained.

The variation in $K_{GT}{}^a$ values between the CFC and CFN may be explained on the basis of the mineralogical composition of the CFC and CFN. The alluvial clay separates are dominated by montmorillonite, kaolinite and illite (hydrous mica) whereas the calcareous clay separates are dominated with attapulgaite. The mica impurities might contribute to the high affinity of the CFN for K as expressed by K_{GT}^{a} selectivity coefficients .

Vanselow's selectivity coefficient :

Likewise, values of K_G^a and K_{GT}^a, values of K_V^a in the clay fractions separated from both the calcareous and Nile alluvial noncalcareous soils seemed to decrease by increasing K/Ca ratio in equilibrium solution or by, in other words, increasing the equivalent fraction of K on exchanger. Similar findings were reported by **Evangelou and Philips (1987)** and **Levy et al., (1988)**.

The larger values of Vanselow's selectivity coefficient for the CFC relative to those characterizing the CFN indicates to the possibility of a pronounced preference of the CFC over the CFN for K .

4.5.3. K-Ca exchange on the calcareous and Nile alluvial noncalcareous soils after removal of organic matter:

Values of the equivalent fractions of exchangeable K i.e. Ex_K corresponding to the different K/Ca ratios in the equilibrium solutions seemed, generally, somewhat higher after removal of the organic matter relative to those of the untreated soils (Table, 11 and Figs., 10 and 11). The low organic matter content of the studied soils might have resulted in a small decrease in the active surface responsible for sorption and exchange of K cations due to the blocking action of organic materials to some of the exchange sites particularly those located in the interlayer of the 2:1 clay mineral group (**Al-Araby, 1978; Abbady, 1980; Zein, 1988 and Abou-Agwa and Abou-Hussein, 1993**). Removal of

Table (11): Concentrations and activities of soluble K and Ca, exchangeable K and Ca, equivalent and mole fractions of exchangeable K, selectivity coefficients, for K-Ca equilibria for calcareous and Nile alluvial noncalcareous soils after removal of organic matter.

Type of the exchange material	K/Ca ratio in equilibrium solution	C_K	a_K	C_{Ca}	a_{Ca}	Ex_K	Ex_{Ca}	E K	NK	$K_G{}^a$	$K_{GT}{}^a$	$K_V{}^a$
		mol L^{-1}				c mol_c kg^{-1}						
The calcareous after removal of the organic matter	10:90	0.002	0.0017	0.009	0.0045	2.31	26.19	0.08	0.15	3.53	11.42	42.26
	25:75	0.006	0.0051	0.007	0.0036	4.04	24.20	0.14	0.25	1.97	3.34	11.67
	50:50	0.01	0.0085	0.005	0.0026	6.98	20.90	0.25	0.40	2.01	3.04	9.71
	75:25	0.014	0.0120	0.003	0.0016	8.19	19.50	0.30	0.46	1.41	1.40	4.31
	90:10	0.018	0.0155	0.001	0.0006	11.70	16.87	0.41	0.58	1.05	0.65	1.85
The noncalcareous soil after removal of the organic matter	10:90	0.002	0.0017	0.009	0.0045	7.40	43.00	0.15	0.26	6.88	40.37	140.81
	25:75	0.006	0.0051	0.007	0.0036	13.80	36.20	0.28	0.43	4.51	14.70	46.07
	50:50	0.01	0.0085	0.005	0.0026	15.60	28.20	0.36	0.53	3.33	7.15	21.10
	75:25	0.014	0.0120	0.003	0.0016	28.30	19.60	0.59	0.74	4.84	9.59	24.11
	90:10	0.018	0.0155	0.001	0.0006	31.40	17.70	0.64	0.78	2.69	2.60	6.35

See footnote Table (9).

the organic matter might have resulted in general decrease in preferential adsorption of Ca i.e. general decrease in the exchangeable equivalent Ca fractions relative to the corresponding values attained in presence of the organic material. This finding points to a slight decrease in Ca preference due to removal of the organic matter but at the same time a corresponding increase in K preference.

Values of K_G^a, K_{GT}^a, and K_V^a were generally higher in both the studied soils after removal of the organic matter than the corresponding values of soils without removal of the organic matter. This occurred at all the used C/K ratios in the equilibrium solutions of both the investigated soils except for the Nile alluvial noncalcareous soil at C/K ratio of 10:90 where the K_G, K_{GT} and K_V^a values recorded were higher for soil without removal of the organic matter than the corresponding ones after removal of organic matter.

It is also of importance to indicate that both soils showed the same trend of decreasing K_G, K_{GT} and K_V^a, values with increasing saturation of soils with exchangeable K or decreasing their saturation with exchangeable Ca.

4.5.4. <u>K- Ca exchange on the commercial used clay minerals</u> :

Data in Tables (12&13) reveal values of exchangeable K and Ca in relation to K/Ca ratios in equilibrium solutions.

Increasing K/Ca ratio in equilibrium solution resulted in increases in equivalent exchangeable K on both attapulgite and bentonite clay minerals but, on the other hand, decreased equivalent exchangeable Ca fraction on both the studied

Table (12): Concentrations and activities of soluble K and Ca, exchangeable K and Ca, equivalent and mole fractions of exchangeable K, selectivity coefficients, for K-Ca equilibria for commercial attapulgite clay mineral.

Type of the exchange material	K/Ca ratio in equilibrium solution	C_K	a_K	C_{Ca}	a_{Ca}	Ex_K	Ex_{Ca}	E K	NK	$K_G{}^a$	$K_{GT}{}^a$	$K_V{}^a$
		mol L^{-1}				c mol_c kg^{-1}						
Attapulgite	10:90	0.002	0.0017	0.009	0.0045	4.60	105.60	0.04	0.08	1.74	2.91	11.16
	25:75	0.006	0.0051	0.007	0.0036	10.70	97.80	0.10	0.18	1.29	1.51	5.49
	50:50	0.010	0.0085	0.005	0.0026	14.80	91.80	0.14	0.24	0.97	0.81	2.85
	75:25	0.014	0.0120	0.003	0.0016	26.60	81.60	0.25	0.39	1.09	0.90	2.89
	90:10	0.018	0.0155	0.001	0.0006	30.70	77.60	0.28	0.44	0.60	0.26	0.80

See footnote Table (9).

