RESULTS AND DISCUSSION

4.RESULTS AND DISCUATION

Concentration of micronutrients in soil solution and hence their availability to plants are probably controlled by sorption and desorption on surfaces of soil colloidal materials .Although many studies dealt with sorption of these micronutrients on soil and soil components only few have examined the reverse process, i.e. desorption of these nutrients into soil solution .

4.1. Adsorption isotherms of copper on soils, clay minerals and Fe and Al oxides :

4.1.1-Soils :

Two calcareous soils differed in their $CaCO_3$ content were chosen, i.e., sandy loam soil (with 11.84 % $CaCO_3$) and sandy clay loam (21.15 % $CaCO_3$).

Adsorption isotherms of Cu on soils were plotted in Figs. (1-6) and data of equilibrium concentration of Cu as well as the amounts of adsorbed Cu per the unit of adsorbent were presented in Tables (2-5).

The amount of Cu adsorbed ($\mu g\ g^{-1}$) on sandy loam and sandy clay loam soils under different concentration of back-ground electrolyte increased with increasing initial concentration from 0 to 50 μg Cu mL^{-1} until a condition of surface saturation is reached. Adsorption maxima of Cu on sandy clay loam soil under different concentrations of the back- ground electrolyte were higher than the corresponding ones observed with sandy loam soil.

The high values of adsorbed Cu on sandy clay loam soil could be due to its high content of clay, $CaCO_3$ and O.M. These results stand in well agreement with those of **Wassif (1973),**

Sabet et al., (1975) Shuman (1980), Mehta et al., (1984) Mohey El-Din (1985), and Abbas et al., (1996), Mesquita (1996).

The highest adsorption was observed in case of without back-ground electrolyte and decreased with increasing the concentration of $Ca(NO_3)_2$ (the back-ground electrolyte) from 0.001 M to 0.1 M (Fig. 7).

Data of Cu adsorption on both soils were fitted to the linear form of the following adsorption isotherm equations :

(1) Langmuir equation : $C/q= 1/ab + C/b$

(2) Ferundlich equation : $\ln q= \ln K+n \ln C$

Where C : equilibrium concentration , q: the amount of Cu adsorbed (µg g^{-1} soil), b: maximum adsorption of Cu on the unit weight of soil and a : constant related to the bonding energy. In case of Freundlich, q :the amount of Cu adsorbed (µg g^{-1}), K and n are constants ($n<1$) and C: equilibrium concentration(µg mL^{-1}).

In case of sandy loam soil (Fig. 2), the adsorption of Cu obeyed the Langmuir adsorption isotherms with coefficients of determinations (r) of 0.997***, 0.985***, 0.977*** and 0.985*** for back-ground electrolyte of 0, 0.001, 0.01 and 0.1M $Ca(NO_3)_2$ (Table 6). Also, in case of sandy clay loam soil, adsorption of Cu was highly fitted to Langmuir isotherms with coefficient of determination (r) of 0.976***,0.970***, 0.990*** and 0.950*** for back-ground concentrations of 0, 0.001, 0.01, and 0.1 M $Ca(NO_3)_2$, respectively.

Data of Table (6) reveal that the highest adsorption maximum (1719.1µg g^{-1}) was observed in case of without Ca $(NO_3)_2$ electrolyte. With increasing electrolyte concentration, the adsorption maximum was decreased being 1191.8 μg g^{-1} in presence 0.1 M $Ca(NO_3)_2$. The adsorption maximum of Cu was decreased by 19.5, 24.5 and 30.7 % with 0.001, 0.01 and 0.1 M $Ca(NO_3)_2$, respectively.

In case of sandy clay loam soil, the corresponding adsorption maximum of Cu was 2254.8, 2084.6, 1717.0 and 1516.9 μg g^{-1}. The adsorption maximum was decreased by 7.5, 23.9, and 32.7 with 0.001, 0.01 and 0.1 M $Ca(NO_3)_2$, respectively.

The decrease in adsorption maximum in both soils accompanied with increasing the background electrolyte indicates that copper may partially formed outer sphere complex with the surfaces of soils. Copper in the outer sphere could be replaced easily by Ca^{2+} ions. Adsorption isotherms of Cu indicate that high proportion of Cu was adsorbed on specific sites and formed inner sphere complexes. In case of the highest back-ground concentration [0.1 M $Ca(NO_3)_2$] the decreases in adsorption maximum were 30.7 and 32.7 % with sandy loam and sandy clay loam soil, respectively.

Data of Table (7) represent adsorption isotherms of Freundlich, adsorption data of Cu obeyed the Freundlich in a manner like that obtained with Langmuir .In case of sandy loam soil the coefficients of determination (r) were 0.975***, 0.956***, 0.966*** and 0.972*** with the following back-ground concentrations 0, 0.001, 0.01 and 0.1 M $Ca(NO_3)_2$ respectively. The corresponding (r) values with sandy clay loam soil were 0.959***, 0.971***,0.976*** and 0.989*** with the following back-ground concentrations 0, 0.001, 0.01 and 0.1 M $Ca(NO_3)_2$ respectively. The adsorption maxima of Cu in both soils were affected by the concentration of the back-ground electrolyte in a way similar to that obtained with Langmuir isotherms.

Data presented in Table (8) and illustrated by Fig. (8) show the relationship between the adsorbed Cu on sandy loam and sandy clay loam soils ($\mu g\ g^{-1}$) versus pH. In the tested soils there was an increase in Cu adsorption ($\mu g\ g^{-1}$) with increasing the equilibrium pH from 4.3 to 7.0 . The increases in Cu adsorption resulted from increasing pH (4.3 to 7.0) were 38 and 22.5 % with sandy loam and sandy clay loam soil, respectively. An obvious increase in Cu adsorption was noticed at pH 5.0 and 5.5 on sandy loam and sandy clay loam soils, receptively, then gradual increases in Cu adsorption were observed with the tested two soils up to pH 7.0.

The obtained results are in agreement with those of ***Barrow(1986)*** in which increasing the pH causes a change in the adsorbing copper species from Cu^{2+} to $Cu(OH)^{+}$and increase the negative charge of the soil surface. Also the strong pH dependence of copper adsorption by soil could be interpreted in terms of preferential adsorption of hydrolyzed copper cations such as $CuOH^{+}$, where as the hydration energy resisting the adsorption is smaller for these ions than those of Cu^{+}.

Regardless of the mechanism, the net effect is that the adsorption of each copper ion results in a release of protons **(Kinniburgh, 1983 and Ankomah, 1991)** . Thus the effect of increasing pH on copper adsorption could be explained by two complimentary trends an increasing proportion of $Cu\ OH^{+}$ ions and a decreasing electrostatic potential of the soil surface which , for positively charged copper ion, favors adsorption . **(Sewailem et al., 2000).**

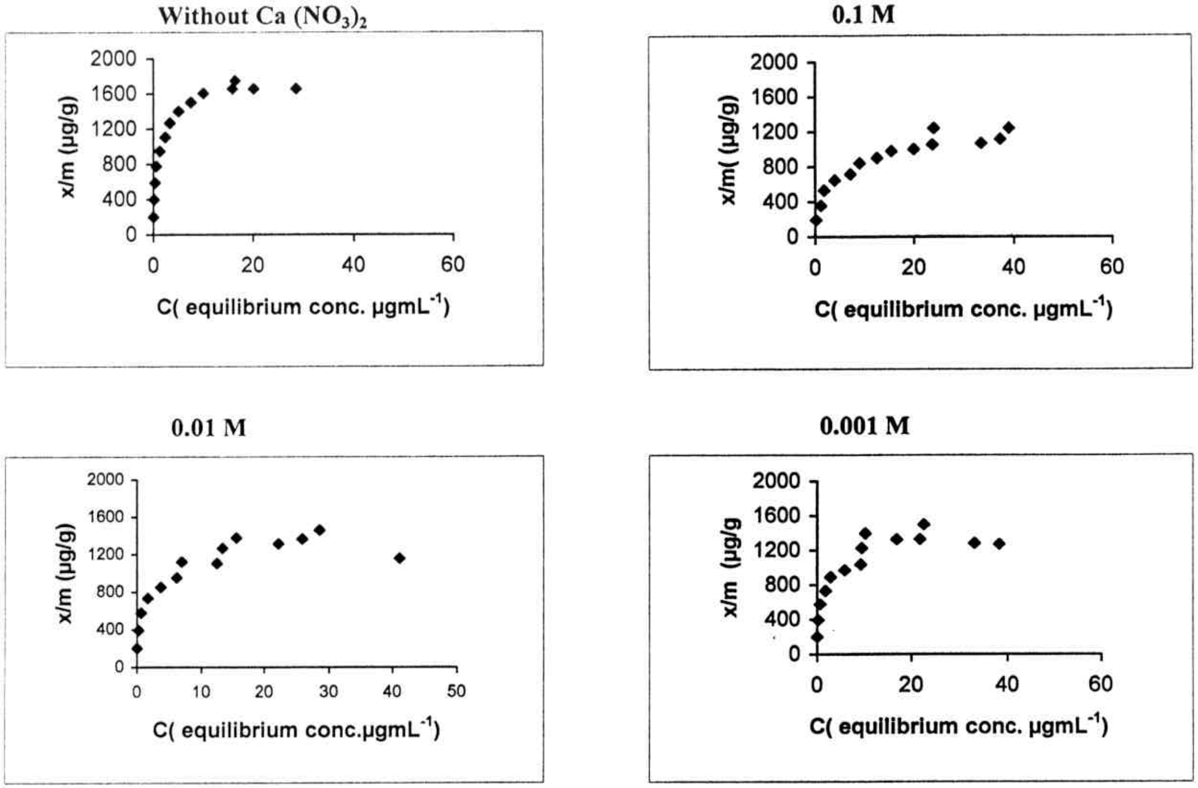


Fig. (1):Adsorption isotherms (Langmuir) for Copper by sandy loam soil. Experimental conditions: ionic strength (without, 0.1,0.01and0.001M Ca(NO3)2,Cu concentration, 0-70 µgmL-1.

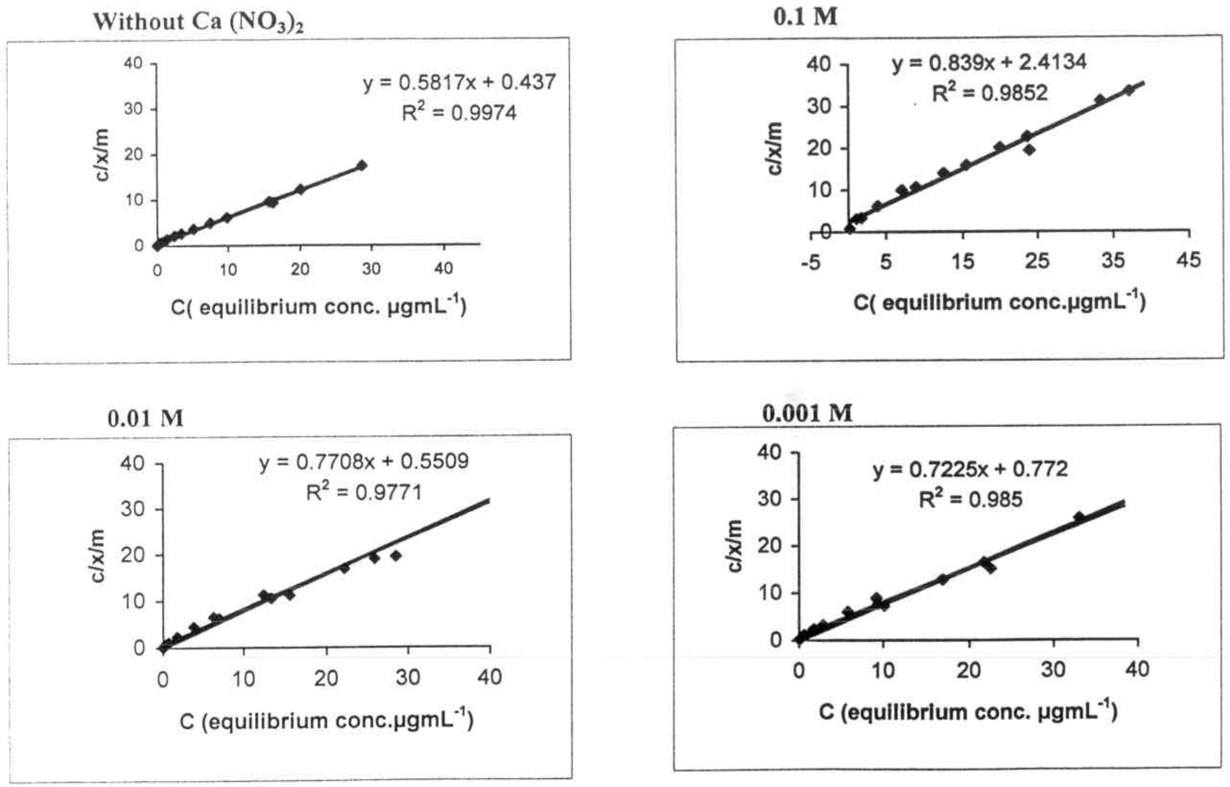


Fig.(2): Adsorption isotherms (Langmuir linear) for Copper by sandy loam soil. Experimental conditions: ionic strength (without , 0.1, 0.01, and 0.001M) Ca(NO3)2, Cu concentration, 0-70 µgmL-1.

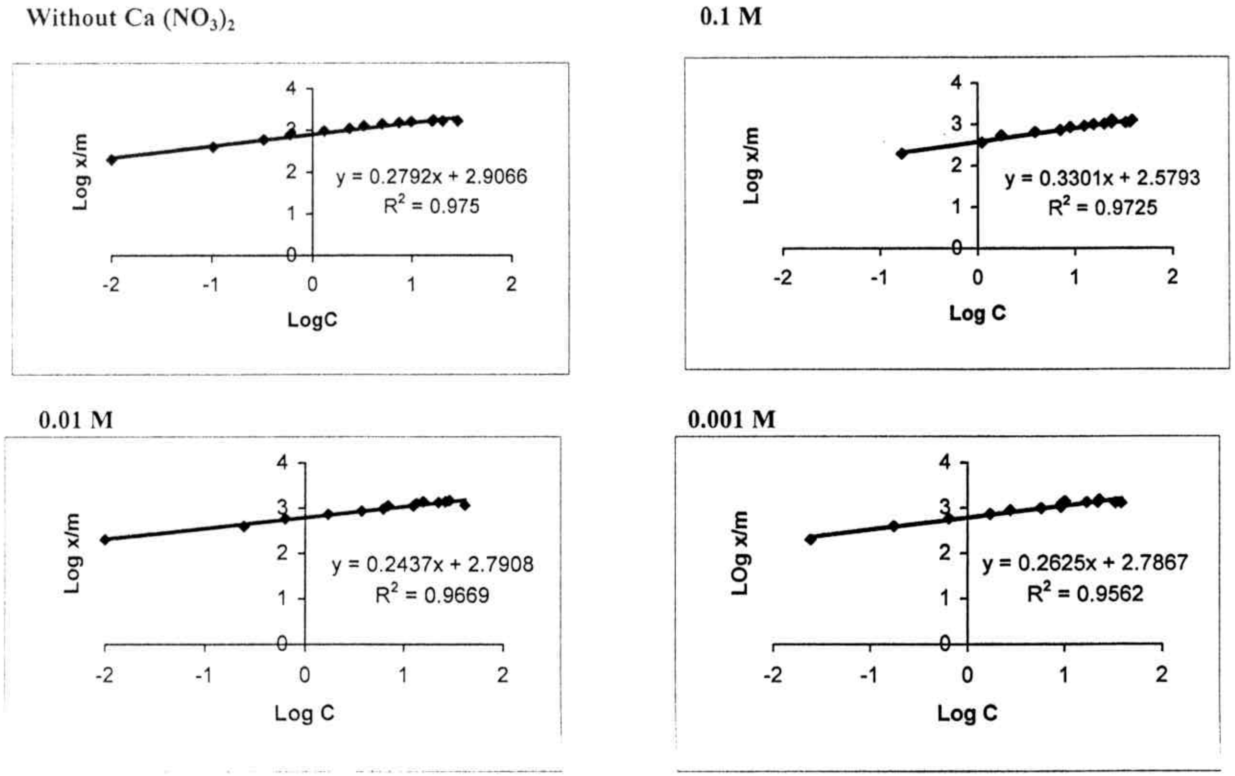
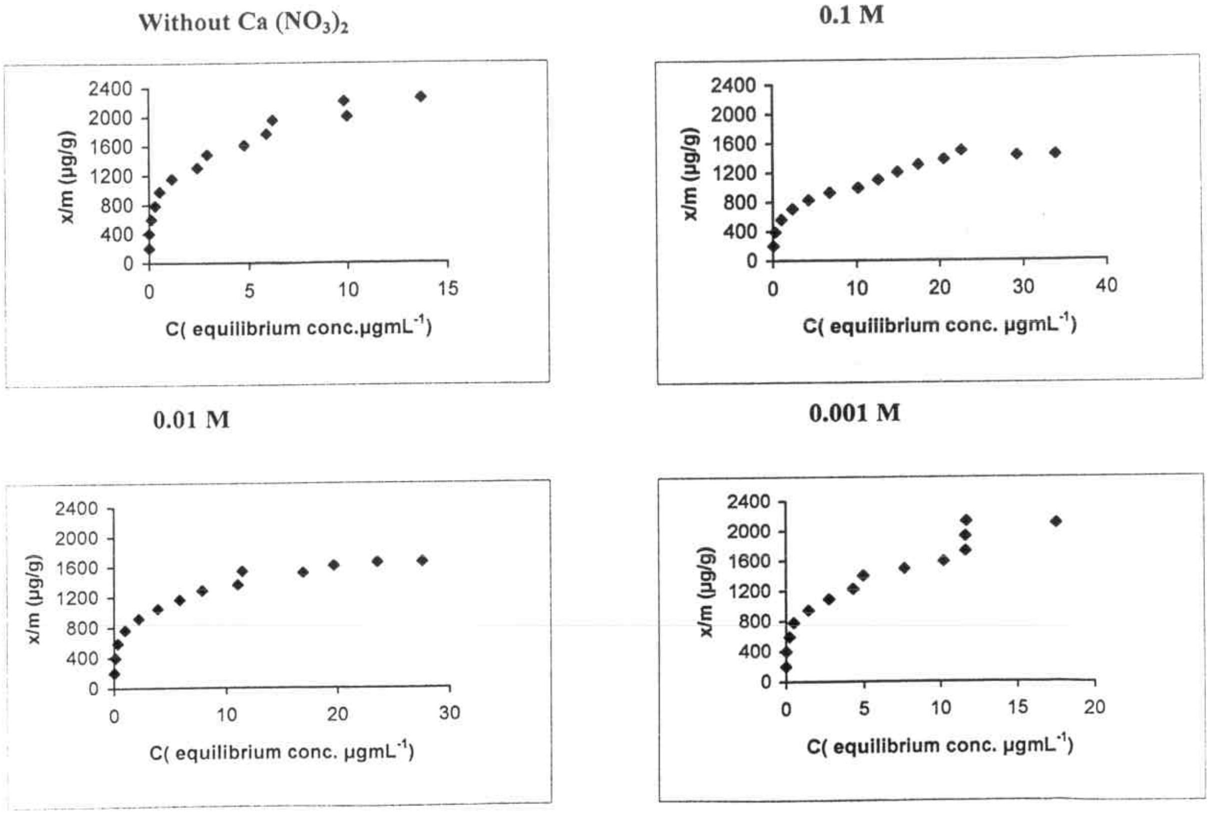


Fig. (3):Adsorption isotherms (Freundlich linear) for Copper by sandy loam soil. **Experimental conditions: ionic strength (without, 0.1 ,0.01, and 0.001M) Ca(NO3)2, Cu concentration, 0-70 µgmL-1.**



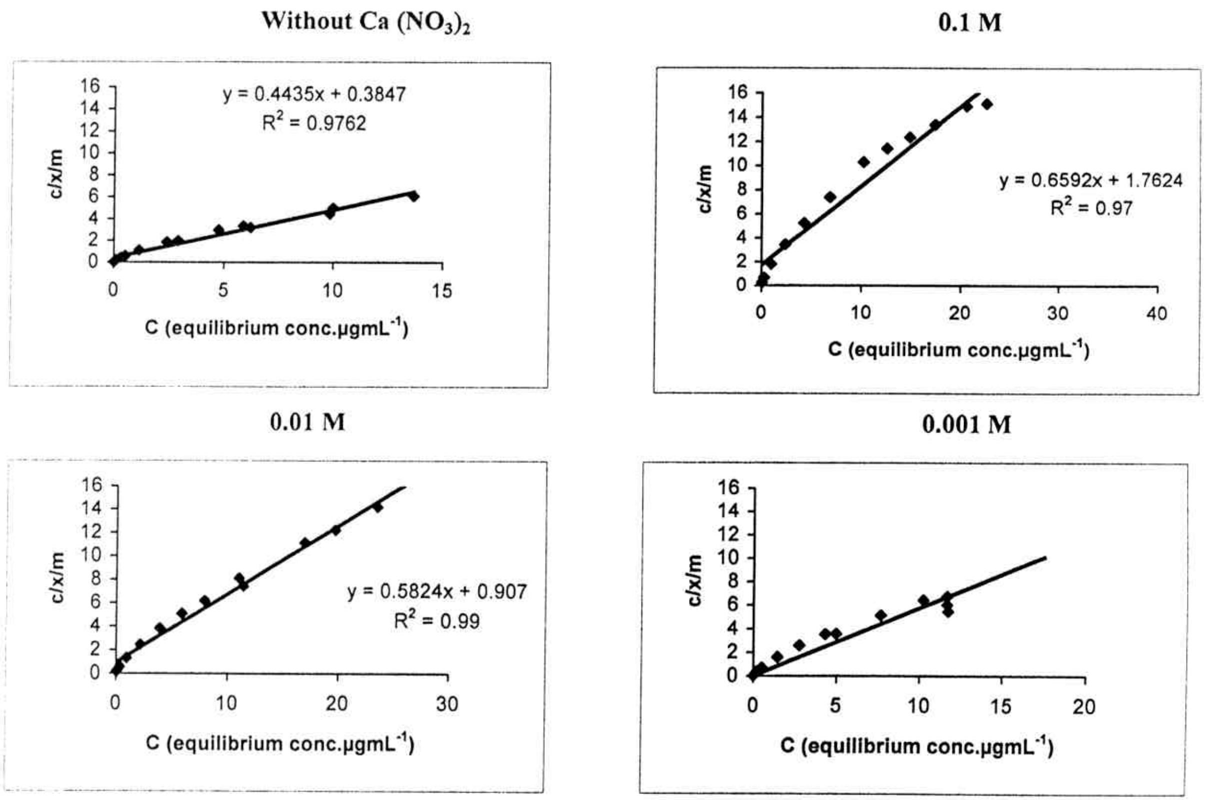
Without Ca $(NO_3)_2$

0.1 M

0.01 M

0.001 M

Fig. (4): Adsorption isotherms (Langmuir) for **Copper by sandy clay loam soil.Experimental conditions:** ionic strength (without , 0.1, 0.01, and **0.001M)$Ca(NO_3)_2$, Cu concentration, 0-70 µgmL^{-1}.**