Table (13): Concentrations and activities of soluble K and Ca, exchangeable K and Ca, equivalent and mole fractions of exchangeable K, selectivity coefficients, for K-Ca equilibria for commercial bentonite clay mineral.

Type of the exchange material	K/Ca ratio in equilibrium solution	C_K	a_K	C_{Ca}	a_{Ca}	Ex_K	Ex_{Ca}	E K	NK	K_G^a	K_{GT}^a	K_V^a
		mol L^{-1}				c mol_c kg^{-1}						
Bentonite	10:90	0.002	0.0017	0.009	0.0045	3.89	22.60	0.15	0.26	6.88	40.38	140.85
	25:75	0.006	0.0051	0.007	0.0036	7.96	18.55	0.30	0.46	5.07	18.00	55.37
	50:50	0.010	0.0085	0.005	0.0026	11.40	15.35	0.43	0.60	4.48	11.49	32.23
	75:25	0.014	0.0120	0.003	0.0016	15.60	10.95	0.59	0.74	4.78	9.41	23.71
	90:10	0.018	0.0155	0.001	0.0006	20.40	5.90	0.78	0.87	5.24	6.15	13.86

See footnote Table (9).

exchangers. The changes in E_K and consequently E_{Ca} were higher in the K-Ca system of bentonite than in that of attapulgite.

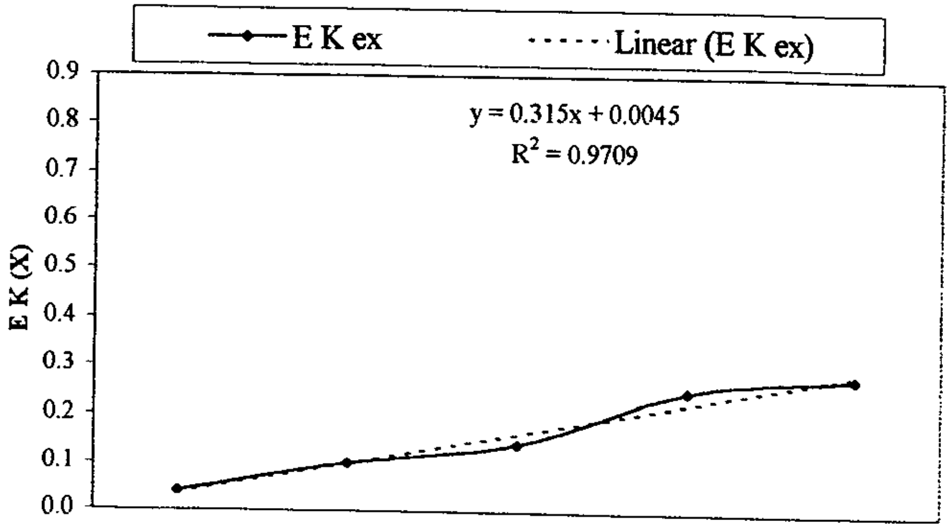
Values of the selectivity coefficients calculated according to Gapon, Gaines-Thomas and Vanselow's equations tended generally to decrease by increasing K/Ca ratio in the equilibrium solutions and consequently increasing value of exchangeable K fraction on the both exchanger types. This indicates to the increase in K preference at low E_K values and at the same time, the low preference for Ca at the high E_{Ca} values i.e. the affinity for Ca decreases as E_{Ca} increases. This occurred with bentonite and attapulgite as well. However, the selectivity coefficients K_G, K_{GT} and K_V^a showed a decreasing relationship with clay mineralogy in the order bentonite > attapulgite.

The relatively higher selectivity coefficients for K in case of attapulgite clay mineral (Fig. 12) might be attributed to extreme compatibility of K with certain individual exchange sites. **Bolt et al., (1978)** reported that depending on the mechanism of formation of exchanger there will often exist failures in the crystal lattice leaving very small crevices, which could accommodate on ion of a particular size and valence much better than any other ion

4.6. Cd-Ca exchange isotherms:-

Data presented in Tables (14-18) and illustrated graphically in Figs. (13-15), show values of Cd/Ca ratios as

Attapulgite clay mineral



Bentonite clay mineral

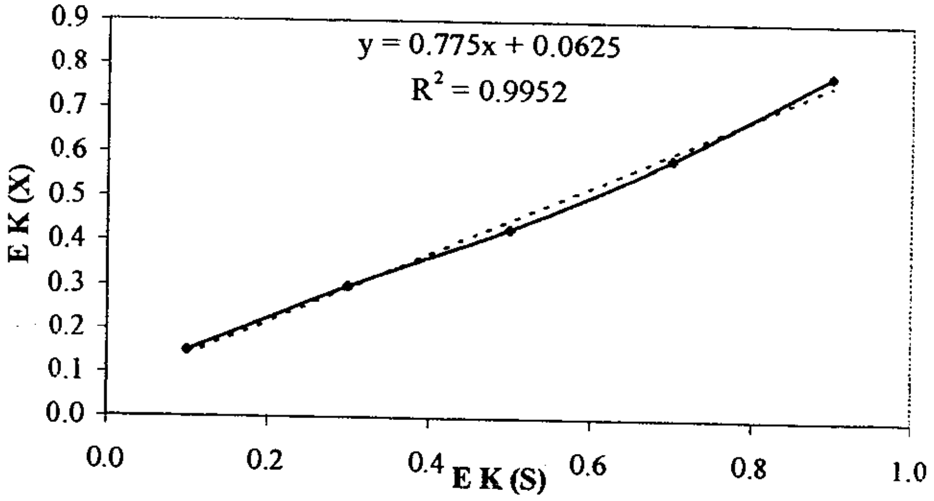


Fig. (12): Relationship between equivalent fractions of soluble K in equilibrium solution and equivalent fractions of exchangeable K on the used commercial clay minerals (K-Ca exchange equilibria).

Table (14): Concentrations and activities of Cd and Ca in equilibrium solution, exchangeable Cd and Ca, equivalent and mole fractions of exchangeable Cd and selectivity coefficients for Cd-Ca equilibria of the studied calcareous and Nile alluvial noncalcareous soils.

Type of the exchange material	Cd/Ca ratio in equilibria solution	C_{Cd}	C_{Ca}	a_{Cd}	a_{Ca}	$E_x Cd$	$E_x Ca$	E_{Cd}	$N Cd$	$K_{GT}{}^a$	K_B	$K_V{}^a$
		mmol L^{-1}				c mol_c kg^{-1}						
The calcareous soil (Borg El-Arab)	0.1:99.9	0.005	4.995	0.000003	0.0030	0.012	24.15	0.001	0.0005	0.513	0.513	0.513
	0.2:99.8	0.010	4.990	0.000006	0.0030	0.017	24.65	0.001	0.0007	0.336	0.336	0.336
	0.4:99.6	0.020	4.980	0.000012	0.0030	0.044	24.30	0.002	0.0018	0.455	0.455	0.455
	0.5:99.5	0.025	4.975	0.000015	0.0030	0.038	23.90	0.002	0.0016	0.316	0.316	0.316
	0.8:99.2	0.040	4.960	0.000024	0.0030	0.042	24.10	0.002	0.0017	0.214	0.214	0.214
	1.0:99.0	0.050	4.950	0.000030	0.0030	0.051	23.60	0.002	0.0022	0.214	0.214	0.214
	2.0:98.0	0.100	4.900	0.000060	0.0029	0.126	24.48	0.005	0.0051	0.252	0.252	0.252
	4.0:96.0	0.200	4.800	0.000120	0.0029	0.210	24.16	0.009	0.0086	0.209	0.209	0.209
	8.0:92.0	0.400	4.600	0.000240	0.0028	0.380	23.90	0.016	0.0157	0.183	0.183	0.183
The Nile alluvial noncalcareous soil (Moshtohor)	0.1:99.9	0.005	4.995	0.000003	0.0030	0.026	44.90	0.001	0.0006	0.581	0.581	0.581
	0.2:99.8	0.010	4.990	0.000006	0.0030	0.024	44.40	0.001	0.0005	0.273	0.273	0.273
	0.4:99.6	0.020	4.980	0.000012	0.0030	0.048	44.48	0.001	0.0011	0.269	0.269	0.269
	0.5:99.5	0.025	4.975	0.000015	0.0030	0.039	43.80	0.001	0.0009	0.177	0.177	0.177
	0.8:99.2	0.040	4.960	0.000024	0.0030	0.114	43.49	0.003	0.0026	0.324	0.324	0.324
	1.0:99.0	0.050	4.950	0.000030	0.0030	0.215	44.70	0.005	0.0048	0.476	0.476	0.476
	2.0:98.0	0.100	4.900	0.000060	0.0029	0.269	44.60	0.006	0.0060	0.296	0.296	0.296
	4.0:96.0	0.200	4.800	0.000120	0.0029	0.587	43.90	0.013	0.0132	0.321	0.321	0.321
	8.0:92.0	0.400	4.600	0.000240	0.0028	0.780	43.15	0.018	0.0178	0.208	0.208	0.208

C_{Cd}, C_{Ca} mol L-1 are: concentrations of Cd and ca in solution phase.

a_{Cd}, a_{Ca} are: activity of Cd and Ca, respectively.

$E_{x\,Cd}$, $E_{x\,Ca}$ c mol_c kg-1 are: concentrations of Cd and Ca in adsorbed phase.

E_{Cd} and N_{Cd} are: equivalent and mole fractions of Cd on the exchanger

$K_{GT}a$: Gaines - Thomas selectivity coefficient.

K_B : selectivity coefficient according to Beckett (1965).

K_{Va} : Vanselow selectivity coefficient.

Table (15): Concentrations and activities of Cd and Ca in equilibrium solution, exchangeable Cd and Ca, equivalent and mole fractions of exchangeable Cd and selectivity coefficients for Cd-Ca equilibria for the the clay fraction separated from calcareous and Nile alluvial noncalcareous soils.

Type of the exchange material	Cd/Ca ratio in equilibria solution	C_{Cd}	C_{Ca}	a_{Cd}	a_{Ca}	$E_x Cd$	$E_x Ca$	E_{Cd}	*N Cd*	K_{GT}^*	K_B	K_V^*
		mmol L^{-1}				c mol$_c$ kg^{-1}						
	0.1:99.9	0.005	4.995	0.000003	0.0030	0.014	22.90	0.001	0.0006	0.619	0.619	0.619
The clay fraction	0.2:99.8	0.010	4.990	0.000006	0.0030	0.016	24.48	0.001	0.0007	0.326	0.326	0.326
separated from the	0.4:99.6	0.020	4.980	0.000012	0.0030	0.036	23.80	0.001	0.0015	0.371	0.371	0.371
calcareous soil	0.5:99.5	0.025	4.975	0.000015	0.0030	0.045	23.65	0.002	0.0019	0.379	0.379	0.379
	0.8:99.2	0.040	4.960	0.000024	0.0030	0.055	22.94	0.002	0.0024	0.297	0.297	0.297
(CFC)	1.0:99.0	0.050	4.950	0.000030	0.0030	0.060	23.80	0.003	0.0025	0.250	0.250	0.250
	2.0:98.0	0.100	4.900	0.000060	0.0029	0.188	23.10	0.008	0.0081	0.399	0.399	0.399
	4.0:96.0	0.200	4.800	0.000120	0.0029	0.240	23.49	0.010	0.0101	0.245	0.245	0.245
	8.0:92.0	0.400	4.600	0.000240	0.0028	0.290	23.60	0.012	0.0121	0.141	0.141	0.141
	0.1:99.9	0.005	4.995	0.000003	0.0030	0.021	43.14	0.000	0.0005	0.493	0.493	0.493
The clay fraction	0.2:99.8	0.010	4.990	0.000006	0.0030	0.034	43.90	0.001	0.0008	0.384	0.384	0.384
separated from the	0.4:99.6	0.020	4.980	0.000012	0.0030	0.050	44.40	0.001	0.0011	0.279	0.279	0.279
Nile alluvial	0.5:99.5	0.025	4.975	0.000015	0.0030	0.058	44.00	0.001	0.0013	0.262	0.262	0.262
noncalcareous soil	0.8:99.2	0.040	4.960	0.000024	0.0030	0.095	44.15	0.002	0.0021	0.267	0.267	0.267
	1.0:99.0	0.050	4.950	0.000030	0.0030	0.209	43.85	0.005	0.0047	0.472	0.472	0.472
(CFN)	2.0:98.0	0.100	4.900	0.000060	0.0029	0.498	43.48	0.011	0.0113	0.561	0.561	0.561
	4.0:96.0	0.200	4.800	0.000120	0.0029	0.660	43.48	0.015	0.0150	0.364	0.364	0.364
	8.0:92.0	0.400	4.600	0.000240	0.0028	1.080	44.00	0.024	0.0240	0.282	0.282	0.282

See footnote Table (14).