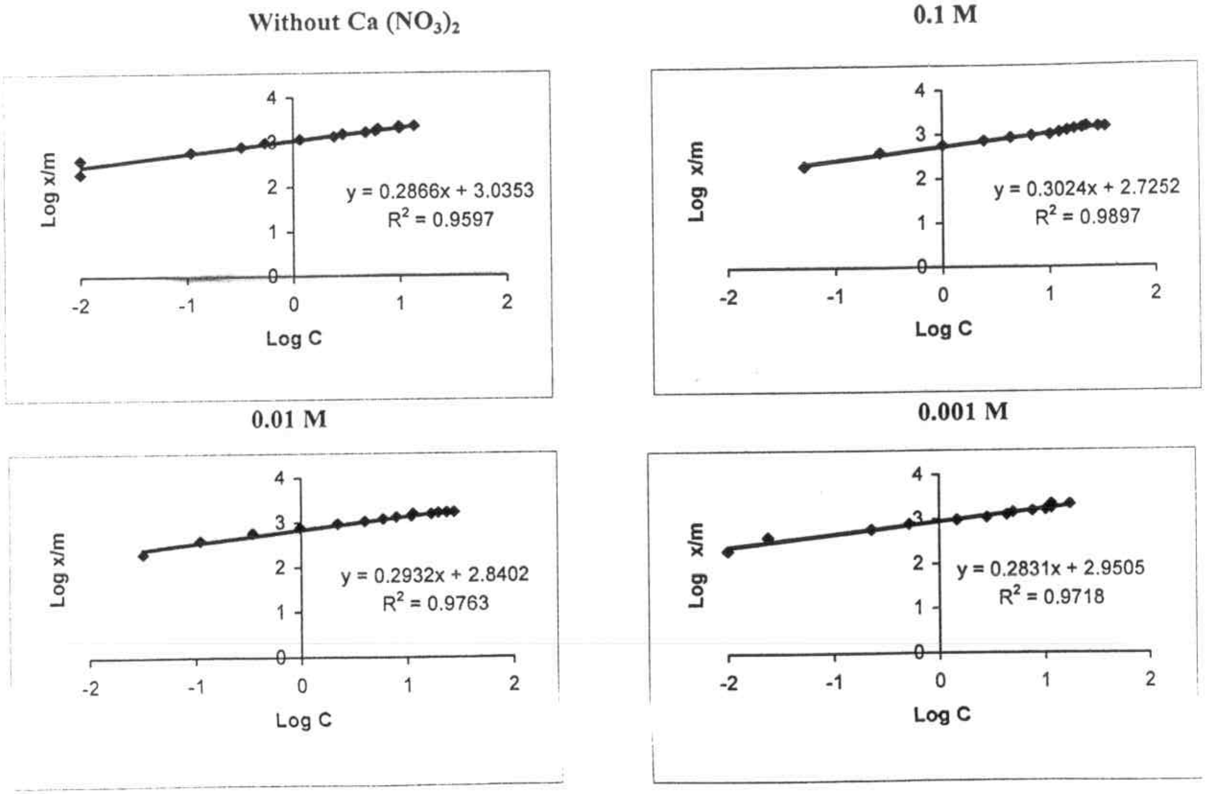

Without Ca $(NO_3)_2$

0.1 M

0.01 M

0.001 M

Fig. (5): Adsorption isotherms (Langmuir linear) for Copper by sandy clay loam soil. **Experimental conditions: ionic strength (without , 0.1, 0.01, and 0.001M)$Ca(NO_3)_2$, Cu concentration, 0-70 µgmL^{-1}.**



Without Ca $(NO_3)_2$

0.1 M

0.01 M

0.001 M

Fig. (6): Adsorption isotherms (Freundlich linear) for Copper by sandy clay loam soil. **Experimental conditions: ionic strength (without , 0.1, 0.01, and 0.001M)Ca$(NO_3)_2$, Cu concentration, 0-70 µgmL^{-1}.**

Table. (2): Adsorption isotherms(Langmuir) of Cu on sandy loam soil ,ionic strength,[without ,0.001,0.01 and 0.1M $Ca(NO_3)_2$]

	Without			0.001 M			0.01M			0.1M		
Initial Cu μg mL^{-1}	C μg mL^{-1}	X/m μg/g	C/X/m	C μg mL^{-1}	X/m μg/g	C/X/m	C μg mL^{-1}	X/m μg/g	C/X/m	C μg mL^{-1}	X/m μg/g	C/X/m
5	0.01	200	0.030	0.02	199	0.121	0.00	200	0.000	0.17	193	0.858
10	0.10	396	0.260	0.18	393	0.445	0.25	390	0.636	1.11	356	3.115
15	0.33	587	0.561	0.64	575	1.109	0.63	575	1.103	1.76	529	3.329
20	0.60	776	0.771	1.73	731	2.370	1.72	731	2.350	3.92	643	6.100
25	1.31	948	1.376	2.78	889	3.130	3.77	849	4.430	7.09	716	9.900
30	2.37	1105	2.140	5.76	970	5.940	6.21	951	6.530	8.96	842	10.640
35	3.32	1267	2.620	9.17	1033	8.870	6.97	1121	6.220	12.52	899	13.920
40	5.07	1397	3.630	9.36	1226	7.630	12.44	1102	11.290	15.51	980	15.830
45	7.46	1502	4.960	10.11	1396	7.240	13.34	1267	10.530	20.01	1000	20.020
50	9.87	1605	6.150	16.86	1326	12.720	15.54	1379	11.260	23.71	1052	22.550
55	15.75	1653	9.520	21.76	1330	16.360	22.21	1312	16.930	23.98	1241	19.320
60	16.31	1748	9.330	22.57	1497	15.070	25.94	1363	19.030	33.30	1068	31.170
65	20.10	1655	12.150	33.02	1279	25.810	28.52	1459	19.540	37.16	1114	33.360
70	28.66	1654	17.330	38.22	1271	30.070	41.10	1156	35.550	38.94	1242	31.350

*c/x/m 10^{-3}

Table.(3):Adsorption isotherms(freundlich) of Cu on sandy loam soil ,ionic strength,[without ,0.001,0.01 and 0.1M $Ca(NO_3)_2$]

Initial Cu µg mL^{-1}	Without		0.001 M		0.01M		0.1M	
	LogC	LogX/m	LogC	LogX/m	LogC	LogX/m	Log	LogX/m
5	-2.00	2.30	-1.60	2.29	0.00	2.30	-0.76	2.28
10	-1.00	2.60	-0.07	2.59	-0.60	2.60	0.04	2.55
15	-0.48	2.77	-0.19	2.75	-0.02	2.77	0.24	2.72
20	-0.22	2.90	0.23	2.86	0.23	2.88	0.59	2.80
25	0.11	2.97	0.44	2.94	0.57	2.92	0.85	2.85
30	0.37	3.04	0.76	2.98	0.79	2.97	0.95	2.92
35	0.52	3.10	0.96	3.01	0.84	3.04	1.09	2.95
40	0.70	3.14	0.97	3.08	1.09	3.04	1.19	2.99
45	0.87	3.17	1.00	3.14	1.12	3.10	1.30	3.00
50	0.99	3.20	1.27	3.12	1.19	3.13	1.37	3.02
55	1.19	3.21	1.33	3.12	1.34	3.11	1.37	3.09
60	1.21	3.24	1.35	3.17	1.41	3.13	1.52	3.02
65	1.30	3.21	1.51	3.10	1.45	3.16	1.57	3.04
70	1.45	3.21	1.58	3.10	1.61	3.06	1.59	3.09

Table. (4):Adsorption isotherms (langmuir) of Cu on sandy clay loam soil ,ionic strength,[without ,0.001,0.01 and 0.1M $Ca(NO_3)_2$]

Initial Cu µg mL^{-1}	Without			0.001 M			0.01M			0.1M		
	C µg mL^{-1}	X/m µg/g	C/X/m	C µg mL^{-1}	X/m µg/g	C/X/m	C µg mL^{-1}	X/m µg/g	C/X/m	C µg mL^{-1}	X/m µg/g	C/X/m
5	0.00	200	0.000	0.00	200	0.000	0.03	199	0.161	0.05	198	0.263
10	0.00	400	0.000	0.02	399	0.060	0.11	396	0.278	0.26	390	0.659
15	0.11	596	0.187	0.22	591	0.380	0.34	586	0.585	1.01	560	1.806
20	0.32	787	0.407	0.52	779	0.665	0.98	761	1.290	2.42	703	3.440
25	0.54	978	0.549	1.48	941	1.570	2.21	912	2.420	4.33	827	5.230
30	1.16	1153	1.090	2.80	1088	2.570	3.96	1042	3.800	6.85	926	7.400
35	2.42	1303	1.859	4.33	1227	3.520	5.90	1164	5.070	10.21	992	10.300
40	2.92	1483	1.960	4.96	1401	3.540	7.90	1284	6.150	12.55	1098	11.420
45	4.76	1610	2.950	7.64	1495	5.110	11.00	1360	8.090	14.88	1205	12.350
50	5.89	1764	3.340	10.22	1591	6.420	11.43	1543	7.410	17.44	1303	13.380
55	6.23	1951	3.190	11.65	1734	6.720	16.96	1522	11.140	20.56	1378	14.920
60	9.98	2001	4.980	11.65	1932	6.030	19.68	1613	12.210	22.63	1495	15.130
65	9.84	2207	4.450	11.71	2132	5.460	23.55	1658	14.200	29.26	1430	20.500
70	13.71	2252	6.090	17.53	2099	8.350	27.61	1666	16.570	33.86	1446	23.400

*c/x/m 10^{-3}

Table.(5):Adsorption isotherms(freundlich) of Cu on sandy clay loam soil ,ionic strength,[without ,0.001,0.01 and 0.1M $Ca(NO_3)_2$]

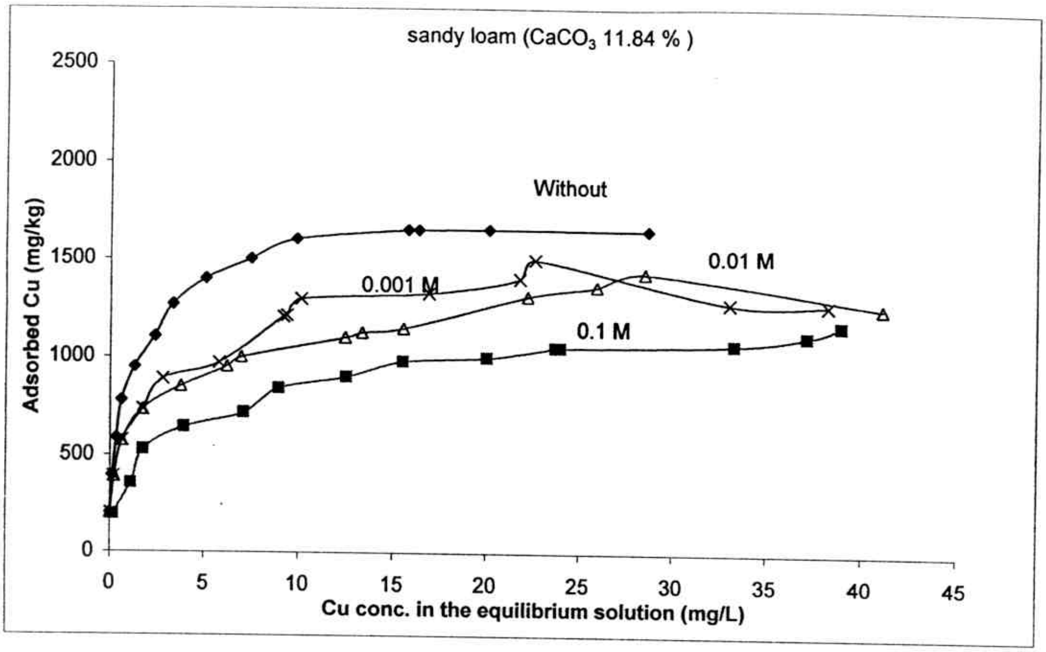
Initial Cu µg mL^{-1}	Without		0.001 M		0.01M		0.1M	
	LogC	LogX/m	LogC	LogX/m	LogC	LogX/m	Log	LogX/m
5		2.30	0.00	2.30	-1.49	2.30	-1.28	2.30
10	0.00	2.60	-1.62	2.60	-0.96	2.60	-0.59	2.59
15	-0.96	2.77	-0.65	2.77	-0.46	2.77	0.00	2.75
20	-0.49	2.90	-0.29	2.89	-0.01	2.88	0.38	2.85
25	-0.27	2.99	0.17	2.97	0.34	2.96	0.64	2.92
30	0.07	3.06	0.45	3.04	0.60	3.02	0.84	2.97
35	0.38	3.11	0.64	3.09	0.77	3.07	1.01	3.00
40	0.46	3.17	0.70	3.15	0.90	3.11	1.10	3.04
45	0.68	3.21	0.88	3.17	1.04	3.13	1.17	3.08
50	0.77	3.25	1.01	3.20	1.06	3.19	1.24	3.11
55	0.79	3.29	1.07	3.24	1.23	3.18	1.31	3.14
60	1.00	3.30	1.07	3.29	1.29	3.21	1.35	3.17
65	0.99	3.34	1.07	3.33	1.37	3.22	1.47	3.16
70	1.14	3.35	1.24	3.32	1.44	3.22	1.53	3.16

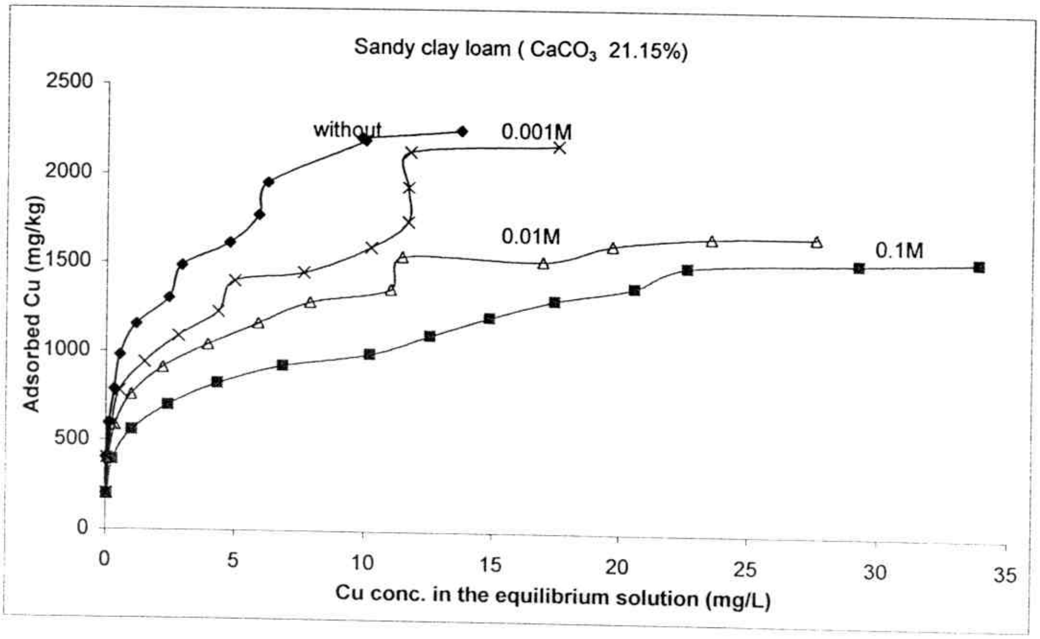
Table (6) Langumir isotherms of Cu adsorption on soils under different back ground concentrations.

Soil	$Ca(NO_3)_2$	Linear equation	b	K	r
Sandy loam	Without	Y=0.0005817X + 0.000437	1719.10	1.33	0.997***
	0.001M	Y=0.0007225 X + 0.000772	1384.10	0.935	0.985***
	0.01M	Y=0.0007708 X + 0.0005509	1297.40	0.714	0.977***
	0.1M	Y=0.000839 X + 0.002413	1191.80	0.347	0.985***
Sandy clay loam	Without	Y=0.0004435 X + 0.0003847	2254.80	1.15	0.976***
	0.001M	Y=0.0004797 X + 0.0006969	2084.60	0.69	0.970***
	0.01M	Y=0.0005824 X + 0.000907	1717.00	0.65	0.990***
	0.1M	Y=0.0006592 X + 0.0017624	1516.90	0.37	0.950***

Table (7) Freundlich isotherms of Cu adsorption on soils under different back ground concentrations.

Soil	$Ca(NO_3)_2$	Linear equation	'a"	'B"	R
Sandy loam	Without	Y=0.2792X +2.9066	806.49	0.279	0.975***
	0.001M	Y=0.2625X + 2.7867	611.92	0.263	0.956***
	0.01M	Y=0.2437 X +2.7908	617.73	0.244	0.966***
	0.1M	Y=0.3301X + 2.5793	379.57	0.33	0.972***
Sandy clay loam	Without	Y=-0.2866X+3.0353	1084.67	0.287	0.959***
	0.001M	Y=0.2831X+2.9505	892.27	0.283	0.971***
	0.01M	Y=0.2932X+2.8402	692.14	0.293	0.976***
	0.1M	Y=0.3024X+2.7252	531.12	0.302	0.989***





g .(7): Adsorption isotherms for copper by sandy loam and sandy clay loam soils xperimental conditions: Ionic strength without ,0.1,0.01 and 0.001 M Ca(NO$_3$)$_2$]

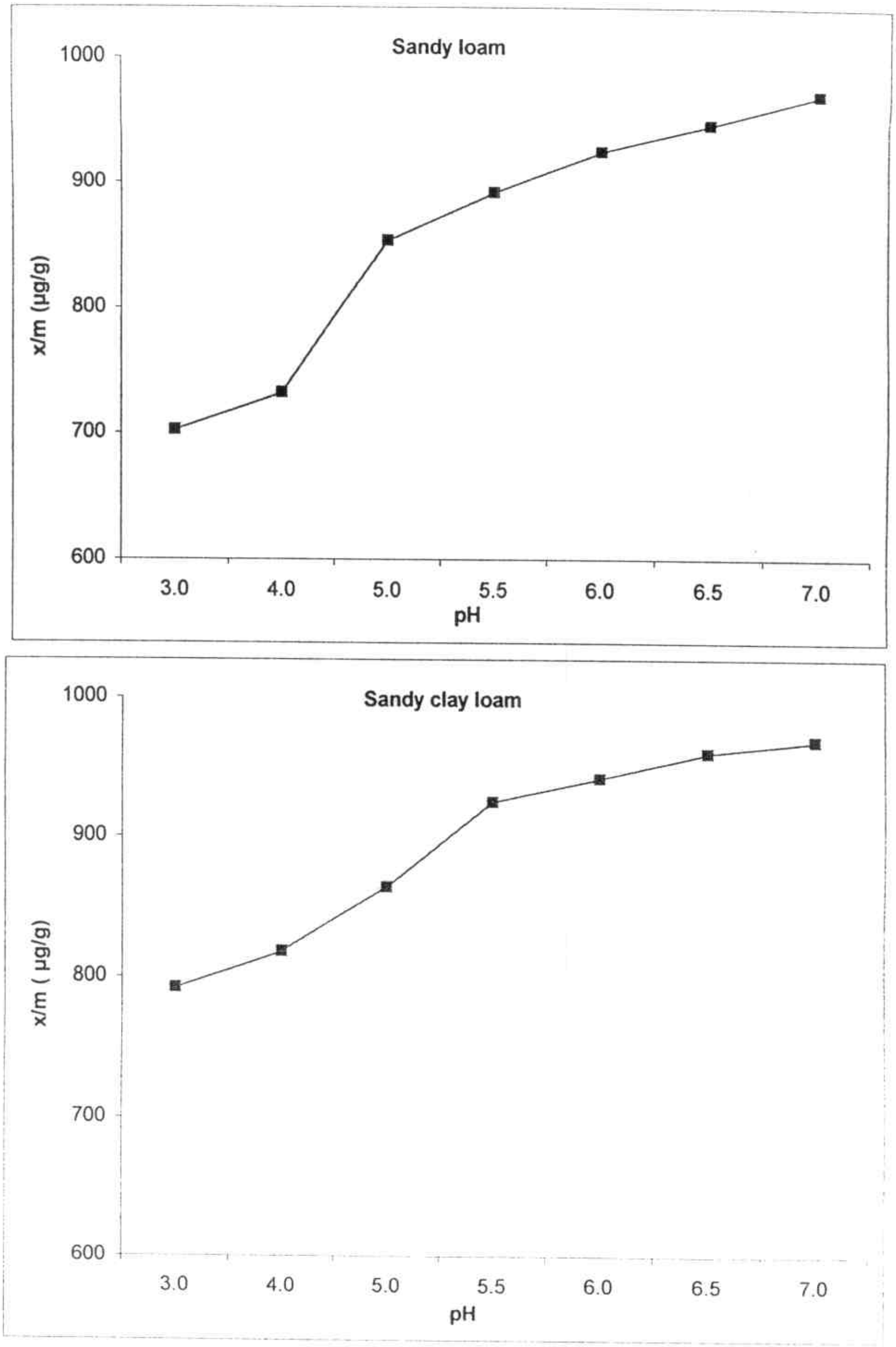


Fig .(8) : Copper adsorption on sandy loam and sandy clay loam soils as a function of pH in presence of 0.1M $Ca(NO_3)_2$ as a back-ground electrolyte

Table . (8):Copper adsorption on a sandy loam, and sandy clay loam soils as a function of pH [Cu conc. (25µg/mL) ionic strength buffer 0.1M Ca $(NO_3)_2$]

Soils	Initial ofCu (µg/mL)	PH	C (µg/mL)	x/m µg/g	PH Final
Sandy loam	25	3.00	7.435	703	4.30
	25	4.00	6.675	733	4.70
	25	5.00	3.645	854	5.00
	25	5.50	2.695	892	5.50
	25	6.00	1.866	925	6.10
	25	6.50	1.321	947	5.50
	25	7.00	0.721	971	7.00
Sandy clay loam	25	3.00	5.188	792	4.30
	25	4.00	4.551	818	4.80
	25	5.00	3.401	864	5.40
	25	5.50	1.876	925	5.60
	25	6.00	1.445	942	6.00
	25	6.50	0.988	960	6.50
	25	7.00	0.759	970	7.00

4.2.1 Clay minerals :

In the pH range generally associated with soils heavy metals interact with oxides , oxyhyroxides, and clays. The extent of the interaction depends on the nature and concentration of the back ground electrolytes ***(Farrah and Pickering 1979; Bengamin and Leckie 1981; Kinniburgh and Jackson 1982; Lowson and Evans 1984; Spark et al. 1995a, 1995b).***

Four clay minerals were used in this study, i.e., bentonite, montmorillonite, kaolinite and atapolgite. Adsorption isotherms of Cu on such clay minerals are graphically illustrated in Figs (9-14) and the data of adsorption are presented in Tables (9-17). Figures (9-14) show the amounts of adsorbed Cu on clay minerals at pH 4 and 6.

Concerning kaolinite and bentonite (Fig. 9 and 10), adsorbed Cu on kaolinite surfaces was increased gradually with increasing initial concentrations from 0 to 50 μg Cu mL^{-1}, such increase was more pronounced at pH 6.0 (more than double of the corresponding increase at pH 4.0). At pH 4.0 , the highest adsorption of Cu on kaolinite was 2734 μg g^{-1} and there is a tendency to increase adsorption with increasing initial concentration and the adsorption maximum was not achieved with the applied concentrations of Cu. At pH 6.0, with initial concentrations of Cu ranged between 0.0 and 50μg Cu mL^{-1} the adsorbed Cu was increased gradually with no observed adsorption maximum and the highest adsorption of Cu was about 7128 μg g^{-1}.

With bentonite mineral (2:1) results similar to those obtained with kaolinite were achieved. At pH 4.0 Cu was adsorbed in a manner almost like that was happened with kaolinite and the highest adsorption was about 3360 μg g^{-1}. In case of pH 6.0, there were tremendous increases in Cu adsorption with increasing initial concentrations of Cu and the highest Cu adsorption was about 13448μg g^{-1}.It could be noted that adsorption of Cu at pH 6.0 was higher than its adsorption at pH 4.0 and with increasing pH values from 4.0 to 6.0 Cu adsorption was doubled in case of kaolinite (1:1) and increased four folds with bentonite (2:1). This result could be attributed to pH increases which cause a change in adsored copper species from $Cu^{2+}$to Cu $(OH)^{+}$and an increase in negative charge at the mineral clays surface ***(Ankomah, 1992)***

With regard to atapolgite and montmorillonite (Fig. 12), the amount of adsorbed Cu increased on atapolgite surfaces with increasing the initial concentration of Cu from 0.0 to 50.0 μg Cu mL^{-1} and the highest increase was about 6540μg g^{-1}. At pH 6.0, atapolgite surfaces showed a tendency to adsorb large quantities of Cu and decreased equilibrium Cu concentration to a large extent with highest Cu adsorption of 17444μg g^{-1}.

Concerning montmorillonite mineral, at pH 4.0 Cu adsorption increased slightly with low initial concentrations and sharply with the high initial concentrations and the highest adsorption was 4714μg g^{-1}. A trend similar to that of atapolgite with a gradual increase in Cu adsorption was observed at pH 6.0.

Langmuir isotherms of Cu adsorption on clay minerals (Figs 10 and 13), reveal that adsorption of Cu on kaolinite at pH 4.0 did not obey the Langmuir isotherms (linear form), while at pH 6.0 the results fitted Langmuir isotherms with determination coefficient (r) of 0.537**.

With bentonite mineral, at pH 4.0 adsorption isotherms did not fit Langmuir isotherms. However, at pH 6.0, data were fitted completely to Langmuir isotherms with(r) value of 0.904***.

In case of atapolgite and montmorillonite minerals, the adsorption data did not fit to the Langmuir isotherms. Testing data with Freundlich equation reveals that adsorption of Cu on kaolinite and bentonite surfaces obeyed Freundlich isotherms at pH 4.0 and pH 6.0 with highly significant (r).Also, testing data with Freundlich equation reveals that adsorption of Cu at pH 6.0 on both of atapolgite and montmorillonite obeyed Freundlich isotherms (linear form) with (r) values of 0.801***and 0.902***,respectively. At pH 4.0 results with atapolgite fitted to Freundlich isotherms with (r) value of 0.806***, but in case of montmorillonite a poor relationship was observed between adsorption isotherms and Freundlich equation. The adsorption of copper was tested for Kaolinite , atapolgite Bentonite and montmorillonite, it was increased with increasing pH from 4.0 to 6.0. Such increase has also been observed in the other studies of trace elements on Fe oxides ***(Bolland et al., 1977 and Brummer et al., 1988)*** and on soils ***(Barrow, 1986).***

4.1.3. Effect of pH on Cu adsorption by clay minerals :

Effect of pH on Cu adsorption by clay minerals was studied and graphically illustrated in Fig. (15),with atapolgite mineral, adsorption of Cu was increased with increasing pH values from 4.0 to 7.0. Similar results were obtained with kaolinite, bentonite and montmorillonite. This result could be attributed to an increase in pH causes a change in adsorbing copper species from $Cu^{2+}$to Cu $(OH)^{+}$and an increase in negative charge at the mineral clays surface ***(Ankomah, 1992).***

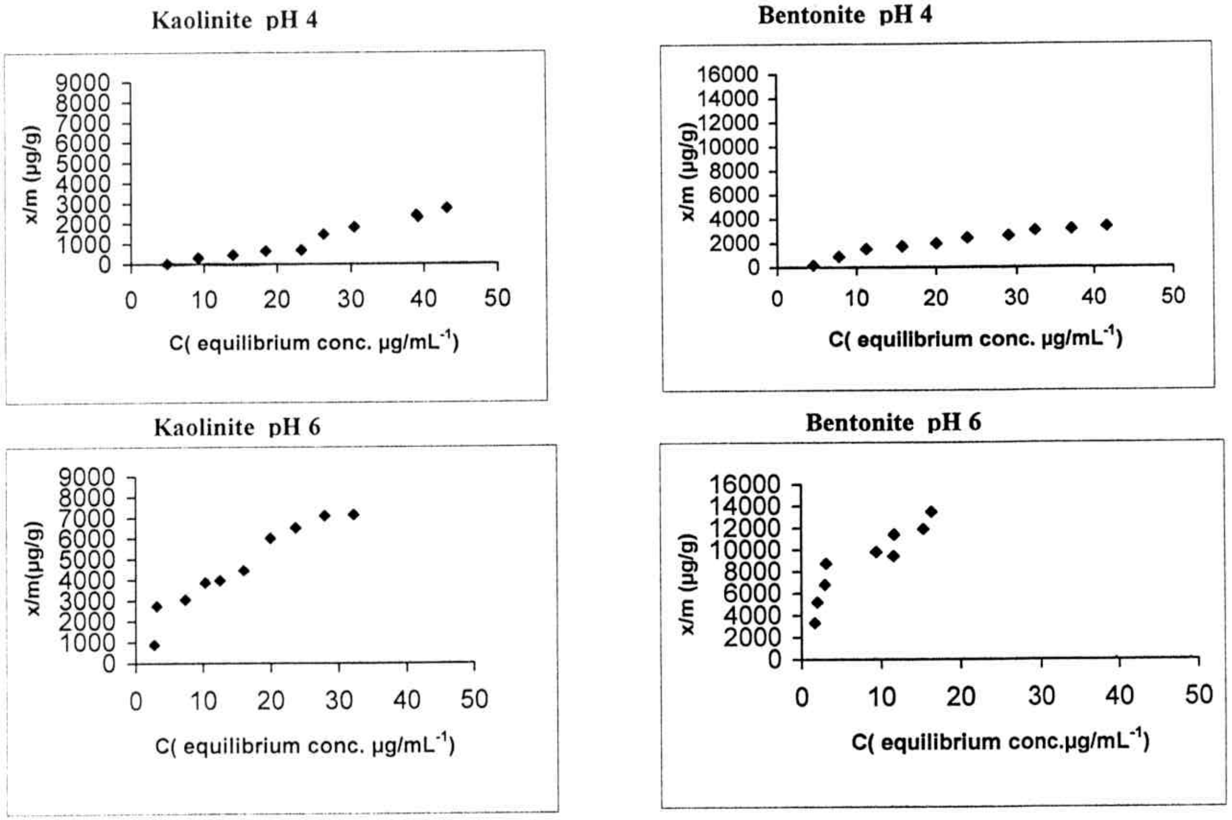


Fig. (9): Adsorption isotherms (Langmuir) for Copper by Kaolinite,Bentonite[Experimental conditions: ionic strength [0.1M $Ca(NO_3)_2$]

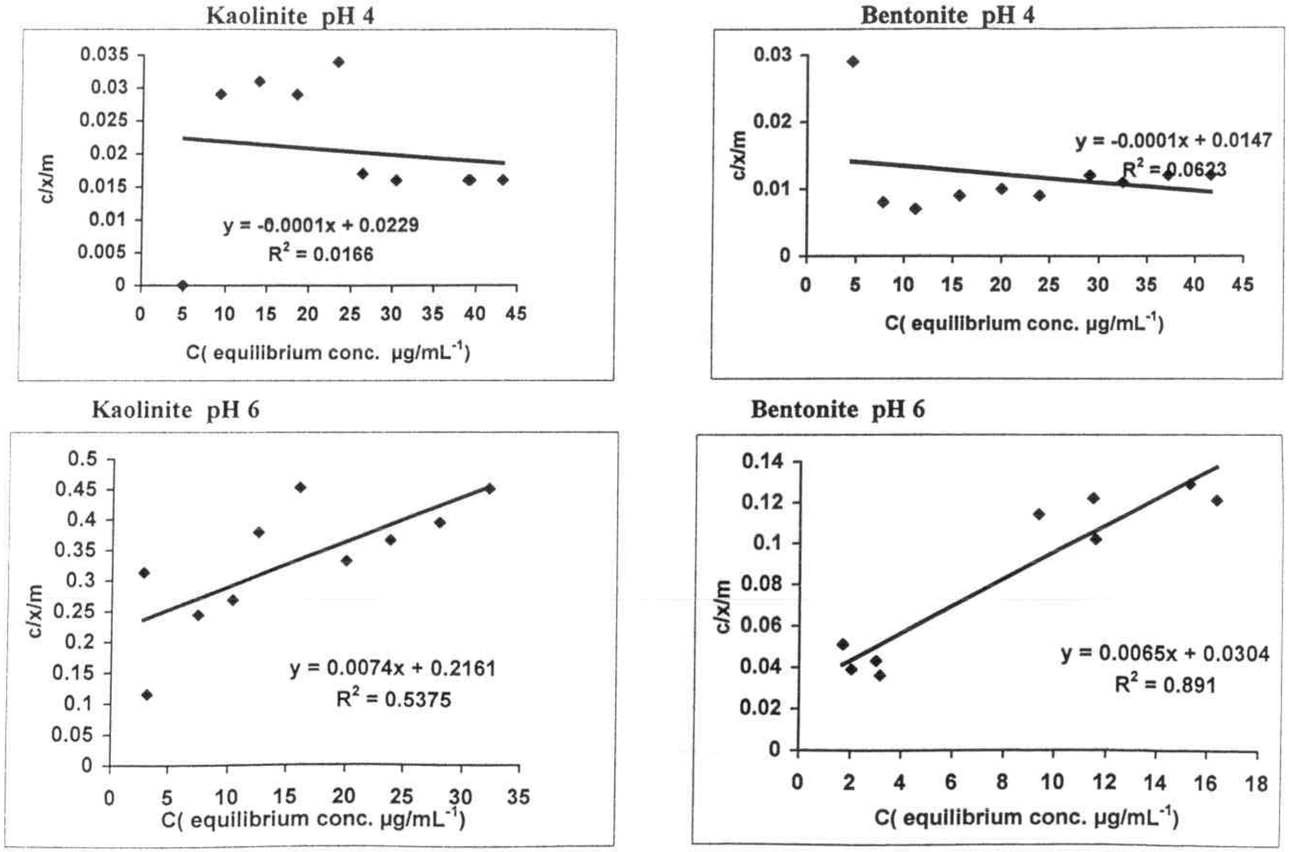


Fig. (10): Adsorption isotherms (Langmuir linear) for Copper by Kaolinite and Bentonite [experimental conditions: ionic strength [0.1M)Ca(NO_3)$_2$]

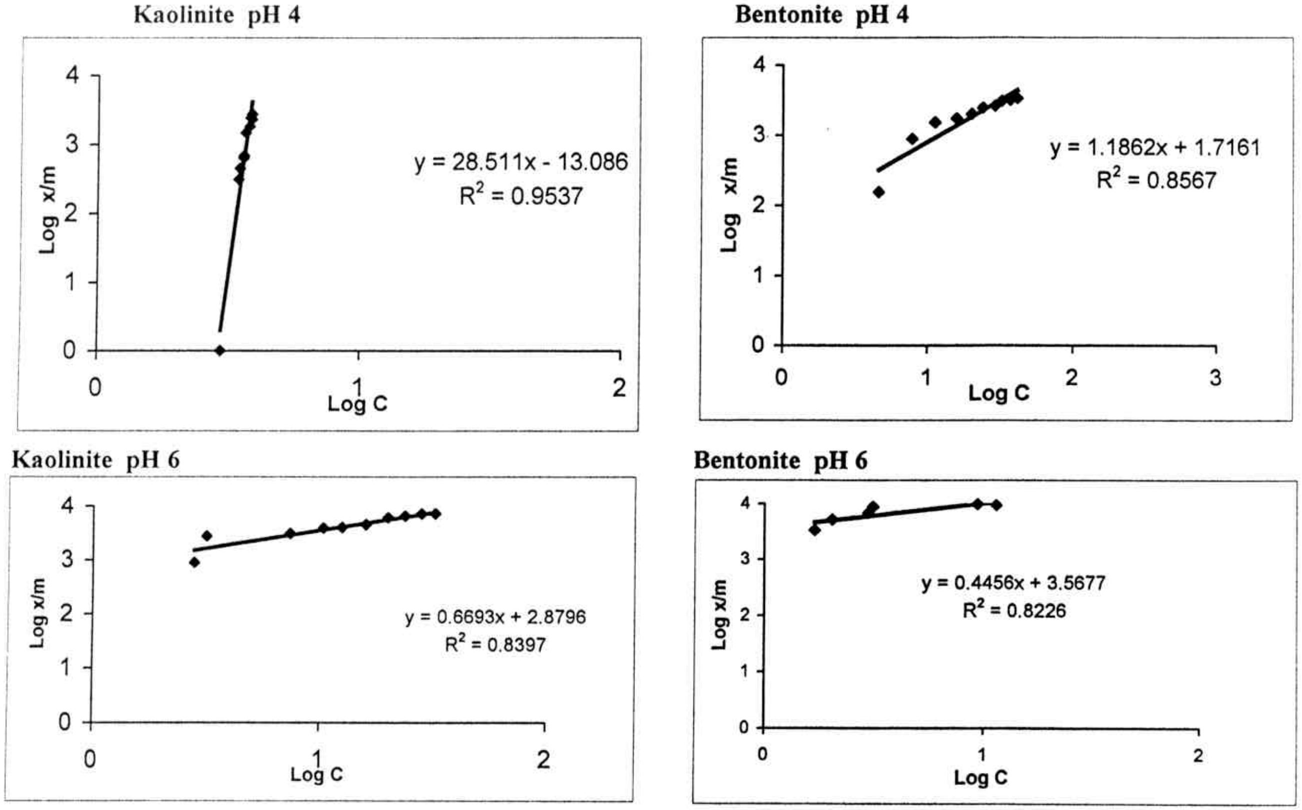


Fig. (11): Adsorption isotherms (Freundlich linear) for Copper by Kaolinite and Bentonite [experimental conditions: ionic strength [0.1M)Ca$(NO_3)_2$]

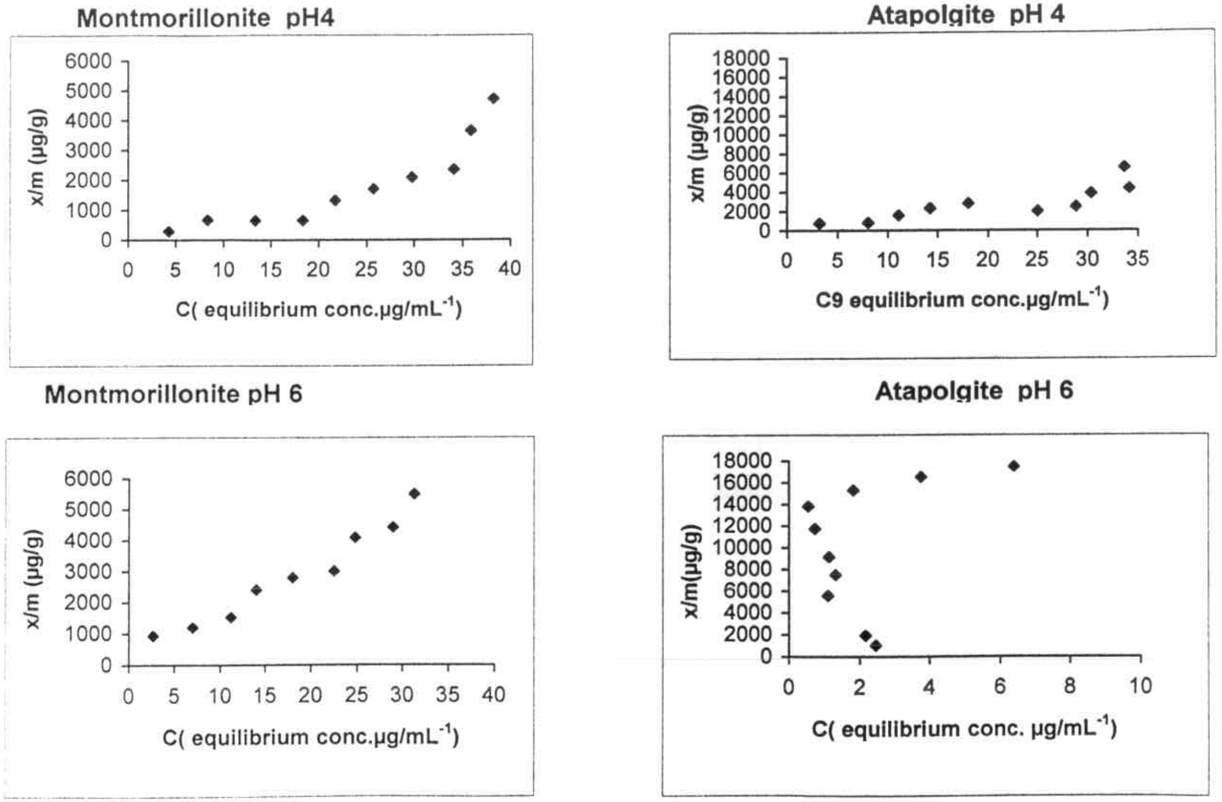
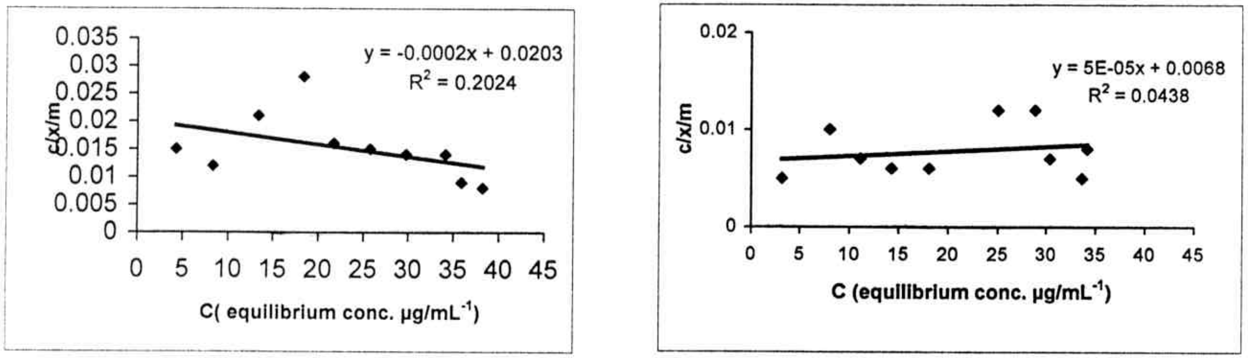


Fig. (12): Adsorption isotherms (Langmuir) for Copper by Atapolgite and Montmorillonite
[Experimental conditions: Ionic strength [0.1M)Ca(NO_3)$_2$]

MontmorillonitepH 4

Atapolgite pH 4



Montmorillonite pH 4

Atapolgite pH 6

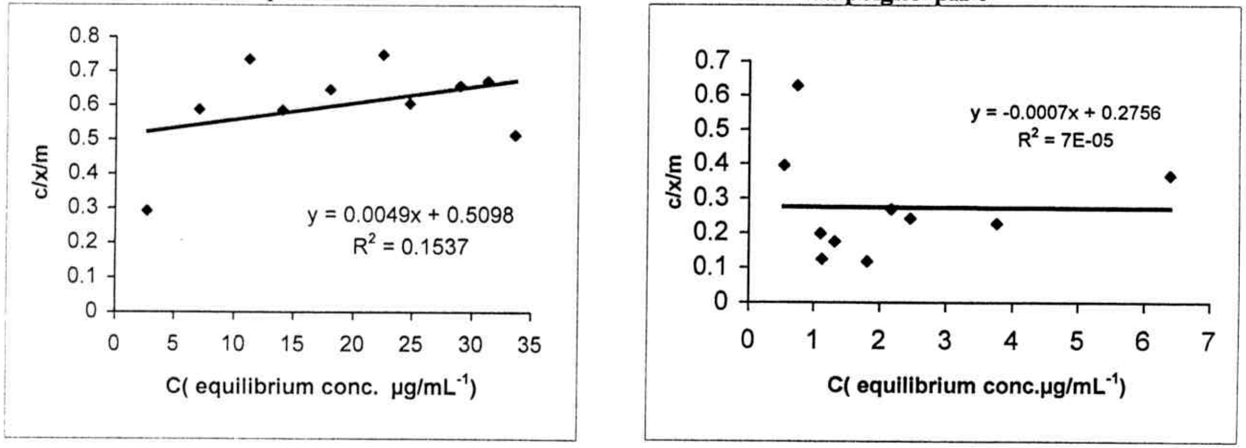


Fig. (13): Adsorption isotherms (Langmuir linear) for Copper by Atapolgite and Montmorillonite [experimental conditions: ionic strength [0.1M)Ca(NO_3)$_2$]

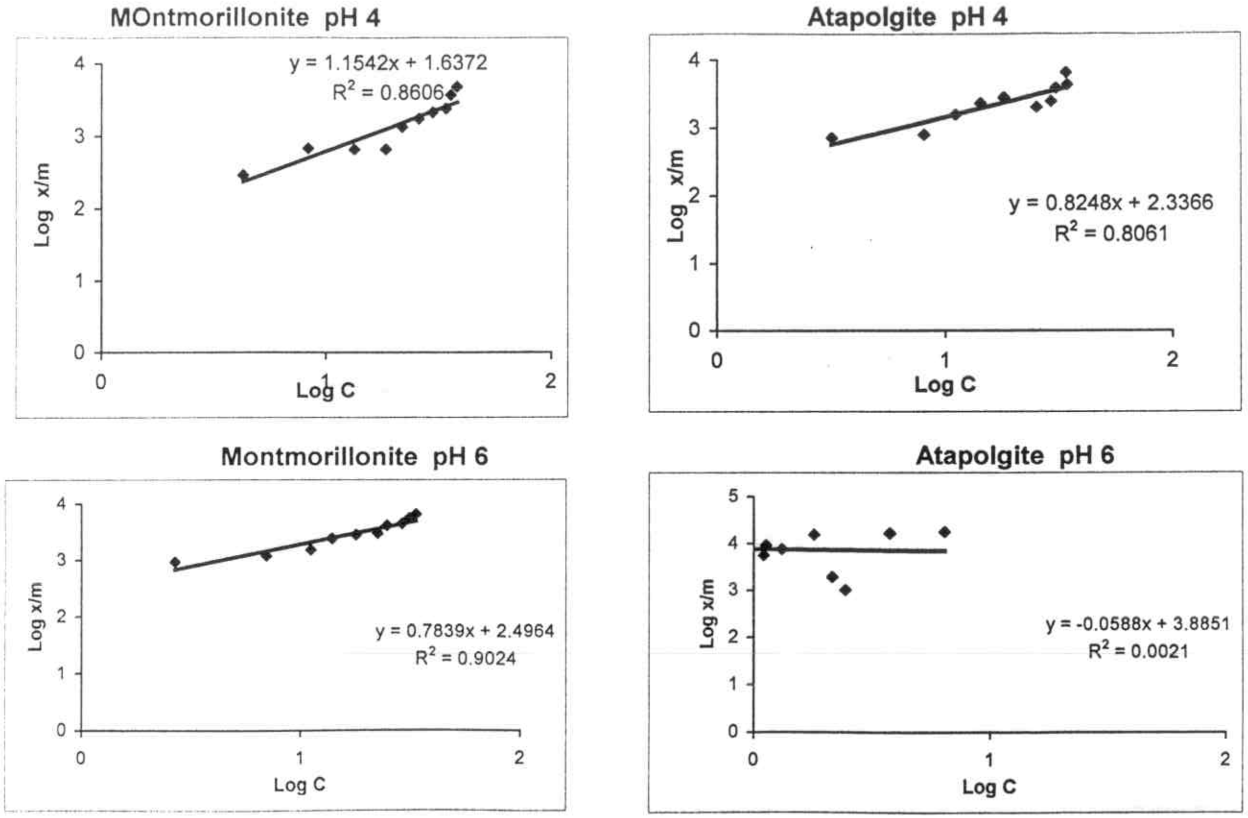


Fig. (14): Adsorption isotherms (Freundlich linear) for Copper by Montmorillonite and Atapolgite [Experimental conditions: ionic strength [0.1M)$Ca(NO_3)_2$]