Table (16): Concentrations and activities of Cd and Ca in equilibrium solution, exchangeable Cd and Ca, equivalent and mole fractions of exchangeable Cd and selectivity coefficients for Cd-Ca equilibria for the studied calcareous and Nile alluvial noncalcareous soils after removal of organic matter.

Type of the exchange material	Cd/Ca ratio in equilibria solution	C_{Cd}	C_{Ca}	a_{Cd}	a_{Ca}	$E_x Cd$	$E_x Ca$	E_{Cd}	*N Cd*	K_{GT}^a	K_B	K_V^a
		mmol L^{-1}				c mol_c kg^{-1}						
The calcareous soil after removal of the organic matter	0.1:99.9	0.005	4.995	0.000003	0.0030	0.013	27.48	0.000	0.0005	0.473	0.473	0.473
	0.2:99.8	0.010	4.990	0.000006	0.0030	0.017	29.00	0.001	0.0006	0.296	0.296	0.296
	0.4:99.6	0.020	4.980	0.000012	0.0030	0.020	28.49	0.001	0.0007	0.176	0.176	0.176
	0.5:99.5	0.025	4.975	0.000015	0.0030	0.039	26.70	0.001	0.0015	0.291	0.291	0.291
	0.8:99.2	0.040	4.960	0.000024	0.0030	0.020	27.95	0.001	0.0007	0.087	0.087	0.087
	1.0:99.0	0.050	4.950	0.000030	0.0030	0.039	27.90	0.001	0.0014	0.138	0.138	0.138
	2.0:98.0	0.100	4.900	0.000060	0.0029	0.060	27.80	0.002	0.0022	0.106	0.106	0.106
	4.0:96.0	0.200	4.800	0.000120	0.0029	0.135	28.10	0.005	0.0048	0.115	0.115	0.115
	8.0:92.0	0.400	4.600	0.000240	0.0028	0.280	25.90	0.011	0.0107	0.124	0.124	0.124
The Nile alluvial noncalcareous after removal of the organic matter	0.1:99.9	0.005	4.995	0.000003	0.0030	0.033	48.20	0.001	0.0007	0.676	0.676	0.676
	0.2:99.8	0.010	4.990	0.000006	0.0030	0.033	49.40	0.001	0.0007	0.329	0.329	0.329
	0.4:99.6	0.020	4.980	0.000012	0.0030	0.057	48.55	0.001	0.0012	0.292	0.292	0.292
	0.5:99.5	0.025	4.975	0.000015	0.0030	0.085	47.55	0.002	0.0018	0.356	0.356	0.356
	0.8:99.2	0.040	4.960	0.000024	0.0030	0.063	48.90	0.001	0.0013	0.159	0.159	0.159
	1.0:99.0	0.050	4.950	0.000030	0.0030	0.094	49.00	0.002	0.0019	0.190	0.190	0.190
	2.0:98.0	0.100	4.900	0.000060	0.0029	0.270	47.90	0.006	0.0056	0.276	0.276	0.276
	4.0:96.0	0.200	4.800	0.000120	0.0029	0.380	48.50	0.008	0.0078	0.188	0.188	0.188
	8.0:92.0	0.400	4.600	0.000240	0.0028	0.738	48.30	0.015	0.0150	0.176	0.176	0.176

See footnote Table (14).

Table (17): Concentrations and activities of Cd and Ca in equilibrium solution, exchangeable Cd and Ca, equivalent and mole fractions of exchangeable Cd and selectivity coefficients for Cd-Ca equilibria for the commercial attapulgite clay mineral.

Type of the exchange material	Cd/Ca ratio in equilibria solution	C_{Cd}	C_{Ca}	a_{Cd}	a_{Ca}	$E_x Cd$	$E_x Ca$	E_{Cd}	*N Cd*	K_{GT}^*	K_B	K_V^*
		mmol L^{-1}				c mol_c kg^{-1}						
Attapulgite	0.1:99.9	0.005	4.995	0.000003	0.0030	0.110	25.00	0.004	0.0044	4.396	4.396	4.396
	0.2:99.8	0.010	4.990	0.000006	0.0030	0.136	26.30	0.005	0.0051	2.580	2.580	2.580
	0.4:99.6	0.020	4.980	0.000012	0.0030	0.157	26.30	0.006	0.0059	1.486	1.486	1.486
	0.5:99.5	0.025	4.975	0.000015	0.0030	0.163	26.00	0.006	0.0062	1.248	1.248	1.248
	0.8:99.2	0.040	4.960	0.000024	0.0030	0.189	26.50	0.007	0.0071	0.884	0.884	0.884
	1.0:99.0	0.050	4.950	0.000030	0.0030	0.204	24.30	0.008	0.0083	0.831	0.831	0.831
	2.0:98.0	0.100	4.900	0.000060	0.0029	0.453	26.90	0.017	0.0166	0.825	0.825	0.825
	4.0:96.0	0.200	4.800	0.000120	0.0029	0.582	24.90	0.023	0.0228	0.561	0.561	0.561
	8.0:92.0	0.400	4.600	0.000240	0.0028	1.369	25.20	0.052	0.0515	0.625	0.625	0.625

See footnote Table (14).

Table (18): Concentrations and activities of Cd and Ca in equilibrium solution, exchangeable Cd and Ca, equivalent and mole fractions of exchangeable Cd and selectivity coefficients for Cd-Ca equilibria for the commercial bentonite clay mineral.