Table. (9) : Langmuir isotherms of Cu adsorption on kaolinite at pH 4 and 6 ionic strength, 0.1 M $Ca(NO_3)_2$

Initial Cu µg/mL	pH 4			pH 6		
	C µg/mL	x / m µg/g	C /x / m	C µg/mL	x / m µg/g	C /x / m $*10^{-2}$
5	5.00	0	0	2.78	887	0.313
10	9.22	310	0.029	3.15	2738	0.115
15	13.88	447	0.031	7.41	3035	0.244
20	18.42	632	0.029	10.35	3862	0.268
25	23.29	684	0.034	15.07	3974	0.379
30	26.33	1470	0.017	19.33	4269	0.453
35	30.45	1820	0.016	19.98	6010	0.332
40	38.98	2408	0.016	23.76	6498	0.366
45	39.21	2316	0.016	27.97	7080	0.395
50	43.17	2734	0.016	32.18	7128	0.451

Table. (10) : Freundlich isotherms of Cu adsorption **on kaolinite at pH 4 and 6 ionic strength, 0.1 M $Ca(NO_3)_2$**

No.	Initial Cu µg/mL	pH 4		PH 6	
		Log C	Log x / m	Log C	Log x / m
1	5	0.70	0.00	0.44	2.95
2	10	0.96	2.49	0.50	3.44
3	15	1.14	2.65	0.87	3.48
4	20	1.27	2.80	1.01	3.59
5	25	1.37	2.84	1.18	3.60
6	30	1.42	3.17	1.29	3.63
7	35	1.48	3.26	1.30	3.78
8	40	1.59	3.38	1.38	3.81
9	45	1.59	3.36	1.45	3.85
10	50	1.64	3.44	1.51	3.85

Table. (11) : **Langmuir isotherms of Cu adsorption on bentonite at pH 4 and 6, ionic strength, 0.1 M $Ca(NO_3)_2$**

	pH 4			**pH 6**		
Initial Cu µg/mL	C µg/mL	x / m µg/g	C /x / m	C µg/mL	**x / m** **µg/g**	C /x / m *10^{-2}
5	4.61	155	0.029	0.65	**1738**	0.038
10	7.81	876	0.008	1.69	**3324**	0.051
15	11.21	1518	0.007	2.03	**5188**	0.039
20	15.69	1724	0.009	2.99	**6804**	0.043
25	20.03	1988	0.01	3.15	**8740**	0.036
30	23.92	2432	0.009	9.40	**8760**	0.114
35	29.03	2388	0.012	11.52	**9392**	0.122
40	32.38	3048	0.011	11.61	**11356**	0.102
45	37.14	3144	0.012	15.35	**11862**	0.129
50	41.60	3360	0.012	16.38	**13448**	0.121

Table. (12) : Freundlich isotherms of Cuadsorption on bentonite pH 4 and 6, ionic strength, 0.1 M $Ca(NO_3)_2$

No.	Initial Cu µg/mL	pH 4		pH 6	
		log C	log x / m	Log C	Log x / m
1	5	0.66	2.19	-0.19	3.24
2	10	0.89	2.93	0.23	3.52
3	15	1.05	3.18	0.31	3.71
4	20	1.20	3.24	0.48	3.82
5	25	1.30	3.30	0.50	3.94
6	30	1.38	3.39	0.97	3.94
7	35	1.46	3.38	1.06	3.97
8	40	1.51	3.48	1.06	4.05
9	45	1.60	3.50	1.19	4.07
10	50	1.62	3.53	1.21	4.13

Table. (13) : Langmuir isotherms of Cu adsorption on atapolgite at pH 4 and 6, ionic strength, 0.1 M $Ca(NO_3)_2$

Initial Cu	pH 4			pH 6		
	C	x / m	C /x / m	C	x / m	C /x / m
µg/mL	µg/mL	µg/g		µg/mL	µg/g	$*10^{-2}$
5	3.21	717	0.005	2.46	1017	0.242
10	8.02	794	0.01	5.17	1932	0.268
15	11.10	1562	0.007	1.10	5560	0.198
20	14.26	2296	0.006	1.31	7475	0.175
25	18.04	2784	0.006	1.13	9128	0.124
30	25.01	1996	0.012	0.74	11706	0.628
35	28.86	2456	0.012	0.55	13782	0.395
40	30.37	3856	0.007	1.81	15278	0.118
45	34.14	4344	0.008	3.76	16498	0.227
50	33.65	6540	0.005	6.39	17444	0.366

Table. (14) :Freundlich isotherms of Cu adsorption on atapolgite at pH 4 and 6, ionic strength, 0.1 M $Ca(NO_3)_2$

No.	Initial Cu µg/mL	pH 4		pH 6	
		Log C	Log x / m	Log C	Log x / m
1	5	0.51	2.86	0.39	3.01
2	10	0.90	2.90	0.71	3.29
3	15	1.05	3.19	0.04	3.75
4	20	1.15	3.36	0.12	3.87
5	25	1.26	3.44	0.05	3.96
6	30	1.40	3.30	-0.13	4.07
7	35	1.46	3.39	-0.26	4.14
8	40	1.48	3.59	0.26	4.18
9	45	1.53	3.64	0.57	4.22
10	50	1.53	3.82	0.81	4.24

Table. (15) : Langmuir isotherms of Cu adsorption on montmorillonite at pH 4and 6, ionic strength, 0.1 M $Ca(NO_3)_2$

	pH 4			pH 6		
Initial Cu µg/mL	C µg/mL	x / m µg/g	C /x / m	C µg/mL	x / m µg/g	C /x / m *10-2
5	4.29	284	0.015	2.69	924	0.291
10	8.32	672	0.012	7.01	1194	0.587
15	13.37	652	0.021	11.20	1522	0.735
20	18.37	652	0.028	14.02	2393	0.585
25	21.71	1318	0.016	18.03	2788	0.646
30	25.75	1700	0.015	22.50	3002	0.749
35	29.80	2082	0.014	24.78	4088	0.606
40	34.11	2356	0.014	28.98	4410	0.657
45	35.88	3648	0.009	31.31	5478	0.671
50	38.22	4714	0.008	33.64	6546	0.513

Table. (16) : Freundlich isotherms of Cu adsorption on montmorillonite pH 4 and 6 ionic strength, 0.1 M $Ca(NO_3)_2$

No.	Initial Cu µg/mL	pH 4		pH 6	
		Log C	Log x / m	Log C	Log x / m
1	5	0.63	2.45	0.43	2.97
2	10	0.92	2.83	0.85	3.08
3	15	1.13	2.81	1.05	3.18
4	20	1.26	2.81	1.15	3.38
5	25	1.34	3.12	1.26	3.45
6	30	1.41	3.23	1.35	3.48
7	35	1.47	3.32	1.39	3.61
8	40	1.53	3.37	1.46	3.64
9	45	1.55	3.56	1.50	3.74
10	50	1.58	3.67	1.53	3.82

Table (17) Langumir isotherms of Cu adsorbed on clay minerals under different back ground concentrations.

clay	pH	Linear equation	b	K	r
Kaolinite	4	Y=0.0001 X +0.0229	10000	0.004	0.017
	6	Y=0.000047X + 0.002161	21276.59	0.022	0.537*
bentonite	4	Y=0.0.0001 X + 0.00147	10000	0.006	0.062
	6	Y=0.00065 X + 0.000312	15384	0.208	0.904***
montmori.	4	Y=-0.0002 X + 0.0203	5000	0.009	0.202
	6	Y=0.000049 X + 0.005098	20408	0.009	0.154
atapulgite	4	Y=5E-05 X + 0.0068	200000	0.0007	0.044
	6	Y=-0.000007X + 0.002756	142857	0.002	0.000

Table (17) Freundlich isotherms of Cu adsorbed onclay minerals under different back ground concentrations.

clay	pH	Linear equation	'a"	'B"	R
Kaolinite	4	Y=2.851 X + 1.3086	20.35	2.851	0.954***
	6	Y=0.6693 X + 2.8796	757.8	0.669	0.839***
bentonite	4	Y=1.1862 X + 1.7161	52.01	1.186	0.857***
	6	Y=0.5476 X + 3.4736	2975.7	0.547	0.879***
montmori.	4	Y=1.1542X + 1.6372	43.37	1.637	0.860***
	6	Y=0.7839 X + 2.4964	313.61	0.783	0.902***
atapulgite	4	Y=1.1862 X + 1.7161	52.01	1.1862	0.857***
	6	Y=-0.0588 X +3.8851	7675.38	-0.058	0.0021

Table. (18):Copper adsorption on Bentonite and kaolinite as a function of pH range of (4-7) [Cu(25µg/mL) ,ionic strength, 0.1M $Ca(NO_3)_2$]

Clay mineral	Initial of Cu µg/mL	pH	C µg/mL	x\m µg/g
Bentonite	25	4.00	20.03	1988
	25	4.50	20.73	1712
	25	5.00	18.62	2552
	25	5.50	15.66	3736
	25	6.00	6.53	7388
	25	6.50	4.11	8356
	25	7.00	1.87	9252
Kaolinite	25	4.00	20.89	1644
	25	4.50	18.56	2578
	25	5.00	17.84	2866
	25	5.50	15.96	3618
	25	6.00	10.54	5784
	25	6.50	9.82	6072
	25	7.00	4.20	8322

Table. (19):Copper adsorption on Montmorillonite and atapoligite as a function of pH range of (4-7) [Cu(25µg/mL) ,ionic strength, 0.1M $Ca(NO_3)_2$]

Clay mineral	Initial Cu µg/mL	pH	C µg/mL	x\m µg/g
Montmorillonite	25	4.00	20.18	1926
	25	4.50	19.93	2028
	25	5.00	19.03	2388
	25	5.50	10.005	5998
	25	6.00	9.145	6342
	25	6.50	5.605	7758
	25	7.00	2.16	9136
Atapoligite	25	4.00	16.665	3334
	25	4.50	15.65	3740
	25	5.00	7.185	7126
	25	5.50	6.285	7486
	25	6.00	1.3	9480
	25	6.50	0	10000
	25	7.00	0	10000

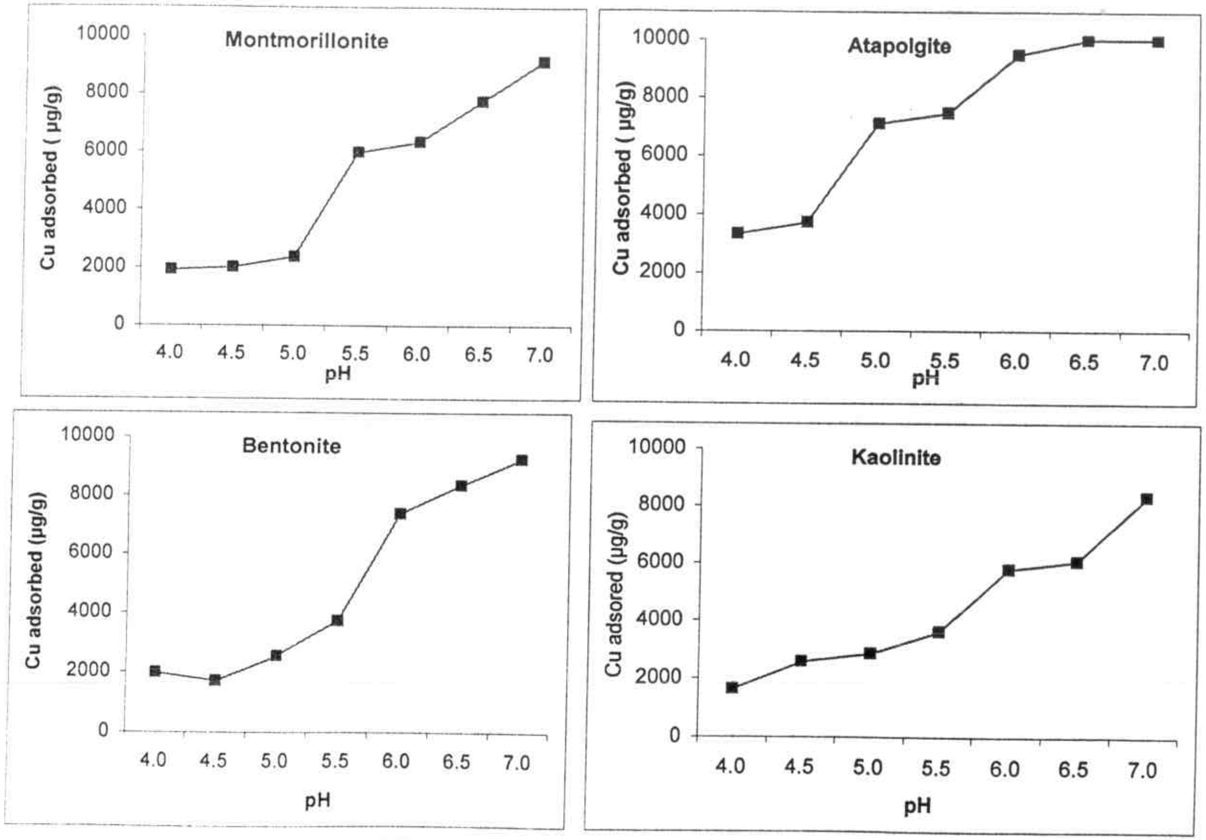


Fig.(15): Copper adsorption on atapolgite, montmorrillonite,bentonite and kaolinite as a funiction of pH.

4.1.4. Adsorption of Cu on aluminum and iron oxides:

Surface adsorption and chemical properties of soils can regulate the solubility of heavy metals in the soil solution and influence their uptake by plants ***(Kuo and Baker, 1980).***

Adsorption of Cu on aluminum and iron oxides was studied through a laboratory experiments and the relationships between equilibrium concentrations and amounts of adsorbed Cu were illustrated in Figs. (15-18). Regarding the adsorption of Cu on aluminum oxide at pH 4.0, adsorbed Cu was increased gradually with increasing equilibrium concentration of Cu and the highest increase of 8760 µg $g^{-1}$was recorded with the highest initial Cu concentration (50µgmL^{-1}).However it seems that surface saturation with Cu was not complete and maximum adsorption was not achieved.

At pH 6.0, Cu was adsorbed in large quantities as compared to pH 4.0 and the amount of adsorbed Cu increased by a proportion higher than that at pH 4.0, the highest amount of adsorbed Cu was 10000 µg g-^{1}.Surfaces of aluminum oxide are still able to adsorb additional amounts of Cu as the saturation condition was not achieved.

With iron oxide at pH 4.0, the adsorbed Cu increased with increasing Cu concentration with the highest adsorption of 4174µgg^{-1}, while at pH 6.0, similar trend was achieved with more increase of Cu adsorption at low and high Cu concentrations as compared to Cu adsorption at pH 4.0. The highest Cu adsorption (10856µgg^{-1}) occurred with highest initial Cu concentration of 50 µgmL^{-1}.

The obtained results reveal that at pH 4.0 there was a superiority of Al oxide over Fe oxide. However, at pH 6.0, both of the two oxides show the same capacity to adsorb Cu. The superiority of Al oxides over Fe oxides at pH 4.0 may be due to one or more of the following:

1-The bounding of aluminum and copper was more stable than copper and iron oxides .

2-The surface area of hydrous aluminum oxides was greater than that of hydrous iron oxides.

3-The exchange sites on hydrous aluminum oxides surfaces were more in number and activity than those on hydrous iron oxide ***(Greenland and Hayes ,1982 and Goldberg, 1985)*** **.** Similar results were obtained by ***Wells (1956) and Sabine et al., (1996) . and Abou hussien et al (2000).*** Data of copper adsorbed on Fe and Al were fitted to the linear form of the Langmuir adsorption isotherms and Freundlich. Investigating Cu adsorption on aluminum and iron oxides using Langmuir adsorption isotherms reveals that adsorption data of Cu on Al oxide at pH 6.0 obeyed Langmuir isotherms with (r) value of 0.899***.However, at pH 4.0, the adsorption data were not fitted with Langmuir isotherms. In case of iron oxide, poor relationships were observed between equilibrium concentrations (C) and c/x/m and data did not obey Langmuir isotherm. These results are in agreement with those of ***(Shuman, 1977and Davis and Leckie,1978).*** Hydrous oxides have high specific surface area and possess OH functional groups capable of reacting with metals, phosphate and other specifically sorbing ions, hydrous oxides are considered important in controlling the concentration of heavy metals in soil solution and natural water ***(Kalbasi et al., 1978).***

Copper adsorption on Al and Fe oxides was tested using Freundlich isotherms (Fig.18). Adsorption of Cu on both oxides showed goodness of fit to Freundlich equation with r^2 values of

0.859***,0.970***, 0.948***and 0.923*** for Al oxide and Fe oxide at pH 4.0 and 6.0, respectively. Soil constituents with a pH –dependent charge such as Fe and Al oxides can cause very highly pH dependent adsorption of zinc and copper and are of permanent importance in controlling the distribution of these trace elements and other heavy metals which are adsorbed by freshly prepared hydrous oxide gels of Fe and Al even when the gels had net positive charge. ***Kuo and Baker (1980)*** studied the sorption of zinc and copper as a function of pH for three acid soils.

4.1.5. Effect of pH :

Adsorption of Cu on Al and Fe oxides under pH range of 4.0 to 7.0 is graphically illustrated in Fig. (19). With Al oxide, there was a gradual increase in Cu adsorption with increasing pH from 4.0 to 7.0. However, with Fe oxide at pH <5.5 (PZC)the adsorption of Cu was minimal with no response to pH.

Increasing the pH by 0.5 unit (5.5), the amount of Cu was increased by almost three times compared to pH 5.0 and this high increase followed by additional increases with increasing pH from 5.5 to 7.0.The obtained results are in agreement with those of ***Ankomah, (1992)*** in which copper was adsorbed at pH values below the point of zero charge (PZC) .As the pH value approaches the (PZC) an increase in the number of positive charge will be neutralized forming neutral and negative charge sites .

4.2.Desorption of copper :

4.2.1 Soils :

While most studies in environmental soil chemistry have focused on the adsorption or sorption of ions and molecules on soils , the desorption process is also extremely important. This is particularly true for soils that are already contaminated. It is often observed that desorption is a more difficult process than adsorption and that not all of the adsorbate is desorbed, i.e., the reactions appear to be irreversible. Such apparent irreversibility is commonly referred to as hysteresis or nonsingularity.

Desorption of Cu from soils was tested and the obtained data are presented in Table (26) and illustrated in Fig (20).

Desorped Cu (μgg^{-1}) from sandy loam soil increased gradually with increasing initial Cu concentration (Table 26).

The highest desorption increases were attained with increasing initial Cu concentration from 10 to 15 (μgmL^{-1}) and from 15 to 20 (μgmL^{-1}). Increasing original copper concentration from 20 to 40 (μgmL^{-1}) in solution resulted in a slight increase in Cu desorption. However, a tremedions increase in the desorbed Cu was observed with initial concentrations of 45 and 50µg Cu mL^{-1}. Desorbed copper % was computed for each initial concentration, the highest desorption percentages, i.e., 60.4 and 62.21 were accompanied with initial concentrations of 20 and 50µg Cu mL^{-1},respectively.

Concerning sandy clay loam soil, a sharp increase in desorped Cu was noticed with increasing the initial Cu concentrations from 5 to 10 µg mL^{-1} followed by gradual increases with increasing initial Cu concentration from 20 to 50µg mL^{-1}Table(26). The highest desorption percentages were observed with the low coverage of Cu which was accompanied with the low initial Cu concentration, i.e., almost 73 and 61 % of adsorbed Cu were desorbed using DTPA solution when the initial Cu concentrations were 5 and 10 µg mL^{-1},respectively .

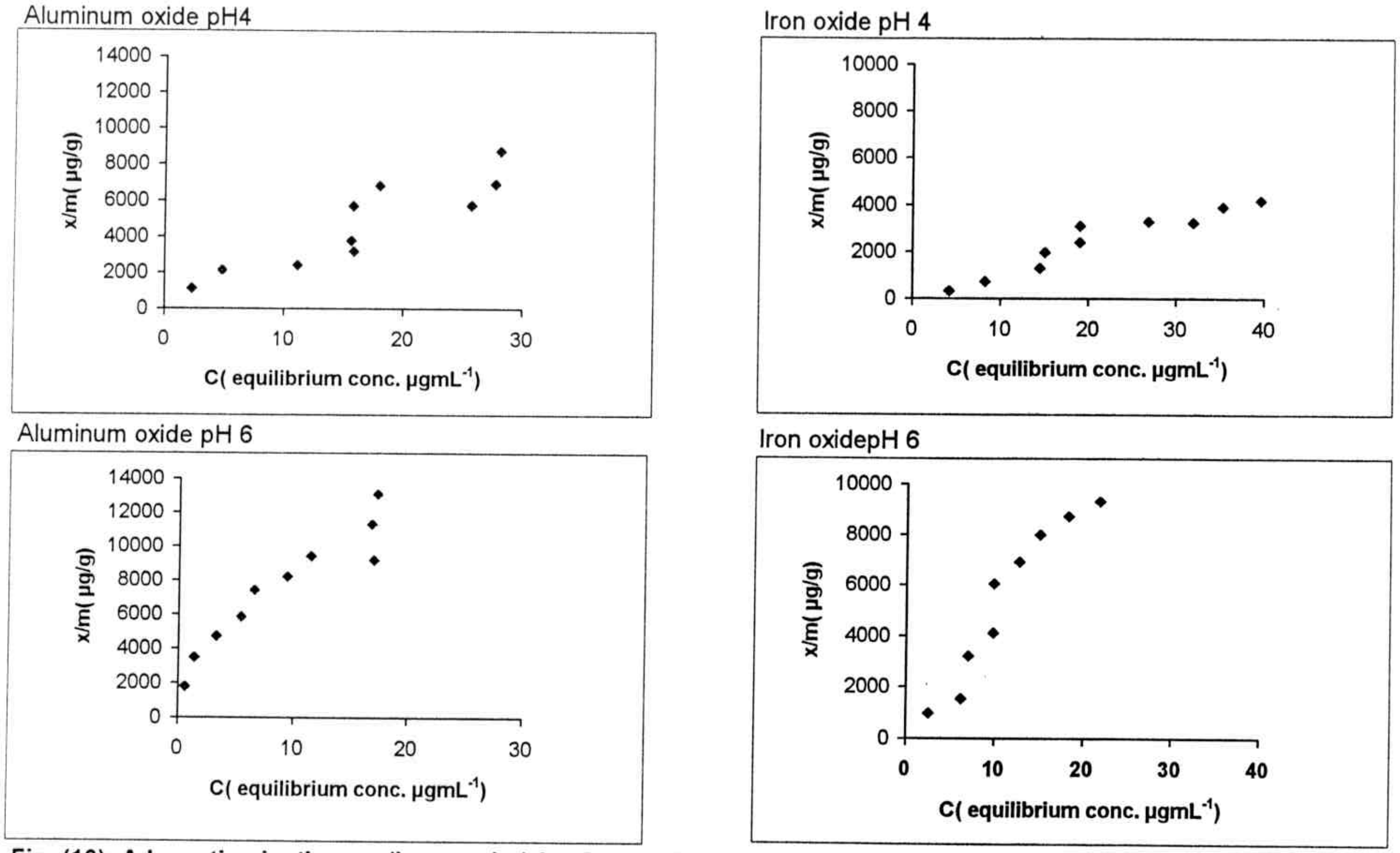


Fig. (16): Adsorption isotherms (Langmuir) for Copper by Iron and Aluminum oxides.
Experimental conditions: ionic strength 0.1M $Ca(NO_3)_2$