Type of the exchange material	Cd/Ca ratio in equilibria solution	C_{Cd}	C_{Ca}	a_{Cd}	a_{Ca}	$E_x Cd$	$E_{x\ Ca}$	E_{Cd}	$N Cd$	K_{GT}^a	K_B	K_V^a
		mmol L^{-1}				c mol_c kg^{-1}						
Bentonite	0.1:99.9	0.005	4.995	0.000003	0.0030	0.192	105.90	0.002	0.0018	1.811	1.811	1.811
	0.2:99.8	0.010	4.990	0.000006	0.0030	0.319	108.20	0.003	0.0029	1.471	1.471	1.471
	0.4:99.6	0.020	4.980	0.000012	0.0030	0.390	103.80	0.004	0.0037	0.936	0.936	0.936
	0.5:99.5	0.025	4.975	0.000015	0.0030	0.576	109.70	0.005	0.0052	1.045	1.045	1.045
	0.8:99.2	0.040	4.960	0.000024	0.0030	0.584	105.90	0.005	0.0055	0.684	0.684	0.684
	1.0:99.0	0.050	4.950	0.000030	0.0030	0.696	109.80	0.006	0.0063	0.628	0.628	0.628
	2.0:98.0	0.100	4.900	0.000060	0.0029	1.800	107.80	0.016	0.0164	0.818	0.818	0.818
	4.0:96.0	0.200	4.800	0.000120	0.0029	2.028	106.20	0.019	0.0187	0.458	0.458	0.458
	8.0:92.0	0.400	4.600	0.000240	0.0028	5.124	103.50	0.047	0.0472	0.569	0.569	0.569

See footnote Table (14).

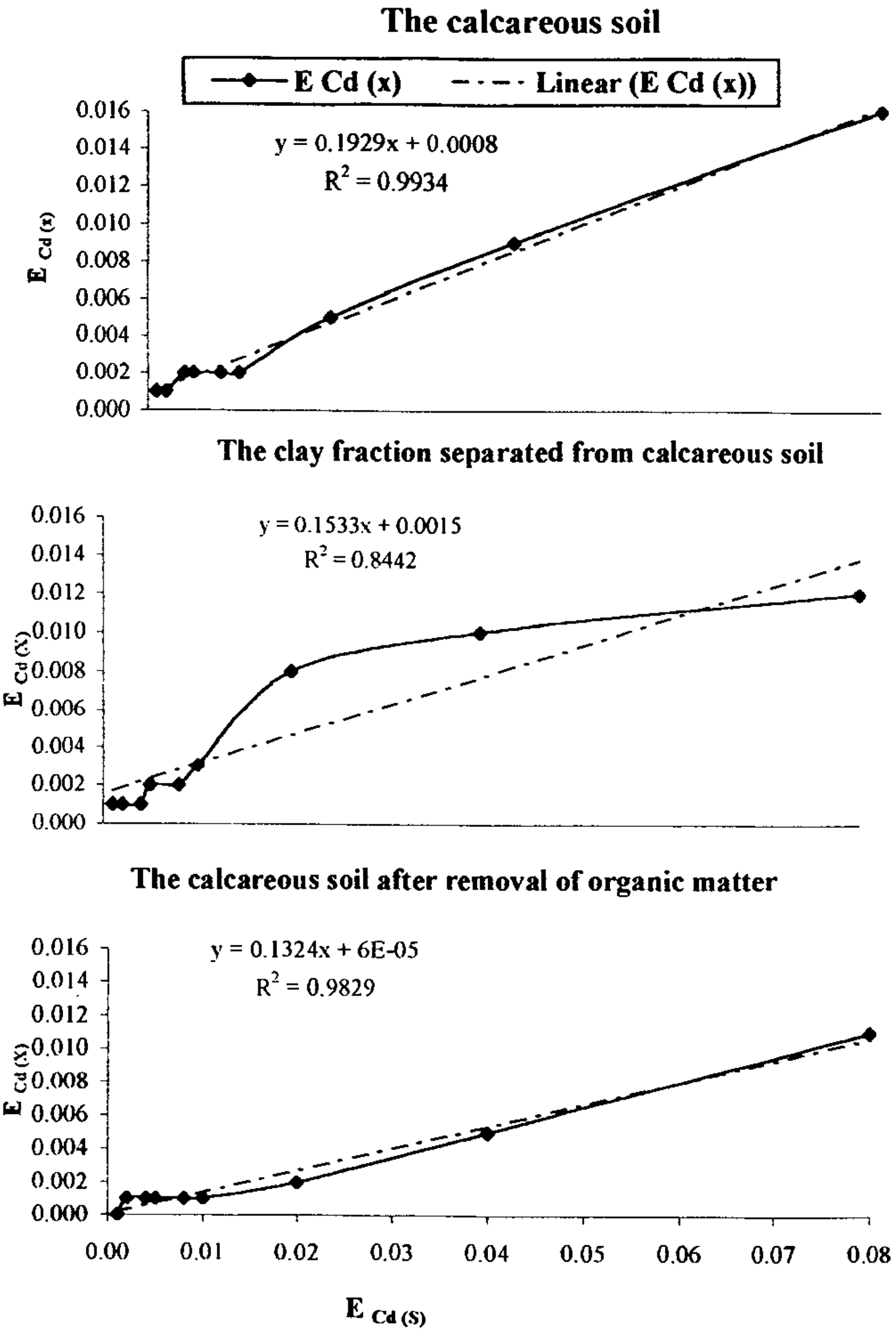
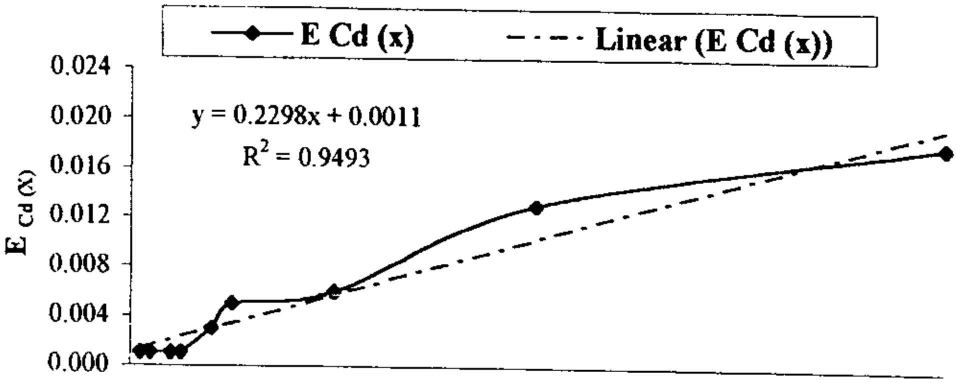
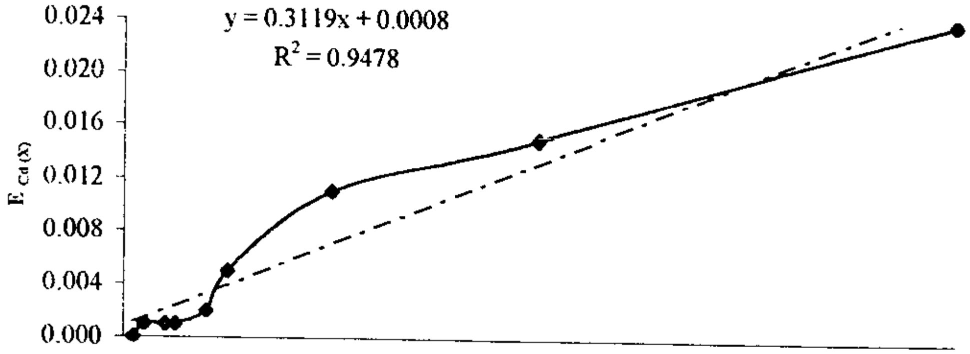


Fig. (13): Equivalent fraction relationship between soluble and exchangeable Cd in Cd-Ca exchange equilibria under differenet treatments for calcareous soils (Borg El-Arab).

The Nile alluvial noncalcareous soil



The clay fraction separated from the Nile alluvial noncalcareous soil



The Nile alluvial noncalcareous soil after removal of organic matter

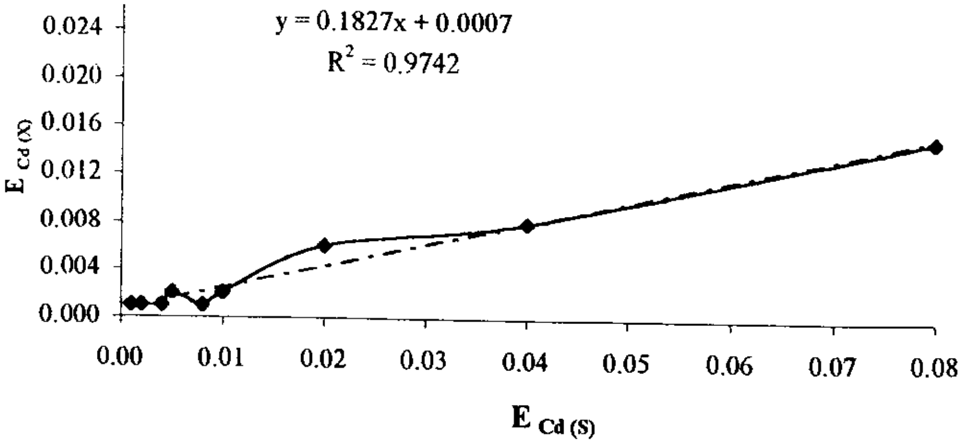


Fig. (14): Equivalent fraction relationship between soluble and exchangeable Cd in Cd-Ca exchange equilibria under differenet treatments for the Nile alluvial noncalcareous soils (Moshtohor).