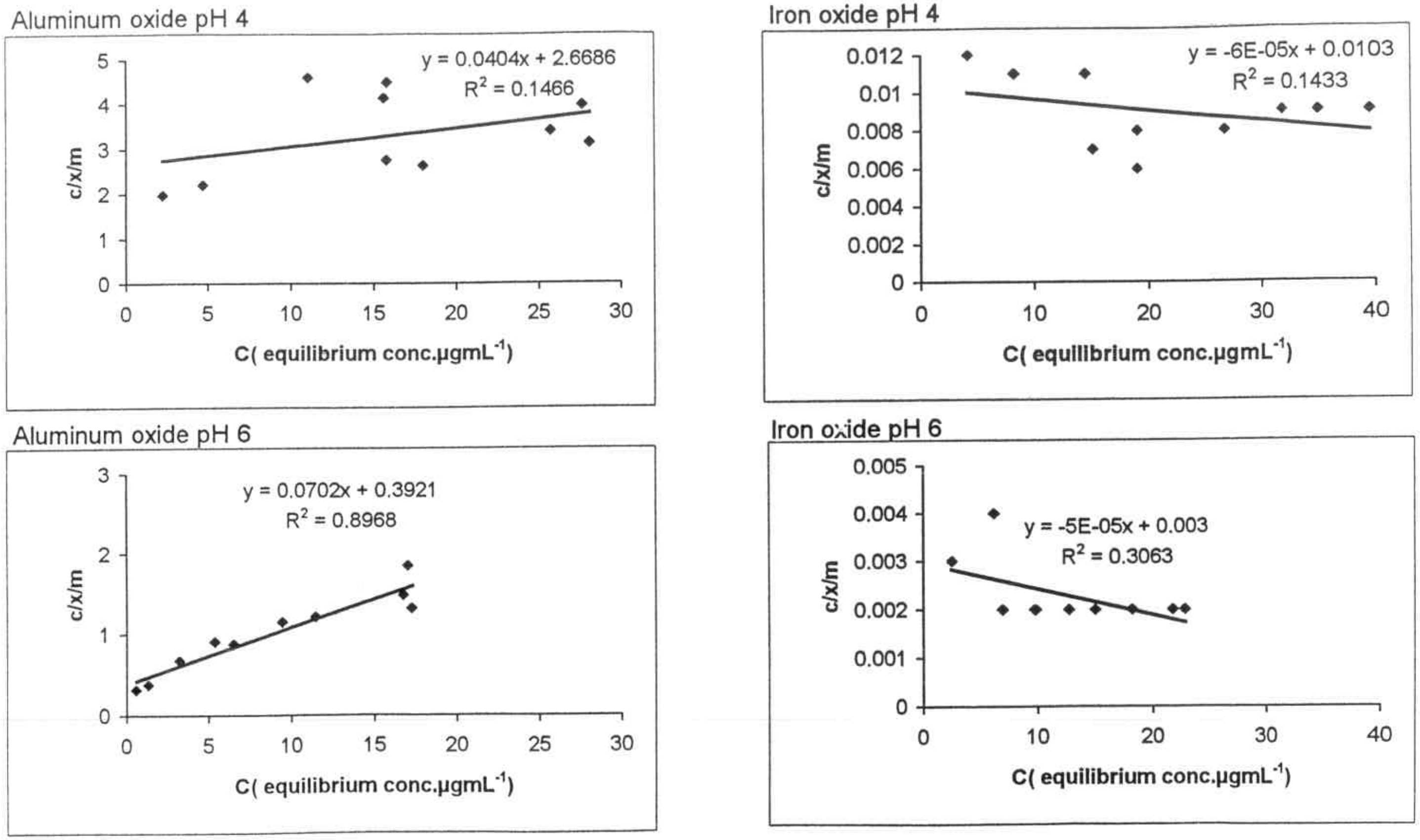


Fig.(17): Adsorption isotherms (Langmuir linear) for Copper by Iron and Aluminum oxides.
Experimental conditions: ionic strength 0.1M $Ca(NO_3)_2$

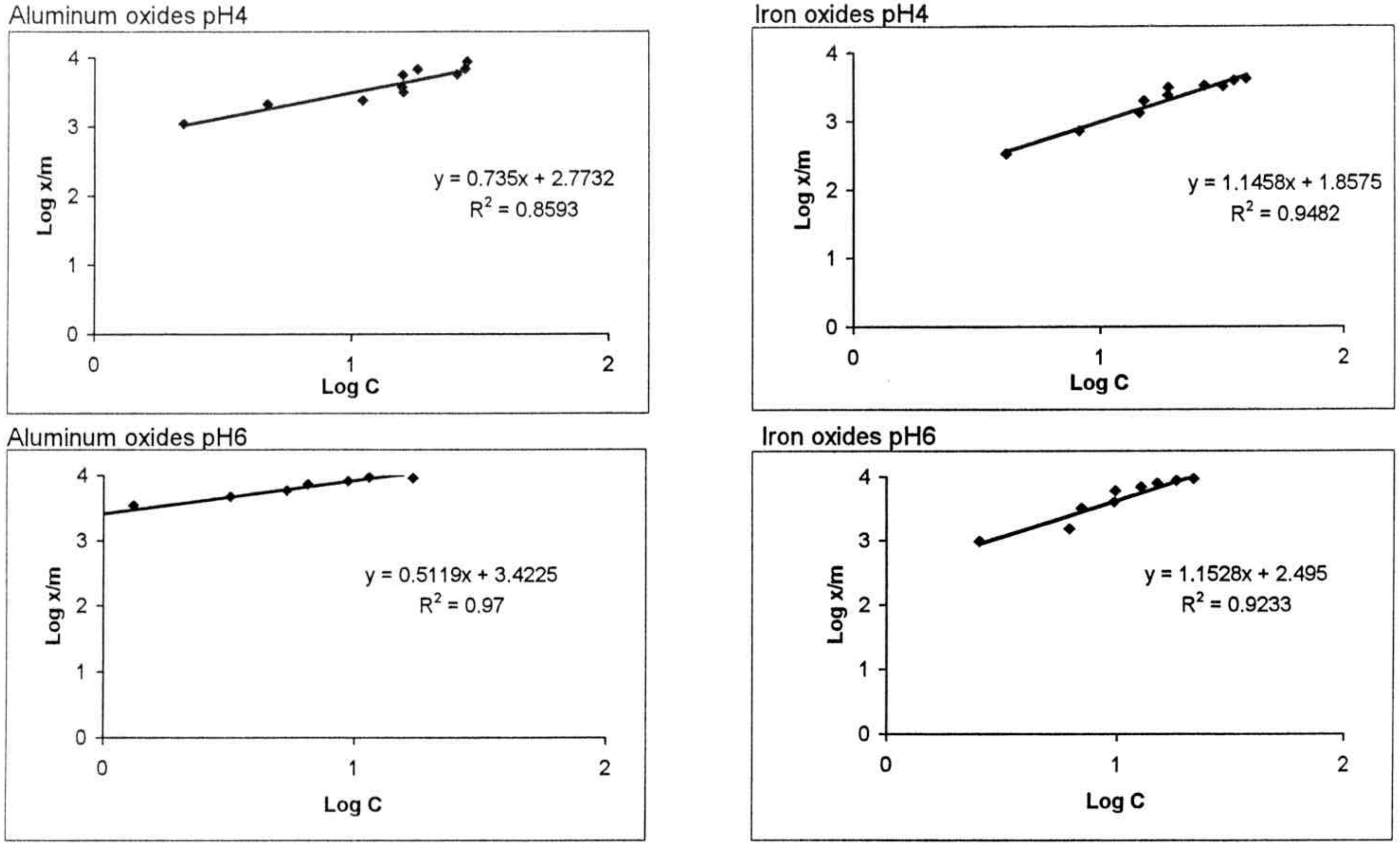


Fig.(18):Adsorption isotherms (Freundlich linear) for Copper by Iron and Aluminum oxides.
Experimental conditions: ionic strength, 0.1M $Ca(NO_3)_2$

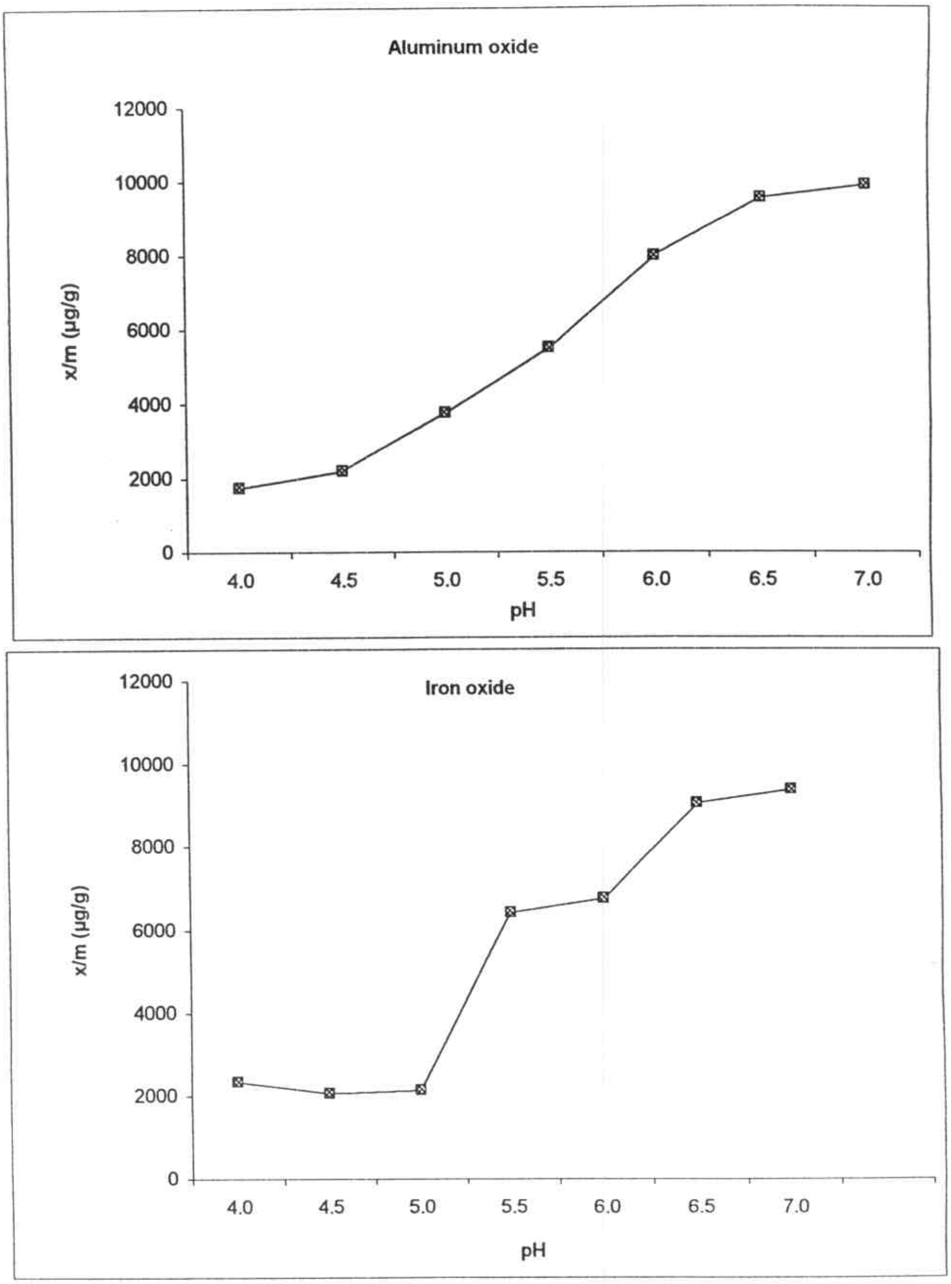


Fig. (19) : Copper adsorption on iron and aluminum oxides as a function of pH in presence of $Ca(NO_3)_2$ as a back-ground electrolyte.

Table (20) Langmuir adsorption isotherms of Cu on aluminum oxide at pH 4 and 6 [ionic strength, 0.1M $Ca(NO_3)_2$]

Initial Cu	pH 4			pH 6		
	C	x / m	C /x / m	C	x / m	C /x / m
μgmL^{-1}	μgmL^{-1}	µg/g	$*10^{-3}$	μgmL^{-1}	µg/g	$*10^{-3}$
5	2.21	1116	1.98	0.56	1778	0.314
10	4.69	2123	2.2	1.31	3478	0.376
15	11.07	2400	4.61	3.19	4724	0.675
20	15.80	3200	4.49	5.34	5864	0.910
25	15.59	3764	4.14	6.47	7410	0.873
30	15.75	5700	2.76	9.43	8228	1.146
35	17.97	6812	2.64	11.43	9427	1.212
40	25.69	5724	4.48	16.98	9210	1.843
45	27.65	6940	3.98	16.73	11308	1.479
50	28.10	8760	3.21	17.24	13104	1.315

Table (21) Freundlich adsorption isotherms of Cu on aluminum oxide at pH 4 and 6 [ionic strength, 0.1M $Ca(NO_3)_2$]

No.	Initial Cu μgmL^{-1}	pH 4		pH 6	
		Log C	Log x / m	Log C	Log x / m
1	5	0.34	3.05	-0.26	3.25
2	10	0.67	3.33	0.12	3.54
3	15	1.04	3.38	0.50	3.67
4	20	1.20	3.51	0.73	3.77
5	25	1.19	3.58	0.81	3.87
6	30	1.20	3.76	0.97	3.92
7	35	1.25	3.83	1.06	3.97
8	40	1.41	3.76	1.23	3.96
9	45	1.44	3.84	1.22	4.05
10	50	1.45	3.94	1.24	4.12

Table (22) Langmuir adsorption isotherms of Cu on iron oxide at pH 4 and 6 [ionic strength, 0.1M $Ca(NO_3)_2$]

Initial Cu μgml^{-1}	pH 4			pH 6		
	C μgmL^{-1}	x / m µg/g	C /x / m	C μgmL^{-1}	x / m µg/g	C /x / m
5	4.16	336	0.012	2.53	989	0.003
10	8.20	722	0.011	6.17	1533	0.004
15	14.50	1300	0.011	6.95	3218	0.002
20	15.10	1960	0.007	9.73	4106	0.002
25	18.98	2408	0.008	9.86	6057	0.002
30	19.01	3100	0.006	12.72	6912	0.002
35	26.78	3288	0.008	15.01	7996	0.002
40	31.90	3242	0.009	18.21	8716	0.002
45	35.23	3908	0.009	21.74	9304	0.002
50	39.57	4174	0.009	22.86	10856	0.002

Table (23) Freundlich adsorption isotherms of Cu on iron oxide at pH 4 and 6 [ionic strength, 0.1M $Ca(NO_3)_2$]

No.	Initial Cu μgmL^{-1}	pH 4		pH 6	
		Log C	Log x / m	Log C	Log x / m
1	5	0.62	2.53	0.40	3.00
2	10	0.91	2.86	0.79	3.19
3	15	1.16	3.11	0.84	3.51
4	20	1.18	3.29	0.99	3.61
5	25	1.28	3.38	0.99	3.78
6	30	1.28	3.49	1.10	3.84
7	35	1.43	3.52	1.18	3.90
8	40	1.50	3.51	1.26	3.94
9	45	1.55	3.59	1.34	3.97
10	50	1.60	3.62	1.36	4.04

Table (24) Langumir isotherms of Cu adsorbed on oxides at pH 4.0and 6.0.

Oxides	pH	Linear equatrion	b	K	R
Iron	4	Y=6E-05X+ 0.0103			0.143
	6	Y=-0.0000365X+0.0017549			0.139
Aluminum	4	Y=0.0000404X+0.00026686	24752.47	0.151	0.147
	6	Y=0.0000703X+0.0003903	14224.75	0.18	0.899***

Table (24) Freundlich isotherms of Cu adsorption on oxides at pH 4.0 and 6.0.

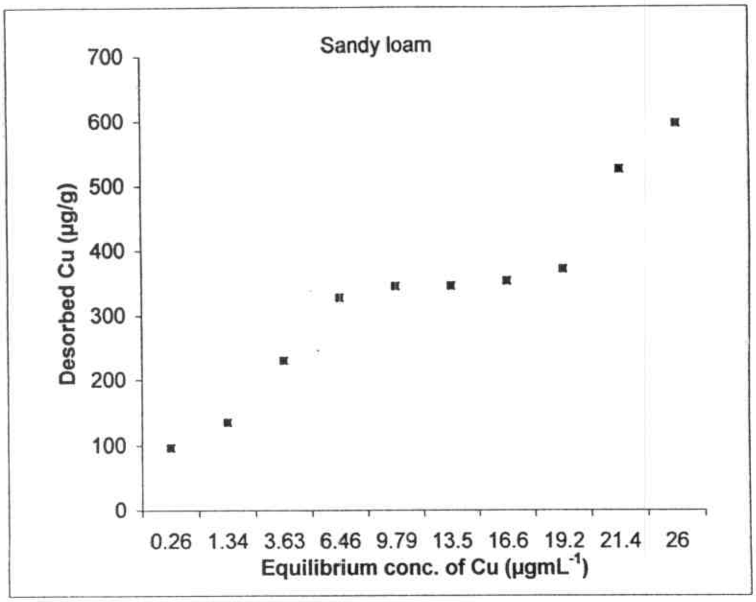
Oxides	$Ca(NO_3)_2$	Linear equation	'a"	'B"	R
Iron	4	Y=1.1458X+1.8575	72.02	1.145	0.985***
	6	Y=1.1528X+2.495	312.60	1.152	0.923***
Aluminum	4	Y=0.735X + 2.7732	593.19	0.735	0.859***
	6	Y=0.5119X+3.4225	2645.00	0.5119	0.977***

Table .(25) : Copper adsorption on Aluminum and iron oxides as a function of pH [Cu, 25 µgml^{-1}, ionic strength , 0.1M Ca(NO$_3$)$_2$

Oxide	No	Initial Cu µgmL^{-1}	pH	C µgmL^{-1}	x/m µg/g
Aluminum	1	25	4.00	20.625	1750
	2	25	4.50	19.515	2194
	3	25	5.00	15.627	3749
	4	25	5.50	11.275	5490
	5	25	6.00	5.080	7968
	6	25	6.50	1.215	9514
	7	25	7.00	0.322	9871
Iron	1	25	4.00	19.12	2352
	2	25	4.50	19.85	2060
	3	25	5.00	19.65	2140
	4	25	5.50	8.98	6410
	5	25	6.00	8.11	6756
	6	25	6.50	2.40	9040
	7	25	7.00	1.59	9364

Table (26):Copper desorption from sandy loam and sandy clay loam soils by DTPA extract[Cu conc 5-50μgmL^{-1}), ionic strength, 0.1M Ca(No$_3$)$_{2]}$

Soil	Initial of Cu (μg/mL)	C (μg/mL)	x/m (μg/g)	C (μg/mL)	Desorbed Cu (μg/g)	Desorbed %
Sandy loam	5	0.255	190	4.84	97	50.95
	10	1.337	347	6.76	135	39.02
	15	3.625	455	11.52	230	50.62
	20	6.459	542	16.36	327	60.4
	25	9.789	608	17.24	345	56.66
	30	13.52	659	17.25	345	52.34
	35	16.595	736	17.65	353	47.94
	40	19.17	833	18.55	371	44.52
	45	21.38	945	26.26	525	55.58
	50	26.035	959	29.79	596	62.21
Sandy clay loam	5	0.848	166	6.08	122	73.22
	10	0.979	361	10.98	220	60.84
	15	1.119	555	13.86	277	49.92
	20	2.916	683	14.37	287	42.05
	25	4.563	817	17.71	354	43.31
	30	6.577	937	19.61	392	41.84
	35	9.096	1036	19.76	395	38.14
	40	11.308	1148	20.02	400	34.89
	45	13.341	1266	20.10	402	31.74
	50	18.57	1257	23.56	471	37.48



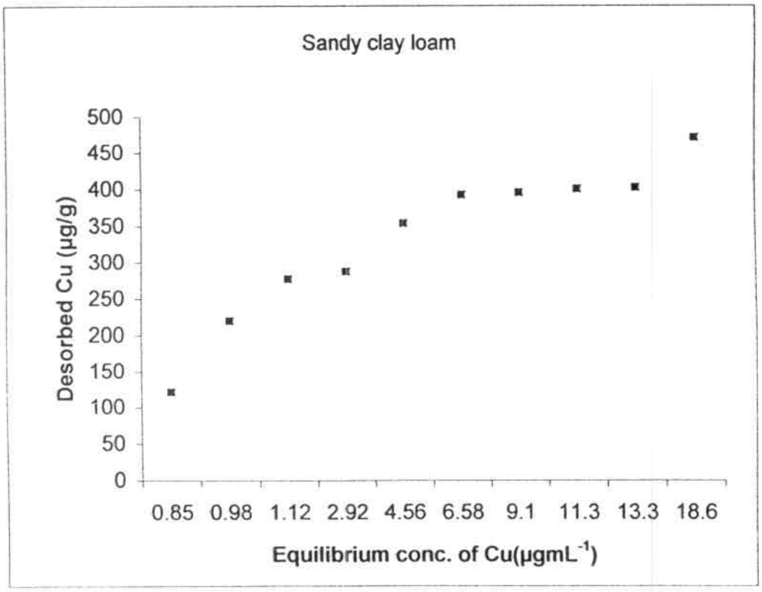


Fig .(20) : Copper desorption from sandy loam and sandy clay loam soils DTPA 0.005 M, ionic strength 0.1M ($Ca(NO_3)_2$

Desorbed Cu % decreased gradually with increasing Cu coverage on the surfaces of sandy clay loam soil. These results are in agreement with those of ***(Mclaren et al. 1983; Padmanabham, 1983 a,b; Mcbride et al., 1984)*** in which sorption of Cu by soil components has been shown to be largely irreversible or only slowly reversible. With initial Cu concentrations ranged between 5 and 40 µg mL^{-1} the desorbed amounts of Cu from sandy loam soil were less than the corresponding ones from sandy clay loam soil. However, at high initial concentrations of 40 and 50 µg mL^{-1}, the dsorbed Cu from sandy loam soil was greater than that desorbed from sandy clay loam soil. The differences in the manner of Cu desorption between the two tested soils could be attributed to the differences in their clay and $CaCO_3$ contents. Such results are comparable with those of ***Barrow (1985)***who showed that initial sorption reactions may be followed by slower reaction that would render a fraction of sorbed copper unavailable for immediate equilibrium with the soil solution. ***Hogget al . (1993)*** indicated that the amount of copper desorbed from soil depends not only on total amount of labile copper in soils but also on soil pH .

4.2.2 Clay minerals :

Desorption of Cu from clay minerals was shown in Tables (27-28) and Figs.(21-22). With all clay minerals except montmorillonite increasing the pH of DTPA solution from 4.0 to 6.5 decreased the desorbed Cu from 1892 to 1454, 2000 to 1904, 2805 to 2442 µg g^{-1} for kaolinite, bentonite and atapolgite minerals, respectively. With increasing pH >6.5,the amounts of desorbed Cu by DTPA were increased again. In case of montmorillonite, the lowest desorption of Cu was observed at pH 5.0 and the highest desorbed Cu %was noticed at pH 6.5. Such results are comparable with those of ***Cavallaro and Mcbride (1984)*** who indicated that desorption of copper from soil clays decreases with increasing soil pH. Copper solubility in soils has been shown to increase at both low and high pH values **(McBride and Blasiak 1977; Swift and Mclaren, (1991). Cavallaro and Mcbride (1984)** have also shown that desorption of copper from soil clays decreases with increasing pH. In the fact, desorption of copper from the labile copper pool in soil is influenced by the pH and the uptake of soil copper by plants might be affected by soil pH. Desorption of Cu was not necessarily provide an effective measure of soil copper availability.

4.2.3.Iron and aluminum oxides :

Desorption of Cu from oxides was shown in Table (29) and Fig. (23), with Al and Fe oxides, increasing pH values of the DTPA solution from 4.0 to 6.0 decreased the desorbed Cu from 2574 to 2450 and from 1800 to 1626μgCu g^{-1} for aluminum and iron oxides, respectively. With increasing pH >6.5, the amounts of desorbed Cu were increased again. These results are in agreement with those indicating that the desorption of Cu increased from goethite surfaces with decreasing pH below 6.5. **(Padmanabham , 1983a).**

Padmanabham (1983a) proposed the existence of specific sites in goethite which are responsible for the irreversible (or very slowly reversible) sorption of copper and showed the proportion of such sites increased with increasing pH.

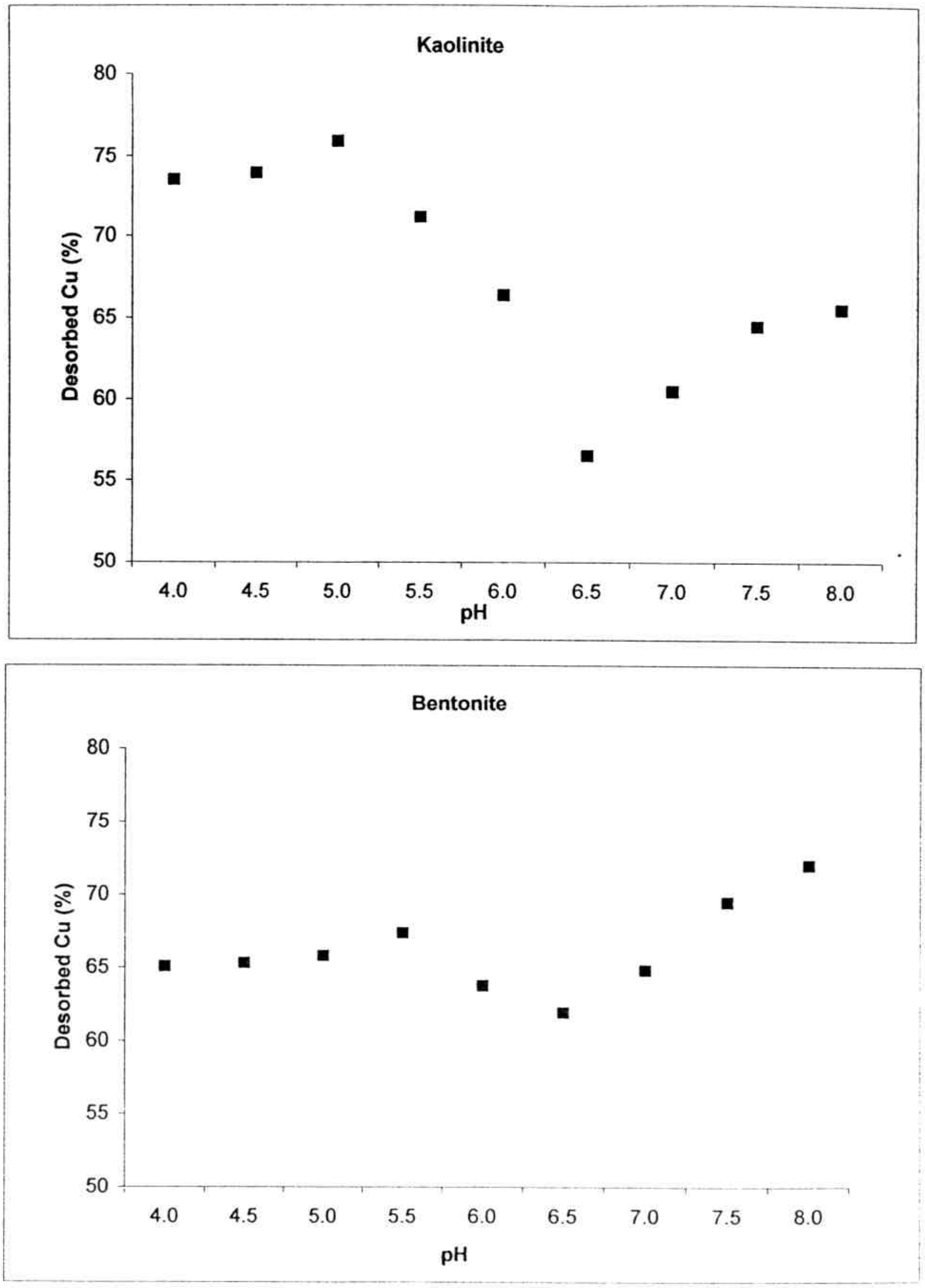


Fig .(21) Copper desorption from Kaolinite and Bentonite by DTPA over a wide range of pH. Experimental conditions : Cu $^{2+}$, 10 μgmL^{-1} ,oxides 2.5gL^{-1}, DTPA 0.005 M ,ionic strength, 0.1M Ca(NO$_3$)$_2$

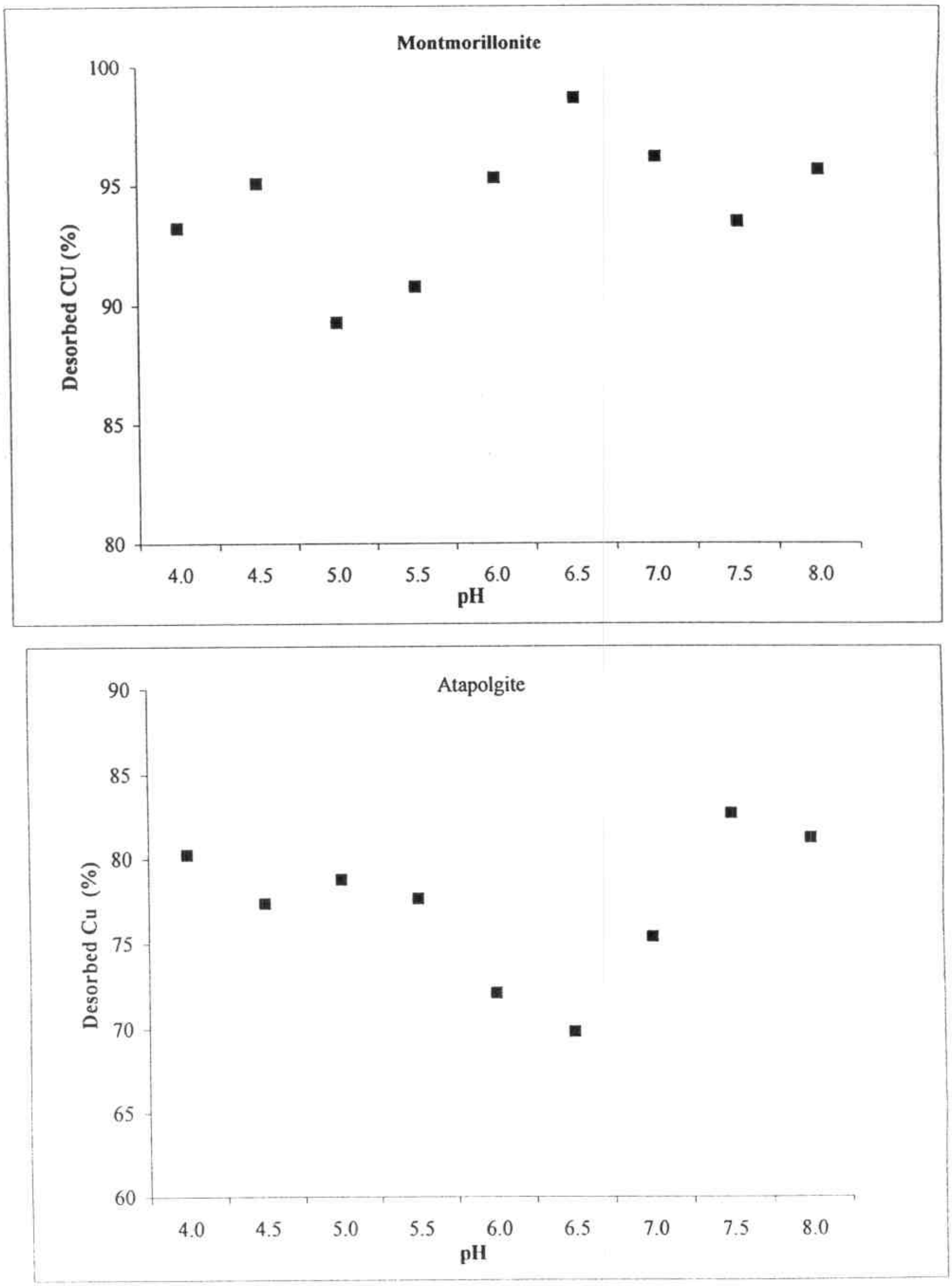


Fig .(22) Copper desorption from Montmorillonite and Atapolgite by DTPA over a wide range of pH. Experimental conditions : Cu $^{2+}$, 10 µgmL^{-1} ,oxides 2.5gL^{-1}, DTPA 0.005 M ,ionic strength, 0.1M Ca(NO$_3$)$_2$

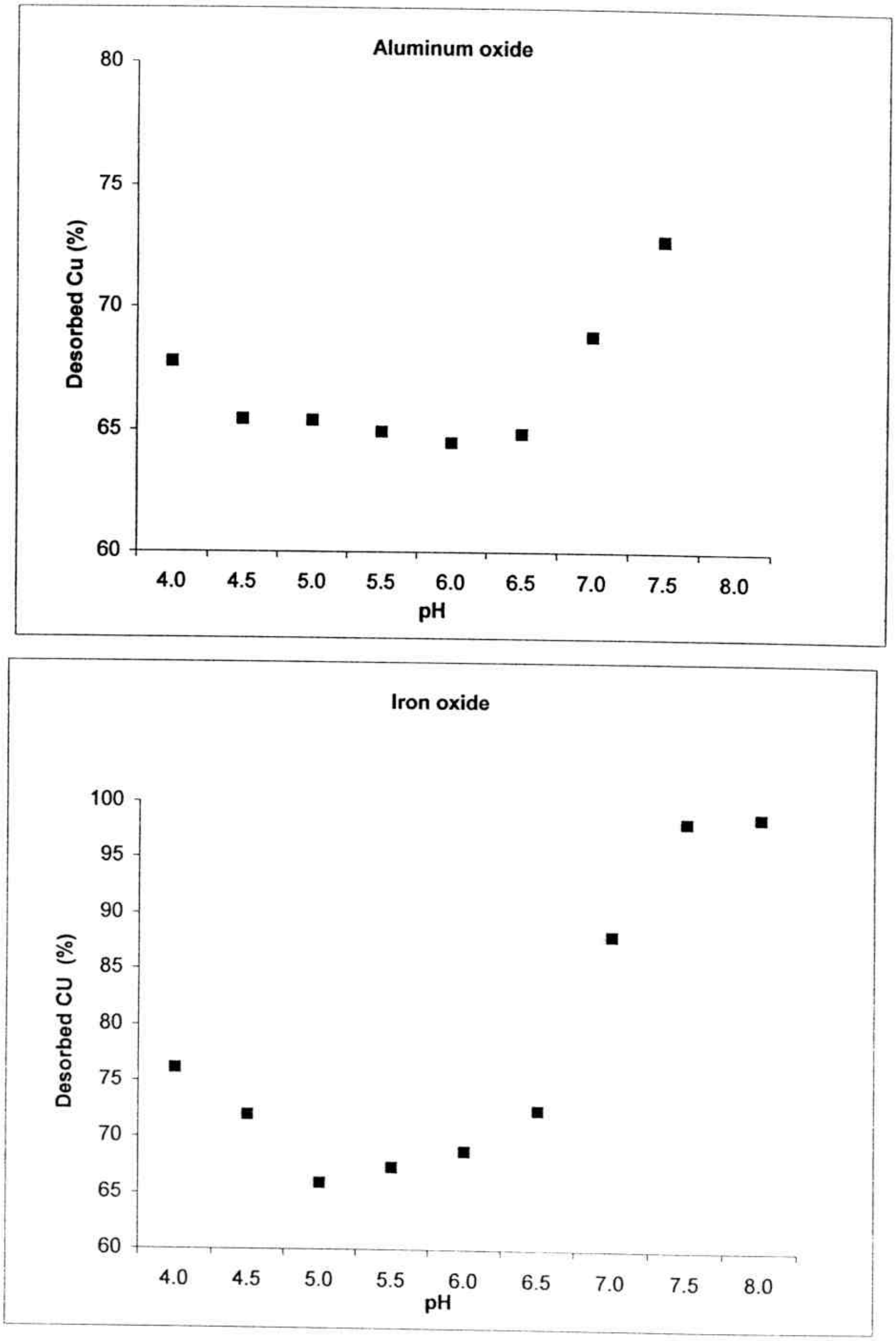


Fig .(23) Copper desorption from aluminum and iron oxides by DTPA over a wide range of pH.Experimental conditions : Cu $^{2+}$, 10 µg mL^{-1} ,oxides 2.5gL^{-1}, DTPA 0.005 M ,ionic strength, 0.1M Ca(NO$_3$)$_2$

Table .(27) :Copper desorption from Kaolinite and bentonite by DTPA extract

[Cu conc. (10 µg/mL) , ionic strength, 0.1M $Ca(NO_3)_2$]

Clay	Adsorption			Desorption			% Desorbed
	pH	C µg/mL	x\m µg/g	pH	Cu conc µg/mL	Desorbed µg/g	
Kaolinite	6.00	3.567	2573.2	4.00	2.365	1892	73.53
	6.00	3.567	2573.2	4.50	2.378	1902	73.93
	6.00	3.567	2573.2	5.00	2.442	1954	75.92
	6.00	3.567	2573.2	5.50	2.289	1831	71.16
	6.00	3.567	2573.2	6.00	2.136	1709	66.41
	6.00	3.567	2573.2	6.50	1.818	1454	56.52
	6.00	3.567	2573.2	7.00	1.947	1558	60.53
	6.00	3.567	2573.2	7.50	2.076	1661	64.54
	6.00	3.567	2573.2	8.00	2.120	1696	65.59
Bentonite	6.00	2.313	3074.8	4.00	2.500	2000	65.04
	6.00	2.313	3074.8	4.50	2.510	2008	65.31
	6.00	2.313	3074.8	5.00	2.529	2023	65.80
	6.00	2.313	3074.8	5.50	2.590	2072	67.39
	6.00	2.313	3074.8	6.00	2.450	1960	63.74
	6.00	2.313	3074.8	6.50	2.380	1904	61.92
	6.00	2.313	3074.8	7.00	2.490	1992	64.78
	6.00	2.313	3074.8	7.50	2.670	2136	69.47
	6.00	2.313	3074.8	8.00	2.766	2213	71.97

Table .(28):Copper desorption from Montmorillonite and atapolgite by DTPA extract [Cu conc. (10 µg/mL) , ionic strength, 0.1M $Ca(NO_3)_2$]

Clay	Adsorption			Desorption			% Desorbed
	pH	C µg/mL	x\m µg/g	pH	Cu conc µg/mL	Desorped µg/g	
Montmorillonite	6.00	5.235	1430.4	4.00	1.667	1334	93.23
	6.00	5.232	1430.4	4.50	1.700	1360	95.08
	6.00	5.235	1430.4	5.00	1.596	1277	89.26
	6.00	5.235	1430.4	5.50	1.623	1298	90.77
	6.00	5.235	1430.4	6.00	1.704	1363	95.30
	6.00	5.235	1430.4	6.50	1.764	1411	98.66
	6.00	5.232	1430.4	7.00	1.720	1376	96.20
	6.00	5.232	1430.4	7.50	1.671	1337	93.46
	6.00	5.232	1430.4	8.00	1.710	1368	95.64
Atapolgite	6.00	1.26	3496	4.00	3.506	2805	80.23
	6.00	1.26	3496	4.50	3.381	2705	77.37
	6.00	1.26	3496	5.00	3.443	2754	78.79
	6.00	1.26	3496	5.50	3.394	2715	77.67
	6.00	1.26	3496	6.00	3.151	2521	72.11
	6.00	1.26	3496	6.50	3.052	2442	69.84
	6.00	1.26	3496	7.00	3.294	2635	75.38
	6.00	1.26	3496	7.50	3.612	2890	82.65
	6.00	1.26	3496	8.00	3.548	2838	81.19

Table .(29) :copper desorption from Aluminum and iron oxides by DTPA extract

[Cu conc. (10 µg/ml) , ionic strength, 0.1M Ca(NO$_3$)$_2$]

Oxides	Adsorption			Desorption			% Desorbed
	pH	C µg/mL	x\m µg/g	pH	Cu conc µg/mL	Desorbed µg/g	
aluminum	6.00	0.656	3800	4.00	3.217	2574	67.73
	6.00	0.656	3800	4.50	3.108	2486	65.43
	6.00	0.656	3800	5.00	3.106	2485	65.39
	6.00	0.656	3800	5.50	3.084	2467	64.93
	6.00	0.656	3800	6.00	3.062	2450	64.46
	6.00	0.656	3800	6.50	3.080	2464	64.84
	6.00	0.656	3800	7.00	3.267	2614	68.78
	6.00	0.656	3800	7.50	3.454	2763	72.72
	6.00	0.656	3800	8.00	3.883	3106	81.75
Iron	6.00	4.09	2364	4.00	2.250	1800	76.14
	6.00	4.09	2364	4.50	2.126	1701	71.95
	6.00	4.09	2364	5.00	1.949	1559	65.96
	6.00	4.09	2364	5.50	1.990	1592	67.34
	6.00	4.09	2364	6.00	2.032	1626	68.76
	6.00	4.09	2364	6.50	2.140	1712	72.42
	6.00	4.09	2364	7.00	2.600	2080	87.99
	6.00	4.09	2364	7.50	2.900	2320	98.14
	6.00	4.09	2364	8.00	2.915	2332	98.64

4. 3.Competitive adsorption of Cu and Zn :

4.3.1. Soils

The competitive adsorption of Cu and Zn on soils was studied using Cu : Zn ratios of 1:0 and 1:1 (Fig.24)

In the absence of Zn, adsorption of Cu on sandy loam soil increased gradually with increasing pH, at pH 4.0 almost 70 % of the added Cu was adsorbed, while at pH 7.0 about 95 % of added Cu was adsorbed. The preference of the adsorbent to Cu over Zn was indicated when they added together as Cu adsorbed % was increased gradually with increasing pH with slight differences as compared with no Zn addition. However, Zn was more affected by Cu and the amount of adsorbed Zn was recorded 35 % at pH 4.0, increased to 42 % at pH 5.5 and increased sharply with increasing pH being 85 % at pH 6.5.

It seems that the preference of sandy loam soil to Cu was high at low pH and with increasing pH the affinity of sandy loam soil to copper was decreased. In the case of sandy clay loam (Fig.24), adsorption of Cu showed the same trend similar to that obtained with sandy loam soil when added alone or with Zn at 1:1 ratio. Adsorption of Zn increased with increasing pH values, with less adsorbed Zn % as compared with the previous soils. It is worthy to note that, Cu was more preferred to soil surfaces comparing to Zn. These results are in agreement with those of ***Pardo (2000)*** in which the selectivity sequences of metals retention were Cu > Zn for soil and also in agreement with those of ***Basta et al. (1992)*** in which general metal affinity by soils was Cu >Zn, and the competition among metals for exchange sites was enhanced as the initial concentration was increased.

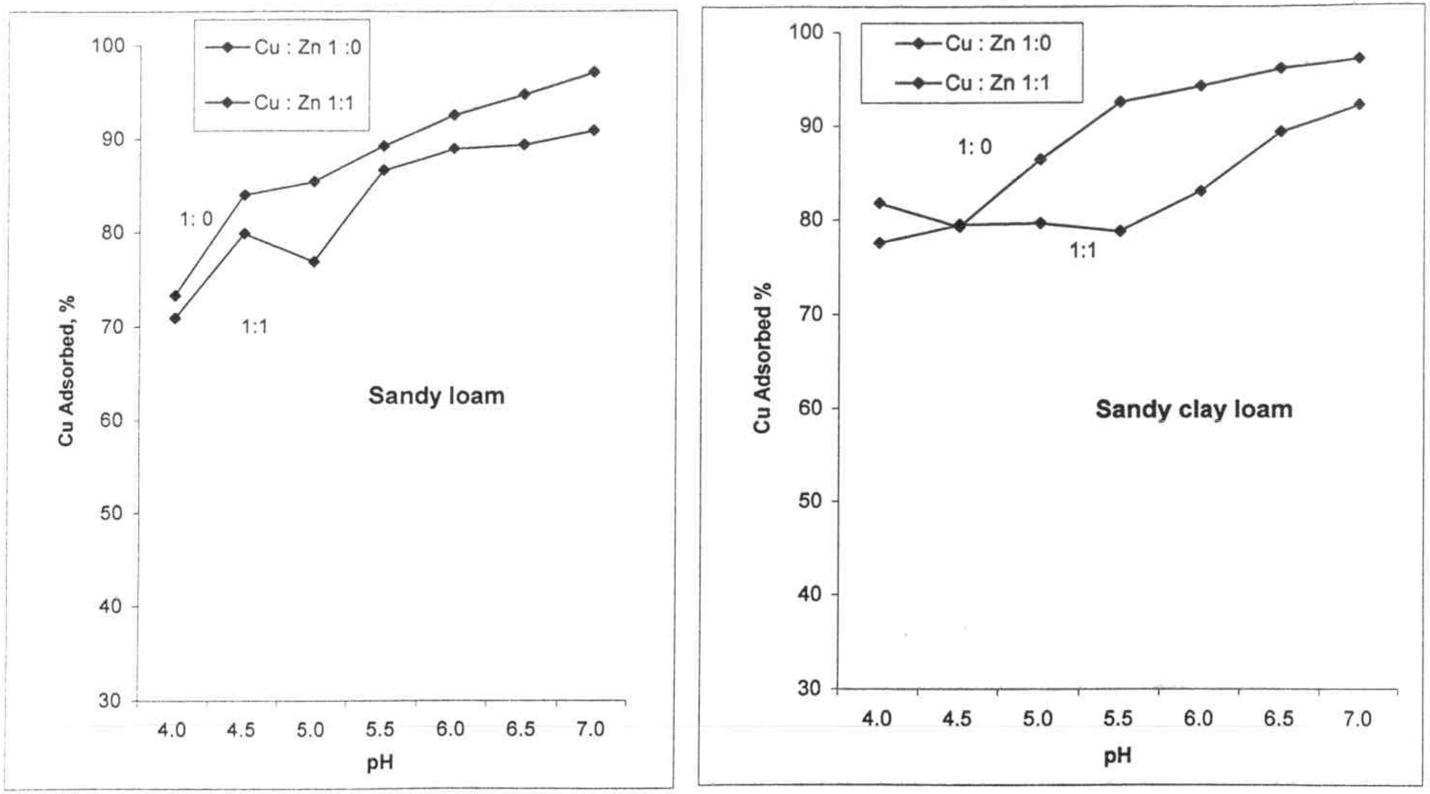


Fig. (24) :Competive adsorption of Cu and Zn on Sandy loam and sandy clay loam soils as a function of pH [Experimental condition:Cu :Zn (1:0, 1:1, 2:1and 1:2), ionic strength buffer, 0.1M $Ca(NO_3)_2$]