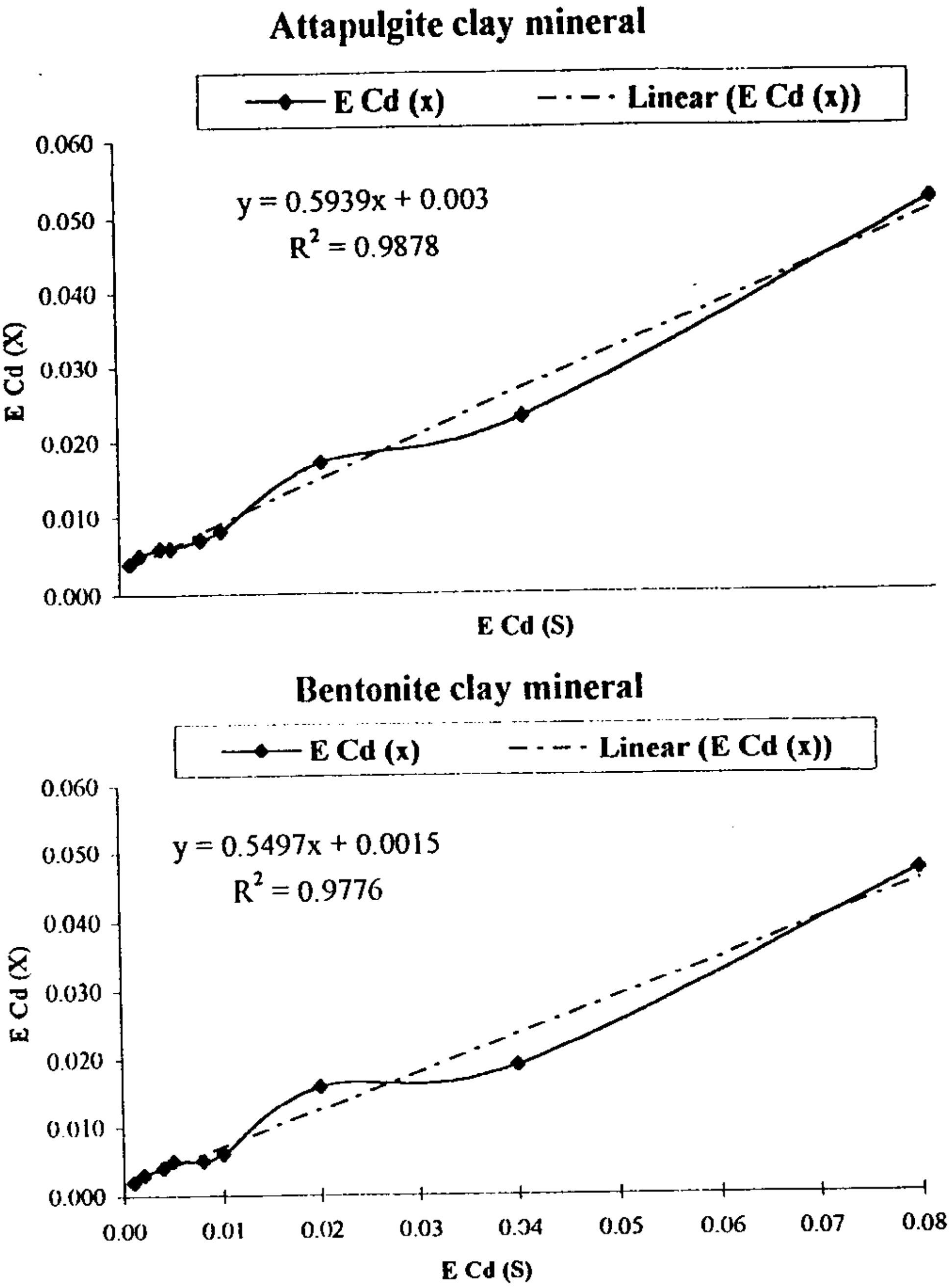


Fig.(15): Equivalent fraction relationship between soluble and exchangeable Cd in Cd-Ca exchange equilibria for the commercial used clay minerals

well as concentrations of Cd and Ca in equilibrium solutions, exchangeable Ca and Ca on the different used exchanger, the Cd equivalent exchangeable fractions and the calculated selectivity coefficients for the different Cd-Ca exchange equilibria.

Generally, it was found that increasing Cd/Ca ratio in the equilibrium solution was associated with a gradual increase in exchangeable Cd and consequently its equivalent exchangeable fractions on the studied exchangers. These results stand in well agreement with those obtained by **Sharma et al., (1994)**, who found that the equivalent fraction of Cd on exchange complex increased as the equivalent fraction of Cd in the equilibrating solution increased.

A comparison among the used exchangers (Tables 14- 18; Fig. 13-15) indicates that values of the equivalent fraction of exchangeable Cd fraction differed depending not only on Cd/Ca ratio in equilibrium solution, but also on type of the exchange materials. These materials could be arranged according to the equivalent fraction of exchangeable Cd retained on their surfaces apparently as follows:-

- The noncalcareous alluvial soil > the calcareous soil.
- The clay fraction separated from the noncalcareous alluvial soil > the clay fraction separated from the calcareous soil.

The mineralogical differences between the noncalcareous alluvial soil or its clay fraction on one hand and the calcareous one or its clay fraction on the other one might account for such a result. Both montmorillonite and kaolinite which are the dominant clay minerals in the Nile alluvial noncalcareous soil might encourage sorption of Cd since kaolinite has a greater percentage of hydroxyl edge sites whereas montmorillonite has a larger percentage of ditigonal cavities formed by six corner-sharing silica tetrahedral on siloxane planer surface. The reactivity of these cavities are dependent on the excess negative charge distribution due to isomorphic substitution in the silicate structure. Relative localization of charge tends to cause the formation of inner-sphere complexes while greater distribution of charge tends to cause the formation of out- sphere complex (**Sposito, 1981**). The excess negative charge in montmorillonite due to isomorphs substitution is spread between the tetrahedra and octahedra within the crystal and lead to the formation of predominantly outer-sphere complexes with cations in solution (**Sposito, 1984**). Thus Cd apparently has a high affinity for the hydroxyl edge sites of kaolinite whereas montmorillonite has a much lower proportion of these sites than kaolinite. Kaolinite tends to stack along the C axis, while montmoriollonite dimensions are 10 to 20 times greater in the horizontal (a b axis) direction **(Garcia- Miragaya et al., 1985).**

The organic matter content of the noncalcareous soil appeared to be also of more pronounced effect on Cd adsorption. On the other hand, **Alloway et al., (1988)** have shown that soils containing free $CaCO_3$ can adsorb Cd and reduce its bioavailability. The chemisorption of Cd at low concentrations was considered to involve the replacement of Ca by Cd in the surface crystals of calcite **(Papadopoulos and Rowell, 1988).**

Data in Table (16) and illustrated in Figs. (13 and 14) indicate that the Nile alluvial noncalcareous soil after removal of the organic matter was of higher equivalent fraction of exchangeable Cd than the calcareous one at the different equivalent fraction of Cd in equilibrium solution. **Alloway (1991)** reported that complexation of Cd with certain organic ligands in the soil solution can have major effects on the amounts sorbed. **Duffy et al., (1988)** reported that Cd forms anionc complexes with humic and fulvic acids.

The comparison between equivalent fractions of Cd sorbed on attapulgite at different equivalent fraction of Cd in equilibrium solution indicates very slightly higher affinity for Cd by attapulgite than bentonite (Tables 17 and 18 and Fig. 15)

Values of the selectivity coefficients shown in Tables (14 - 18) revealed always higher preference of Ca to Cd in both the studied soils, the separated clay fractions as well as the used clay minerals i.e. attapulgite and bentonite. Yet, it is of importance to indicate that values of selectivity coefficients tends generally to decrease by increasing the Cd/Ca ratio in the equilibrating solutions.

Thus, when the concentration of Cd in the equilibrium solution was increased, the values of the exchange coefficients of all the studied exchange complexes, generally decreased. This signifies a decreasing preference of the investigated exchangers to adsorb Cd relative to Ca at the relatively higher Cd concentration. Such a finding is in agreement with that of **Lagerwerff and Brower (1972)** and **Sharma et al., (1994)**.

Adsorption data of Cd on the different studied exchange materials (both the Nile alluvial noncalcareous and calcareous soils, the clay fractions separated from these soils, the same aforementioned soils after removal of the organic matter as well as the commercial clay minerals i.e. attapolgite and bontonite were analyzed according to both Freundlic and Langmuir isotherms.

Freundlich equation **(Freundlich, 1926)** is commonly used for describing the adsorption of ions from dilute solutions and in its linear form is given by:

$$\log x/m = \log K + 1/n \log C_o$$

where:-

x: is amount of adsorbed material (μg)

m: is amount of adsorbent (kg)

C_o: is concentration of Cd in the equilibrium solution (μmol_c L^{-1})

K and n : are empirical constants.

This equation is originally empirical without a theoretical foundation, (Table, 19).