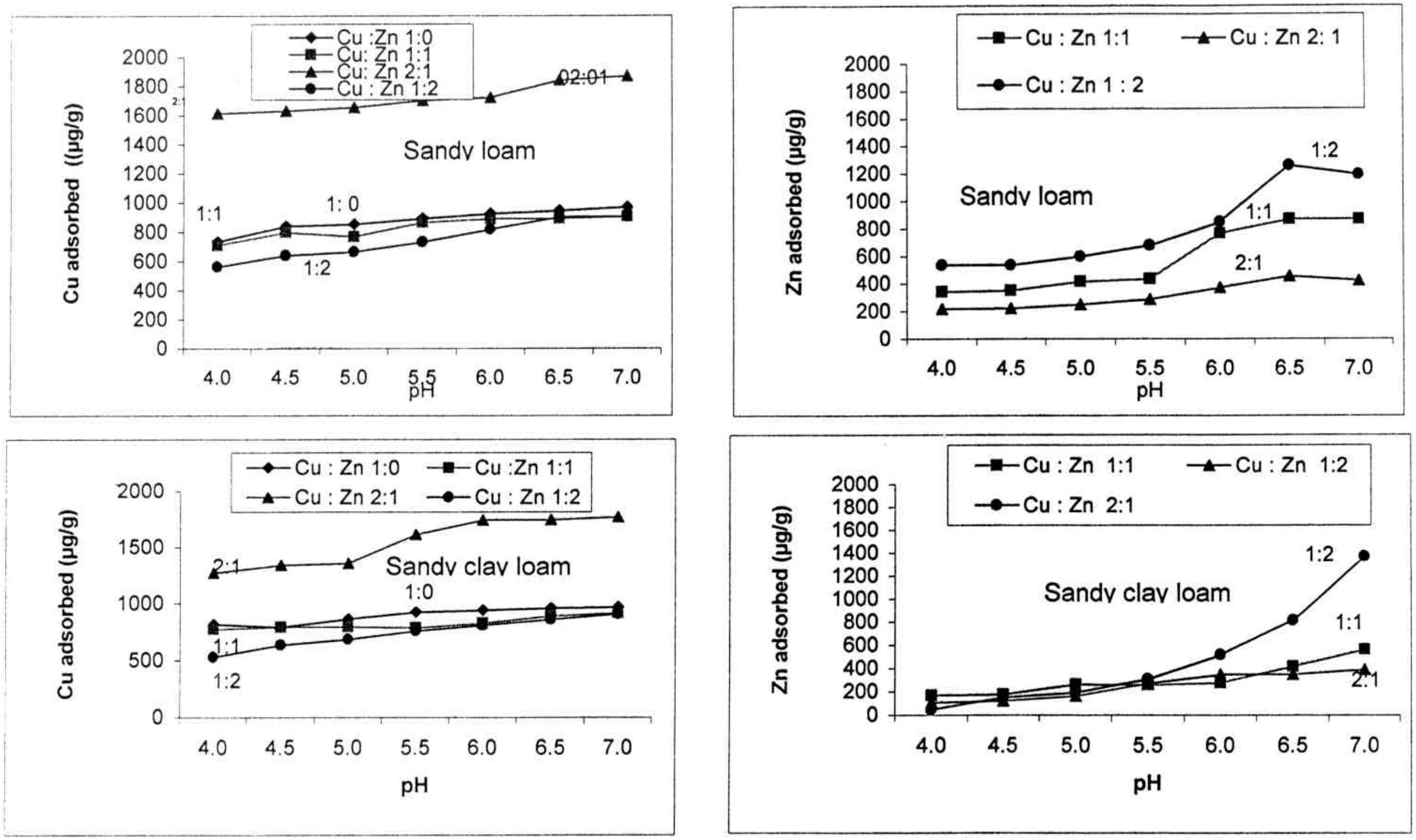


Fig. (24) :Competive adsorption of Cu and Zn on sandy loam and sandy clay loam soils as a function of pH [Experimental conditions:Cu :Zn (1:0, 1:1, 2:1and 1:2), ionic strength buffer, 0.1M Ca(NO$_3$)$_2$]

4.3.2 Clay minerals :

Results of competitive adsorption between Cu and Zn on clay minerals are shown in Figs. (25-26). Concerning atapolgite, adsorption of Cu was increased with increasing pH with very slight differences between the amounts adsorbed on atapolgite in particular when Cu was added alone or with Zn at low Cu : Zn ratio (1: 0 and 1:1). However more pronounced increases in Cu adsorption was noticed when Cu was added at 2:1 Cu :Zn ratio. The affinity of atapolgite to Cu was affected largely by pH and by Cu concentration in the equilibrium solution. Similar trend was observed when Zn was taken into consideration with more differences in Zn adsorption when added at the following ratios 1:2 and 1:1. With regard to montmorillonite, higher amounts of Cu were adsorbed on its surfaces as compared to Zn. The highest adsorption was noticed with Cu :Zn (2:1) ratio particularity at high pH values. Adsorption of Cu was increased with increasing pH in the presence and absence of Zn. Adsorption of Zn on montmorillonite surfaces was affected largely by Cu concentration. Less amounts of Zn were adsorbed on montmorillonite as compared to Cu indicating the preference of montmorillonite to Cu. Competitive adsorption on montmorillonite was less affected by initial pH values. With regard to kaolinite, adsorption of Cu in the presence of Zn was affected by pH values in particular at pH > 5.5, the highest Cu adsorption was noticed with 2 : 1 Cu : Zn ratio. Adsorption of Zn was almost similar to Cu.

Upon bentonite, either Cu or Zn adsorption increased with increasing pH values. The adsorption of the individual Cu or Zn increased with increasing its proportion in Cu : Zn ratios.

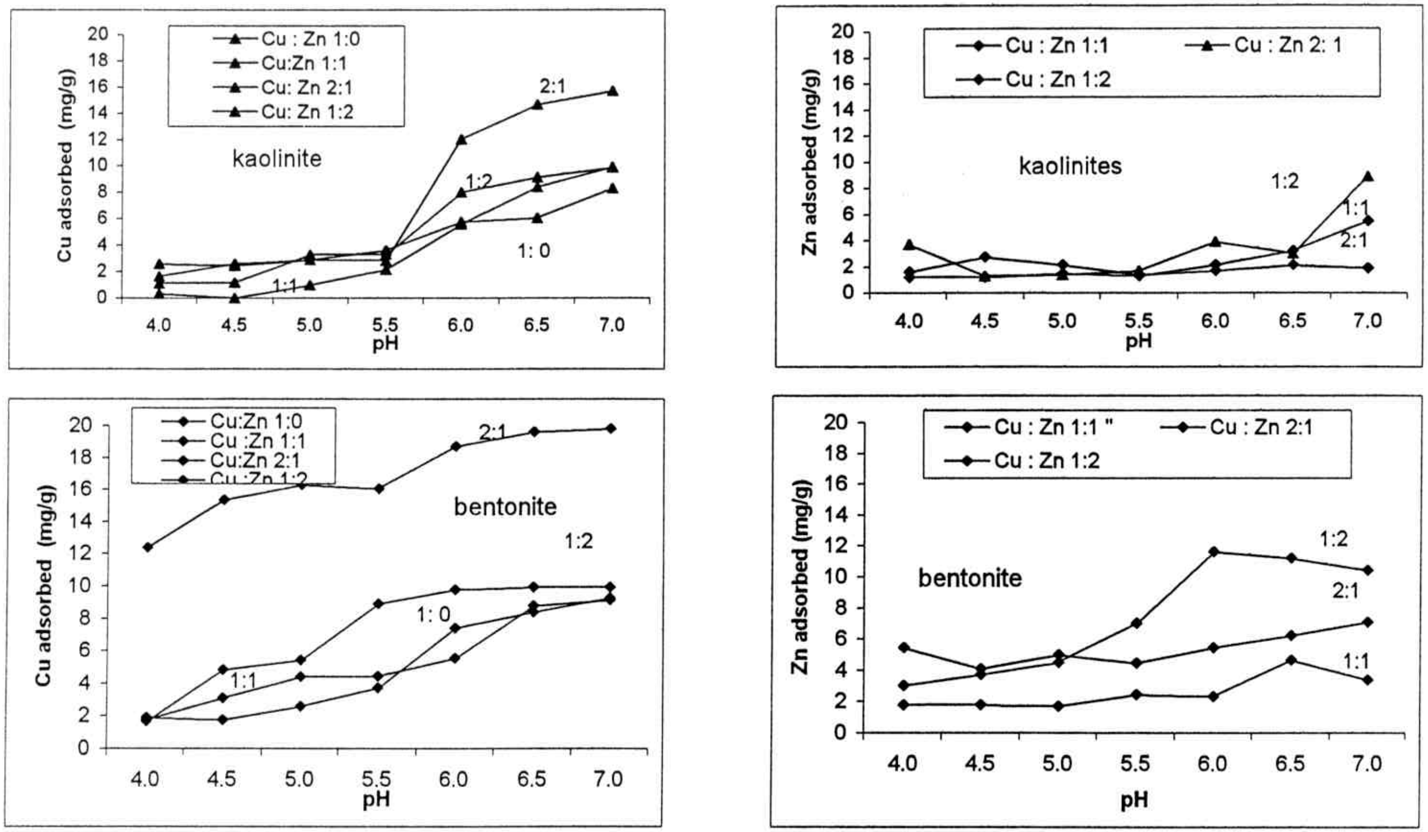


Fig. (25) :Competive adsorption of Cu and Zn on a kaolinite and bentonite as a function of pH
[Experimental conditions : Cu :Zn (1:0, 1:1, 2:1, and 1:2 μg/mL), ionic strength buffer, 0.1M $Ca(NO_3)_2$]

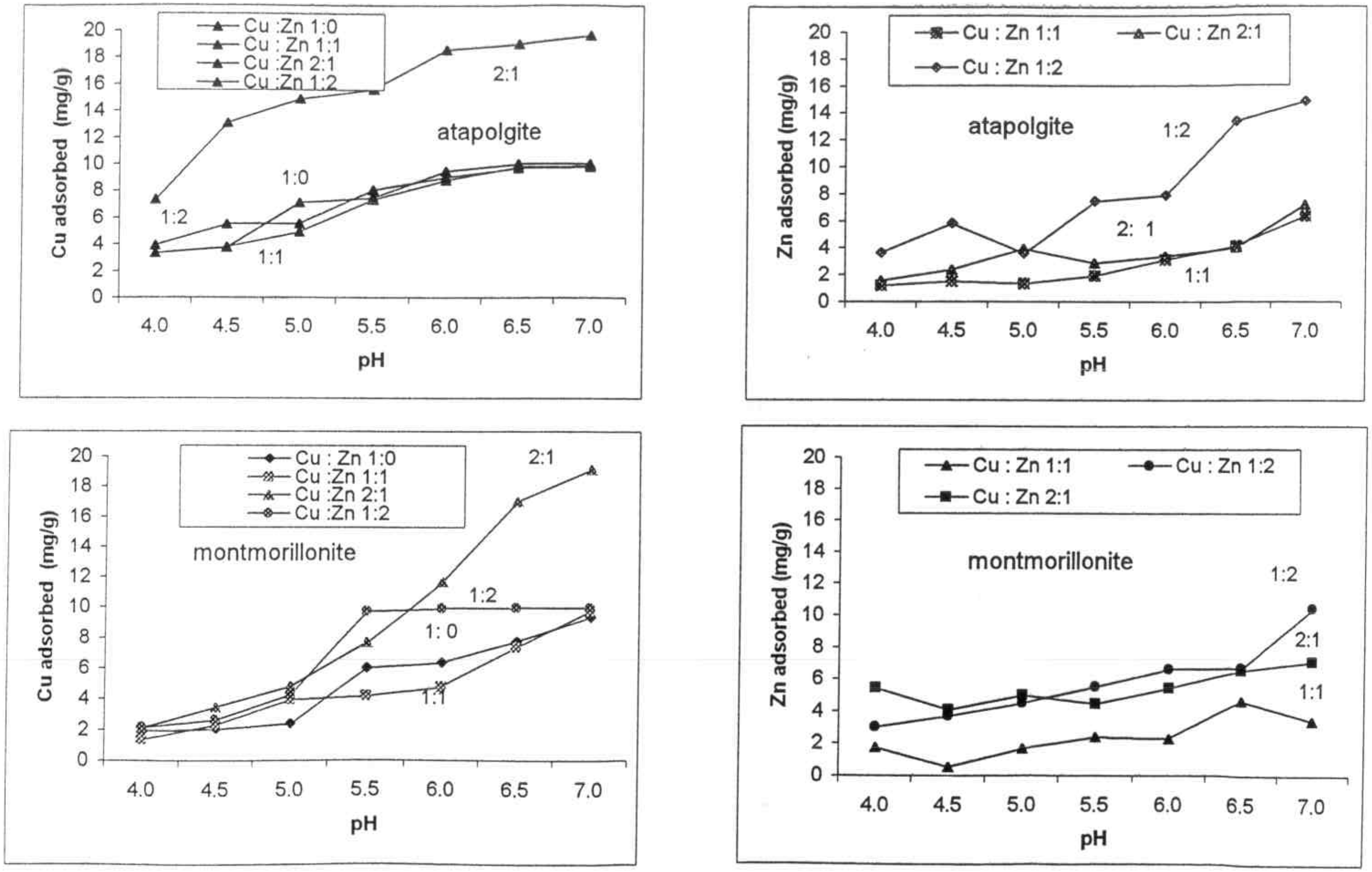


Fig.(26) :Competive adsorption of Cu and Zn on a atapolgite and montmorillonite as a function of pH [Experimental conditions : Cu :Zn (1:0, 1:1, 2:1, and 1:2 µg/mL), ionic strength buffer, 0.1M $Ca(NO_3)_2$]

4.3.3. Iron and aluminum oxides :

Upon iron oxide, as discussed before with clay minerals, adsorption of Cu increased gradually with increasing initial pH from 4.0 to 5.0 and increased dramatically with increasing pH from 5.0 to 7.0, the highest increase was accompanied with 2:1 Cu :Zn ratio. This result indicates that Cu adsorption affected positively by both of pH and its initial concentration. Almost similar trend of Cu adsorption on aluminum oxide in the presence and absence of Zn was observed.

Concerning the adsorption of Zn in the presence of Cu on Fe and Al oxides, data illustrated in Figs. (27-28) reveal that adsorption of Zn was increased with increasing initial pH and highest increase was noted with Cu: Zn ratio of 1:2. While with aluminum oxide, there were high increases in Zn adsorption with increasing initial pH. The highest adsorption of Zn was recorded with Cu : Zn ratio of 1:2.

Increasing the adsorption of Cu and Zn on soils, clay minerals, and Al and Fe oxides with pH could be attributed to the increase in the negative charge of the adsorbent resulted from increasing pH.

Adsorption of Cu on soils , clay minerals and Fe and Al oxides was summarized in Fig. (29). Adsorbed Cu was affected by soil type and sandy clay loam soil was the superior as compared to sandy loam soil. Clay minerals differed in their ability to adsorb Cu on their surfaces and their response to the initial pH with regard to the amount of adsorbed Cu on clay minerals could be arranged in the following descending order : atapolgite >bentonite > montmorillonite > kaolinite particularly at pH > 6.0. Aluminum oxide adsorbed relatively high amounts of Cu on its surfaces as compared to iron oxides Fig.(30).

Effect of initial Cu concentrations on the amount of adsorbed Cu is shown in Figs (31-32). On clay minerals with increasing initial Cu concentration the adsorbed Cu increased gradually with high increases at pH 6.0 as compared to pH 4.0. The minerals could be arranged in the following descending order with regard to their ability to adsorb Cu : atapolgite > bentonite > kaolinite > montmorillonite. At pH 4.0 the order of minerals was changed to the following order : atapolgite > montmorillonite > bentonite > kaolinite.

Concerning aluminum and iron oxides, Al oxide adsorbed higher amounts of Cu as compared to iron oxides when Cu was added at different initial concentrations. Also, the amounts of adsorbed Cu at pH 6.0 were higher than the corresponding ones adsorbed at pH 4.0. these results are in agreement with those of **(Mattes et al. 1999** in which the sorption of Cu and Zn by bentonite was dominated by cation exchange. In artificial leachate, the sorption was reduced due to competition with alkali and alkaline earth cations. The sorption of Cu and Zn at pH 4.9 by Al and Zr-hydroxy – intercalated and pillared Mx80 was governed also by cation exchange. **Shuman (1988)** Stated that copper was not affected siquificantly but Zn increased in Mn and Fe oxides fractions at the expense of the Zn in the other fractions.

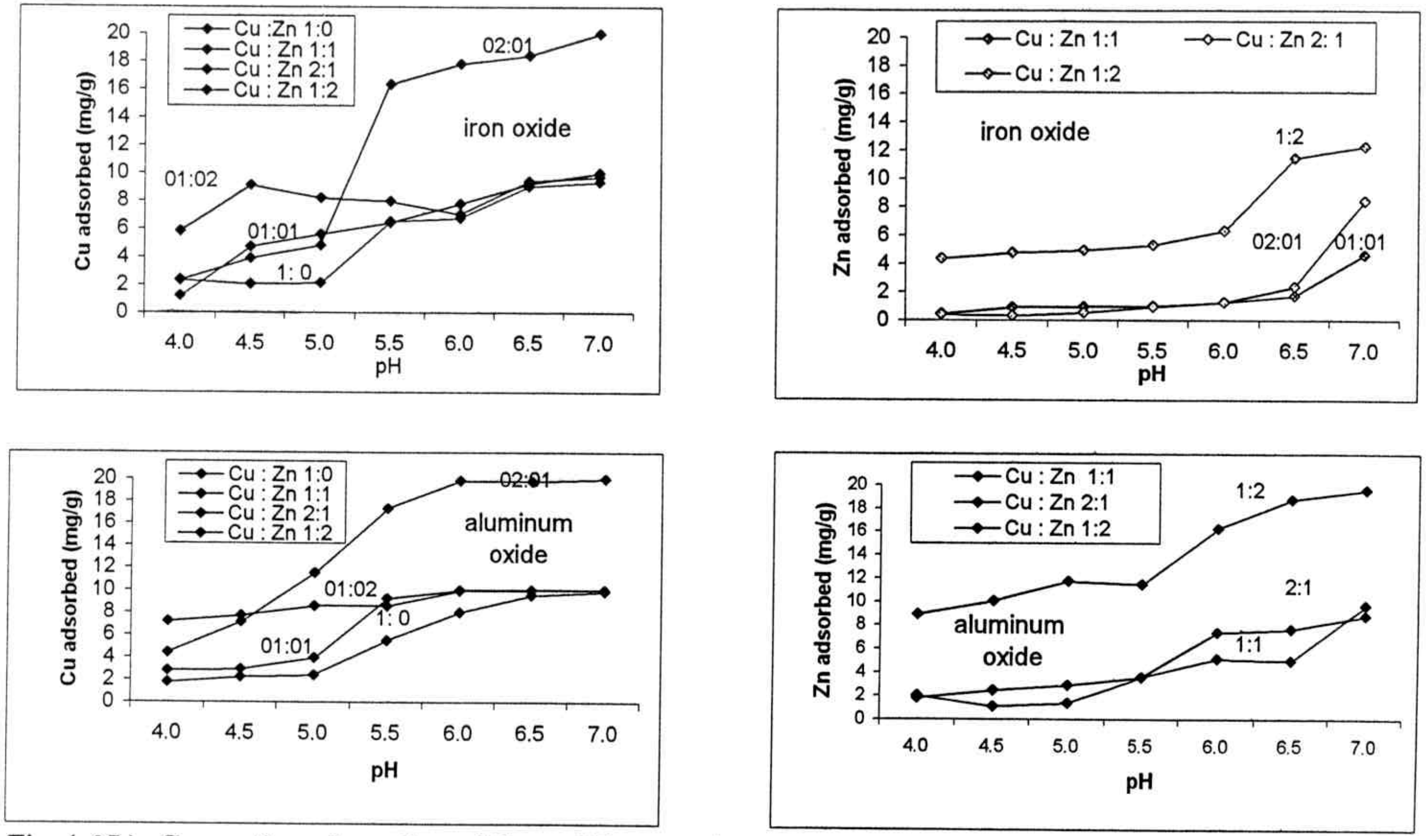


Fig. (27) :Competive adsorption of Cu and Zn on a iron and aluminum oxides as a function of pH
[Experimental conditions : Cu :Zn (1:0, 1:1, 2:1, and 1:2),µg/mL ionic strength buffer, 0.1M $Ca(NO_3)_2$]

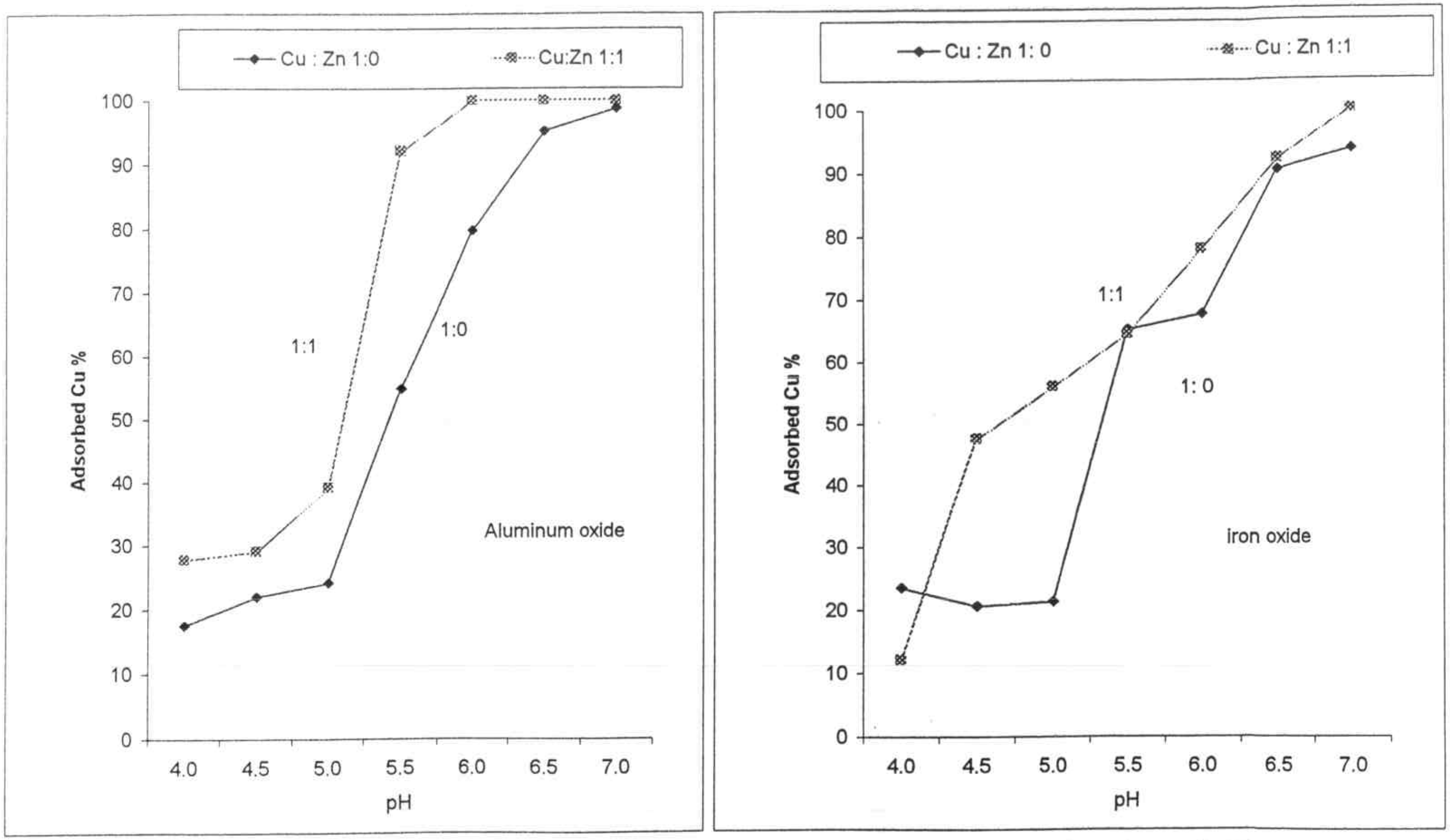


Fig. (28) :Competive adsorption of Cu and Zn on a iron and aluminum oxides as a function of pH [Experimental conditionCu :Zn (without, 1:1),µg/mL ionic strength buffer, 0.1M $Ca(NO_3)_2$]

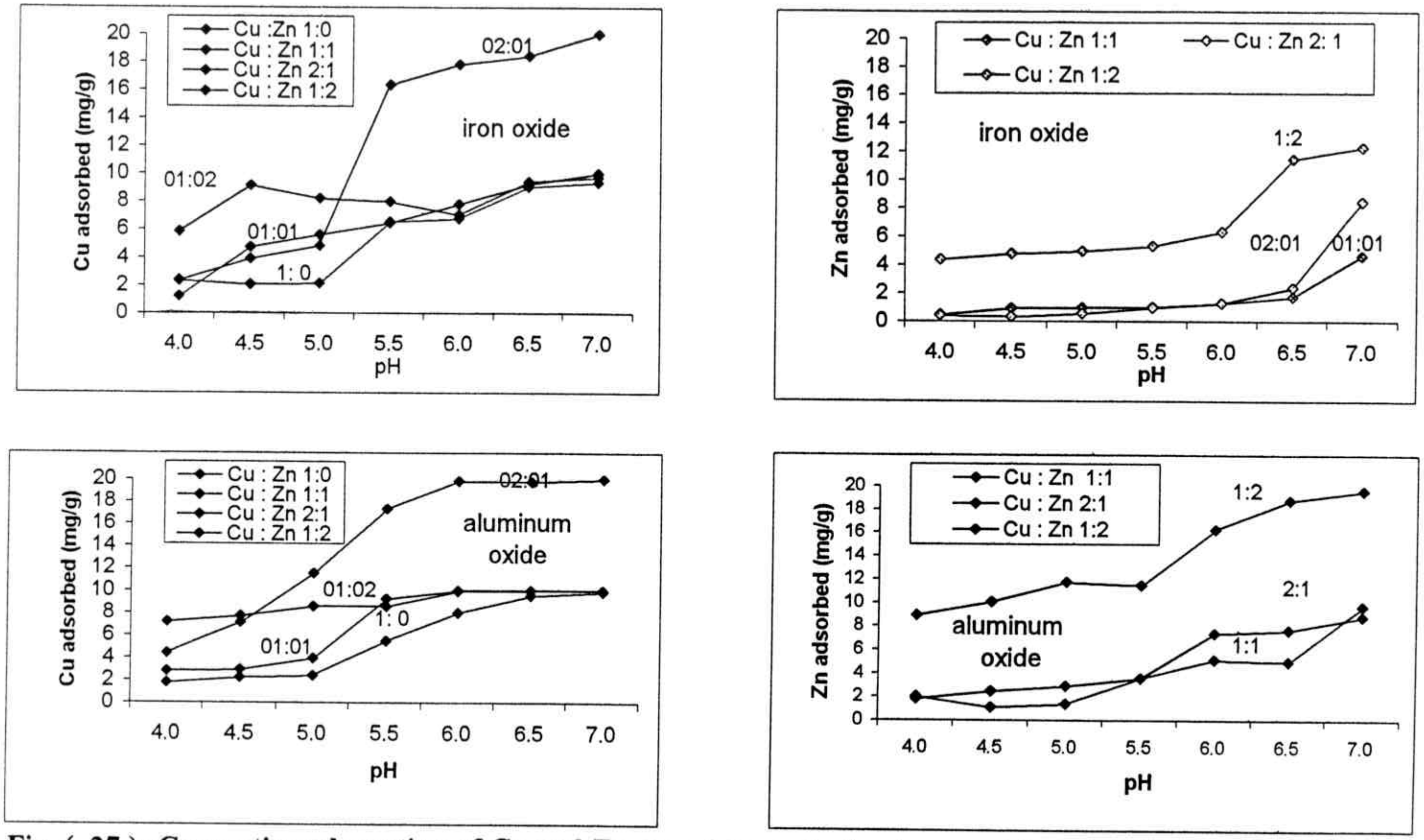


Fig. (27) :Competive adsorption of Cu and Zn on a iron and aluminum oxides as a function of pH
[Experimental conditions : Cu :Zn (1:0, 1:1, 2:1, and 1:2),µg/mL ionic strength buffer, 0.1M $Ca(NO_3)_2$]

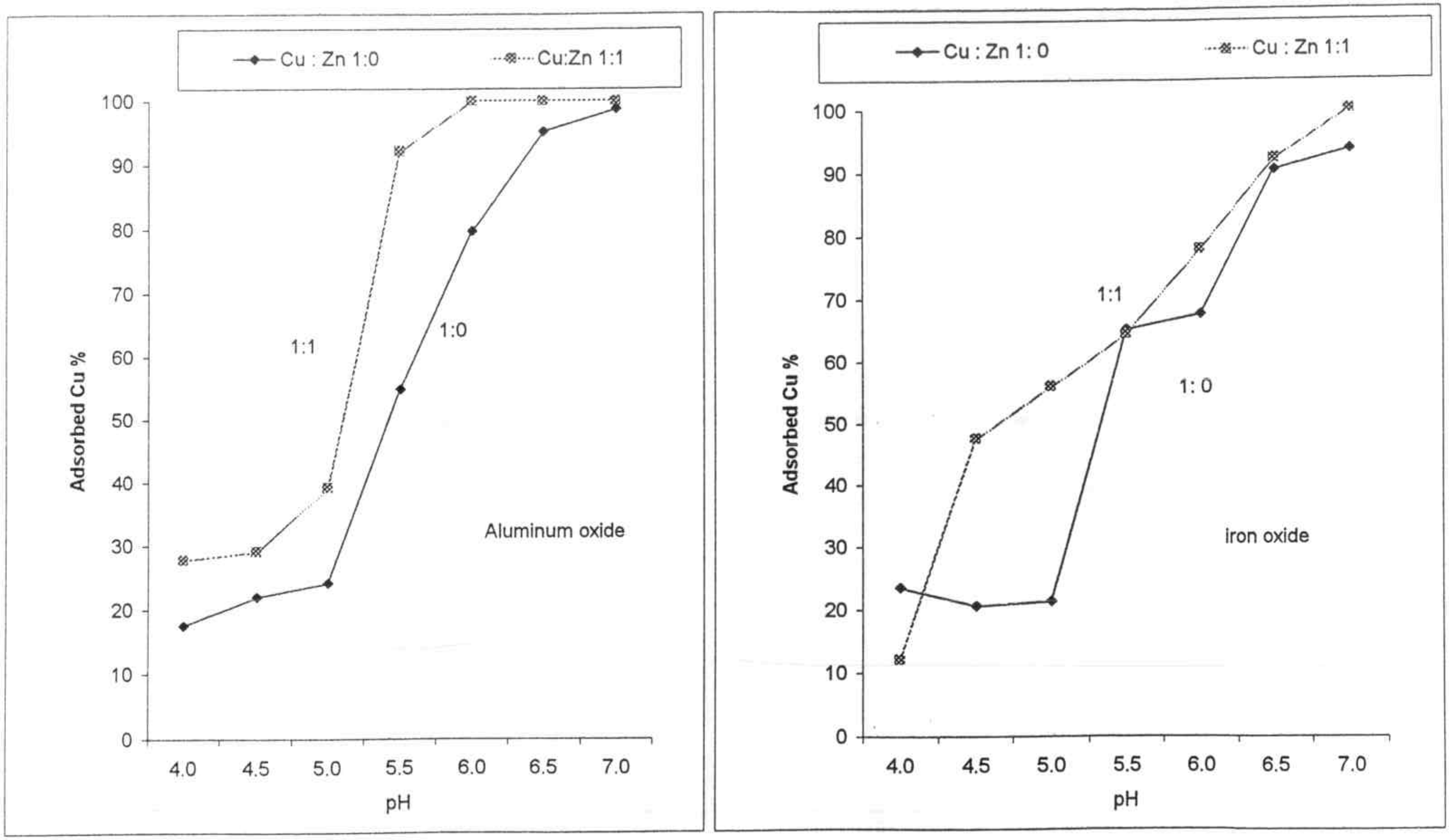
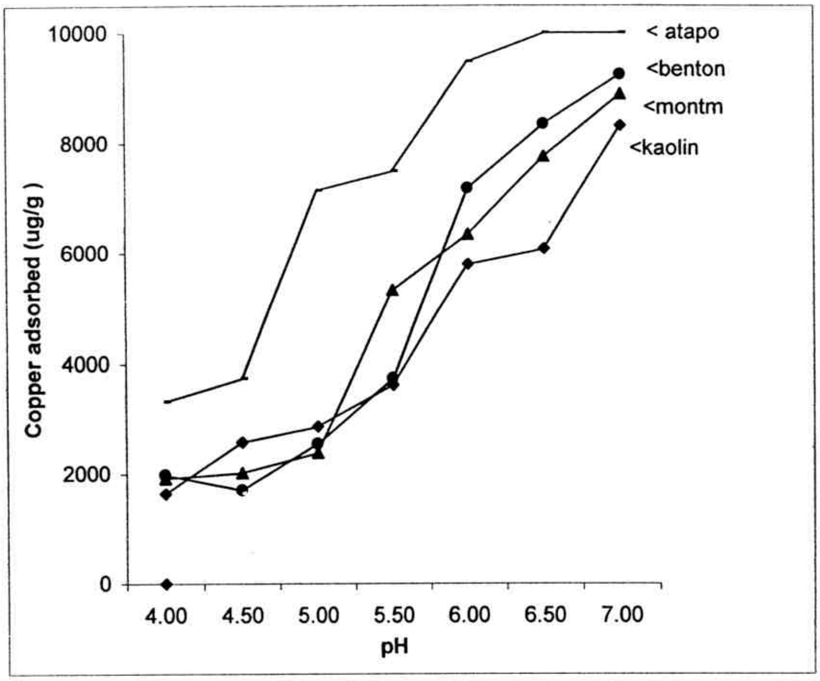


Fig. (28) :Competive adsorption of Cu and Zn on a iron and aluminum oxides as a function of pH [Experimental conditionCu :Zn (without, 1:1),µg/mL ionic strength buffer, 0.1M $Ca(NO_3)_2$]



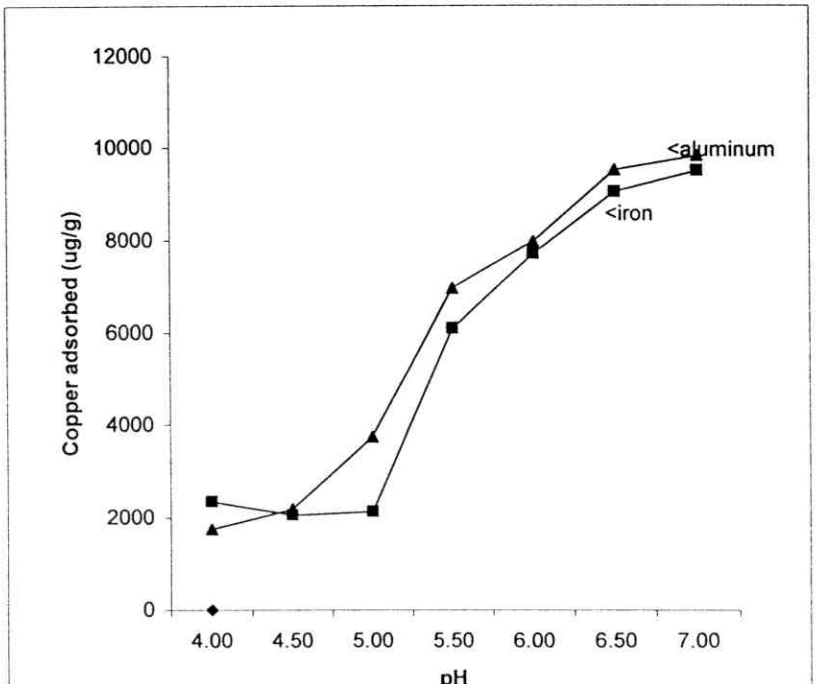


Fig.(29): Adsorption of copper by clay minerals , iron and aluminum oxides over a wide range of pH [Experimental conditions : ionic strength 0.1M $Ca(NO_3)_2$]

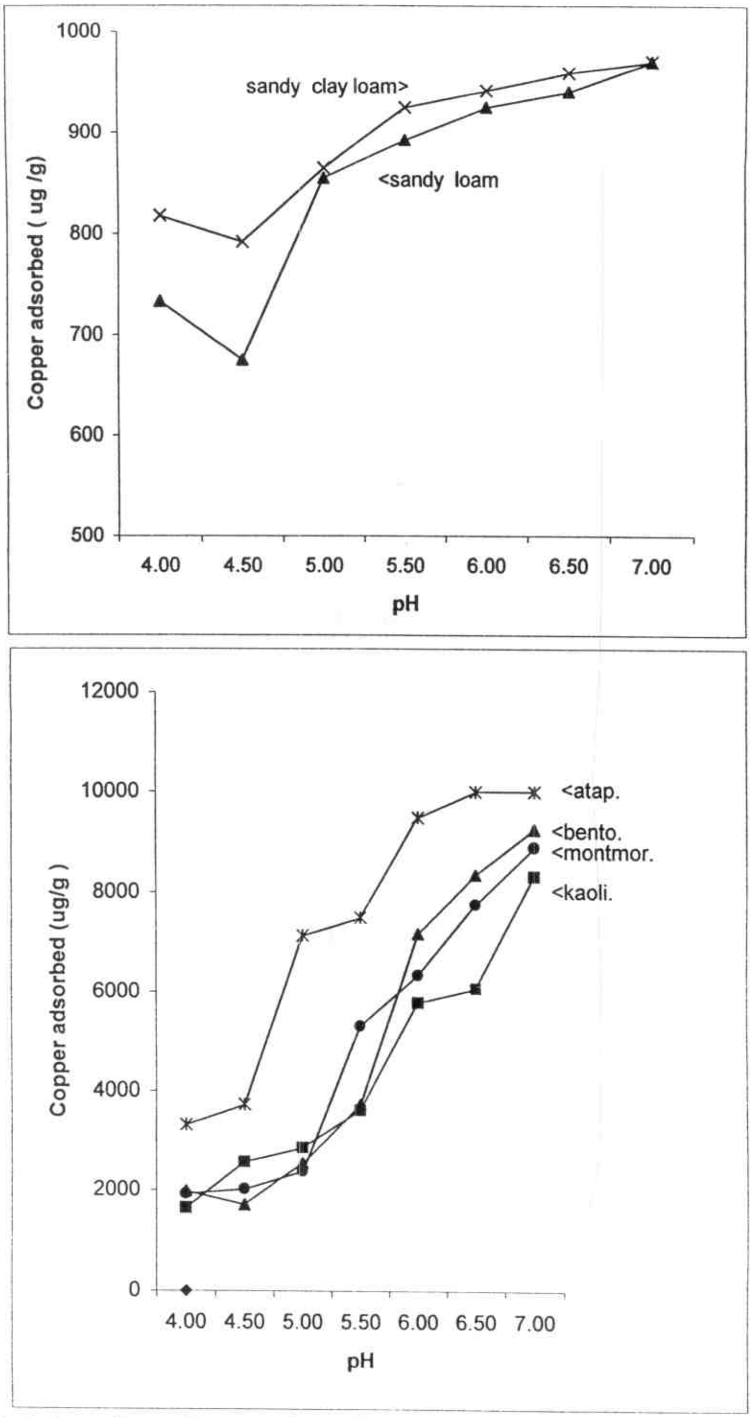


Fig.(30): Adsorption of copper by soil samples and clay minerals over a wide range of pH [Experimental conditions : ionic strength 0.1M $Ca(NO_3)_2$]

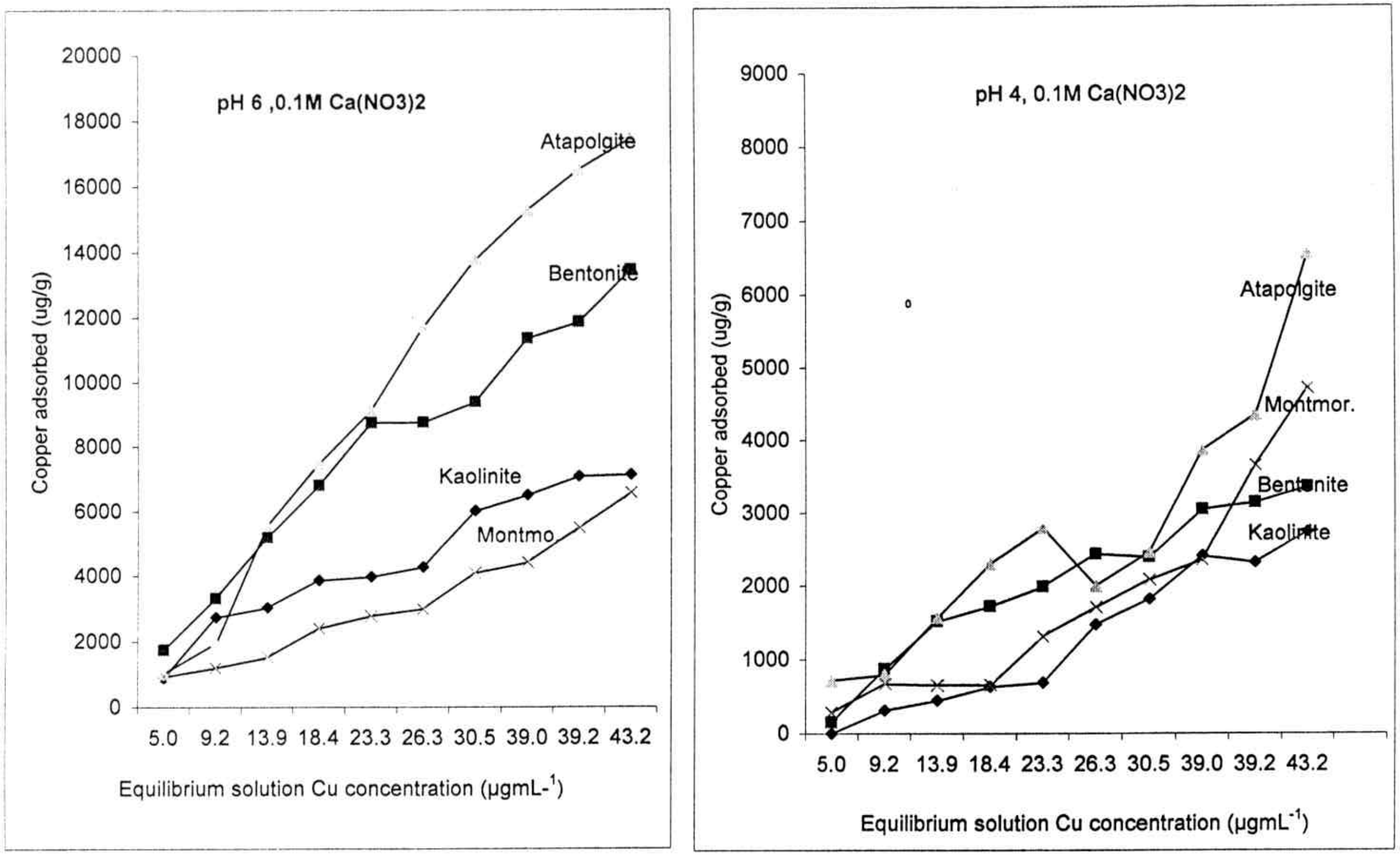


Fig. (31): Adsorption of Copper by(Kaolinite,montmorillinte ,atapolgiteand Bentonite) Experimental conditions : ionic strength (0.1M Ca(NO3)2, 0.1g clay mineral , and Cu conc. ,0-50 µgmL^{-1})

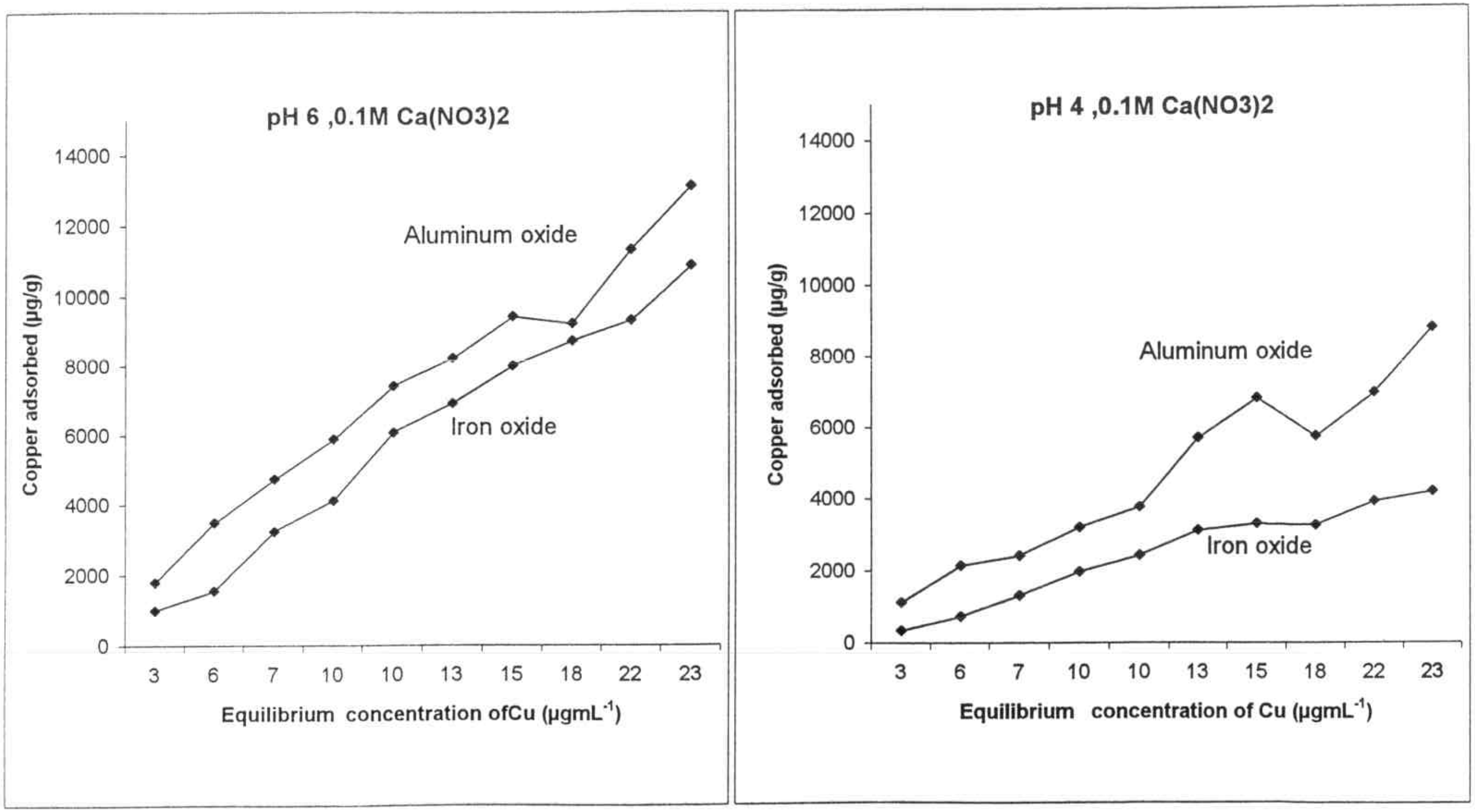


Fig. (32): Adsorption isotherms for copper by aluminum and iron oxides. [Experimental conditions: Cu conc, 5-50 µg mL^{-1} ionic strength 0.1M $Ca(NO_3)_2$]