The statistical significance of the correlation coefficient for log x/m vs log C_o was the criterion by which the fit of adsorption data to the abovementioned equation was tested. The fit was found to be highly significant for Cd adsorption by all the exchange materials where the (r) values (Table, 20) were 0.984**, 0.965**, 0.980**, 0.980**, 0.940**, 0.966**, 0.981** and 0.919** for the calcareous soil, the Nile alluvial noncalcareous soil, the clay fractions separated from the calcareous soil, the clay fractions separated from the Nile alluvial noncalcareous soil, the calcareous soil after removal of organic matter, the Nile alluvial noncalcareous soil after removal of the organic matter, bentonite and attapolgite, respectively.

Table (19): Cont.

Type of the exchange material	C_o Cd u mol$_c$ L^{-1}	x/m u molc kg^{-1}	Log C_o Cd	Log x/m
The calcareous soil after removal of organic matter	10.0	130.0	1.000	2.114
	20.0	172.0	1.301	2.236
	40.0	201.0	1.602	2.303
	50.0	390.0	1.699	2.591
	80.0	195.0	1.903	2.290
	100.0	390.0	2.000	2.591
	200.0	600.0	2.301	2.778
	400.0	1350.0	2.602	3.130
	800.0	2800.0	2.903	3.447
The Nile alluvial noncalcareous soil after removal of organic matter	10.0	326.0	1.000	2.513
	20.0	326.0	1.301	2.513
	40.0	569.0	1.602	2.755
	50.0	850.0	1.699	2.929
	80.0	628.0	1.903	2.798
	100.0	940.0	2.000	2.973
	200.0	2700.0	2.301	3.431
	400.0	3800.0	2.602	3.580
	800.0	7380.0	2.903	3.868
Bentonite clay mineral	10.0	1920.0	1.000	3.283
	20.0	3190.0	1.301	3.504
	40.0	3900.0	1.602	3.591
	50.0	5760.0	1.699	3.760
	80.0	5840.0	1.903	3.766
	100.0	6960.0	2.000	3.843
	200.0	18000.0	2.301	4.255
	400.0	20280.0	2.602	4.307
	800.0	51240.0	2.903	4.710
Attapulgite clay mineral	10.0	110.0	1.000	2.041
	20.0	136.0	1.301	2.134
	40.0	157.0	1.602	2.196
	50.0	163.0	1.699	2.212
	80.0	189.0	1.903	2.276
	100.0	204.0	2.000	2.310
	200.0	453.0	2.301	2.656
	400.0	582.0	2.602	2.765
	800.0	1369.0	2.903	3.136

Table (19): Parameters required for plotting Freundlich equations.

Type of the exchange material	C_o Cd u mol$_c$ L^{-1}	x/m u molc kg^{-1}	Log C_o Cd	Log x/m
The calcareous soil (Borg El- Arab)	10.0	124.0	1.000	2.093
	20.0	166.0	1.301	2.220
	40.0	444.0	1.602	2.647
	50.0	380.0	1.699	2.580
	80.0	415.0	1.903	2.618
	100.0	510.0	2.000	2.708
	200.0	1260.0	2.301	3.100
	400.0	2100.0	2.602	3.322
	800.0	3800.0	2.903	3.580
The Nile alluvial noncalcareous soil (Moshtohor)	10.0	261.0	1.000	2.417
	20.0	243.0	1.301	2.386
	40.0	480.0	1.602	2.681
	50.0	390.0	1.699	2.591
	80.0	1138.0	1.903	3.056
	100.0	2150.0	2.000	3.332
	200.0	2690.0	2.301	3.430
	400.0	5870.0	2.602	3.769
	800.0	7800.0	2.903	3.892
The clay fraction seaparated from the calcareous soil	10.0	142.0	1.000	2.152
	20.0	160.0	1.301	2.204
	40.0	355.0	1.602	2.550
	50.0	450.0	1.699	2.653
	80.0	550.0	1.903	2.740
	100.0	600.0	2.000	2.778
	200.0	1880.0	2.301	3.274
	400.0	2400.0	2.602	3.380
	800.0	2900.0	2.903	3.462
The clay fraction separated from the Nile alluvial noncalcareous soil	10.0	213.0	1.000	2.328
	20.0	338.0	1.301	2.529
	40.0	498.0	1.602	2.697
	50.0	580.0	1.699	2.763
	80.0	950.0	1.903	2.978
	100.0	2090.0	2.000	3.320
	200.0	4980.0	2.301	3.697
	400.0	6600.0	2.602	3.820
	800.0	10800.0	2.903	4.033

Table (20): Freundlich regression equations, correlation coefficients and corresponding calculated parameters.

Type of the exchange material	Freundlich regression equiation	Correlation coefficient (r)	Log K	1/n
The calcareous soil (Borg El-Arab)	log x/m = -1.466 + 1.227 Log Co	0.984 **	-1.466	1.227
The Nile alluvial noncalcareous soil	log x/m = -1.208 + 1.023 Log Co	0.965 **	-1.208	1.023
The clay fraction separated from calcareous. Soil	log x/m = -1.538 + 1.237 Log Co	0.980 **	-1.538	1.237
The clay fraction separated from alluvial soil	log x/m = -1.125 + 0.974 Log Co	0.980 **	-1.125	0.974
The calcareous soil after removal of O.M	log x/m = -1.431 + 1.286 Log Co	0.940 **	-1.431	1.286
The Nile alluvial soil after removal of O.M	log x/m = -1.800 + 1.225 Log Co	0.966 **	-1.800	1.225
Bentonite clay mineral	log x/m = -3.237 + 1.326 Log Co	0.981 **	-3.237	1.326
Attapulgite clay mineral	log x/m = -2.248 + 1.603 Log Co	0.949 **	-2.248	1.603

** = Significant at 1%

These results indicate that adsorption processes rather than precipitation appear to control the distribution of Cd between soluble and soil- bound forms at the concentrations normally encountered even in the majority of polluted soils. In many cases it has been found that Cd adsorption by suspensions of soils or their constituents fits either the Langmuir or Freundlich isotherms equations **(Levy et al., 1976 and Gavallaro and Mc Bride, 1978). Christensen (1984)** reported that adsorption of Cd is normally rapid with more than 90% occurring within the first 10 minutes.