4. RESULTS AND DISCUSSION

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4.1. Effect of pH on copper adsorption isotherm parameters:

4.1. 1. Adsorption of copper on soils:

The obtained results for the adsorbed copper (µg Cu/g soil) were plotted against the concentration of the bulk equilibrium solution (µg Cu/mL) to represent Cu adsorption isotherm at various pH values (Figs., 1 & 2). It is quite clear that the amount of Cu adsorbed on the alluvial and calcareous soils increased gradually with increasing the initial concentration of Cu up to 80 μgmL^{-1}. A slight increase was observed with increasing initial Cu concentration from 80 to 100 µg Cu mL^{-1}. This trend was observed at various pH values. However, the two soils varied appreciably in Cu adsorption from the added copper nitrate electrolyte where adsorption of Cu on calcareous soil under different concentrations of Cu was generally higher than the corresponding one observed with the alluvial soil. This trend was observed at the different pH values. This increase of adsorbed Cu on calcareous soil may be attributed to the high content of $CaCO_3$ in calcareous soil. These results are in agreement with those obtained by **Abd El-Hamid (1981)** and **Abbas et al. (1996)** who showed that the affinity of calcareous soil to adsorb Cu is likely to be dependent on its content of $CaCO_3$.

Data also reveal that sorption did not seem to reach a maximum even at the highest concentration of Cu (100 µg Cu/mL) for both soils. Differences in the amounts of adsorbed Cu between the soils become wider as the concentration of added Cu increased. At low Cu concentration (up to 40 µg Cu/mL), both soils appeared to have the same magnitude of adsorbed Cu, while at high Cu concentration (up to 100 µg Cu/mL) distinct differences were observed. This deviation could be divided into two distinct parts

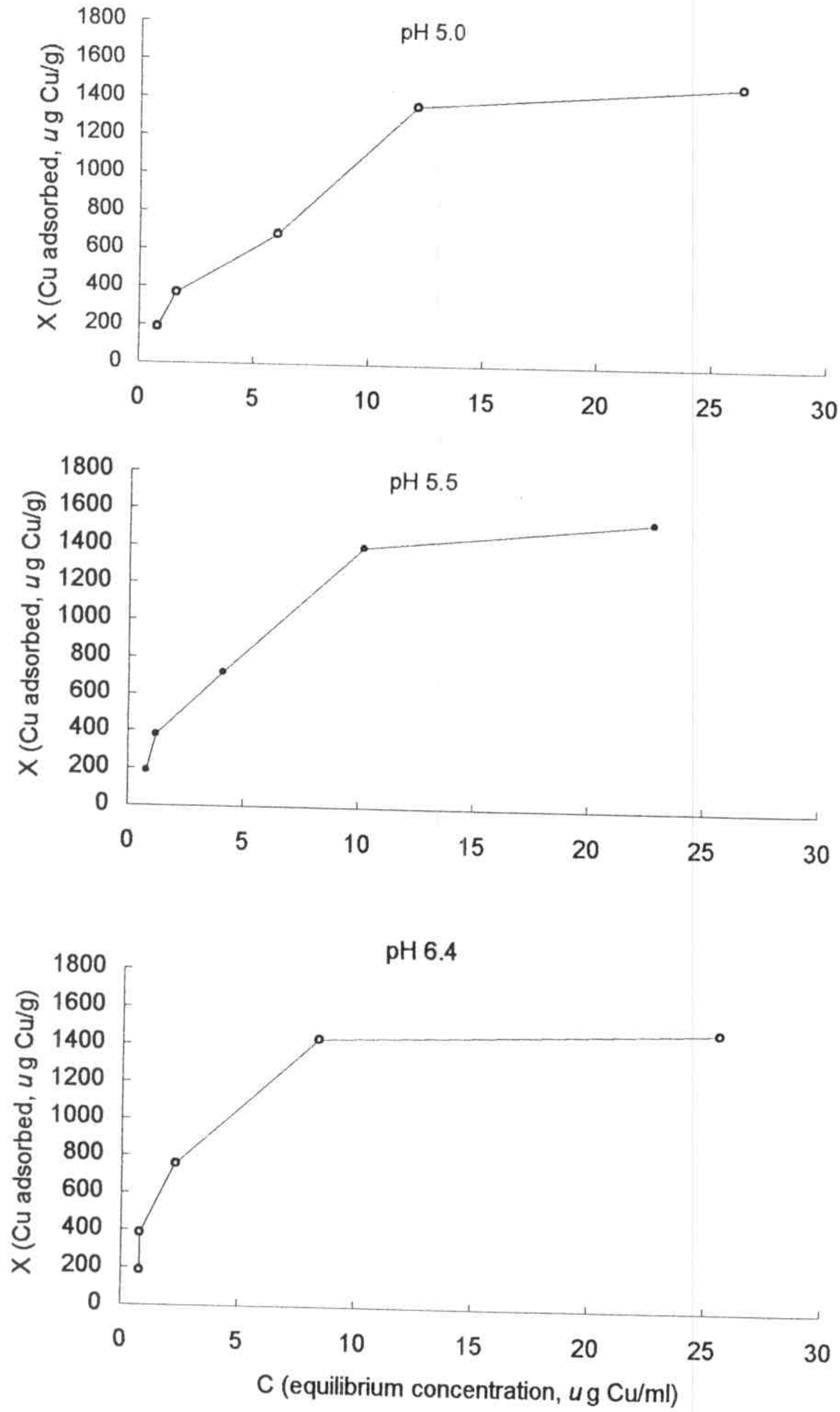


Fig. (1): Copper adsorption isotherms on alluvial soil at various pH values

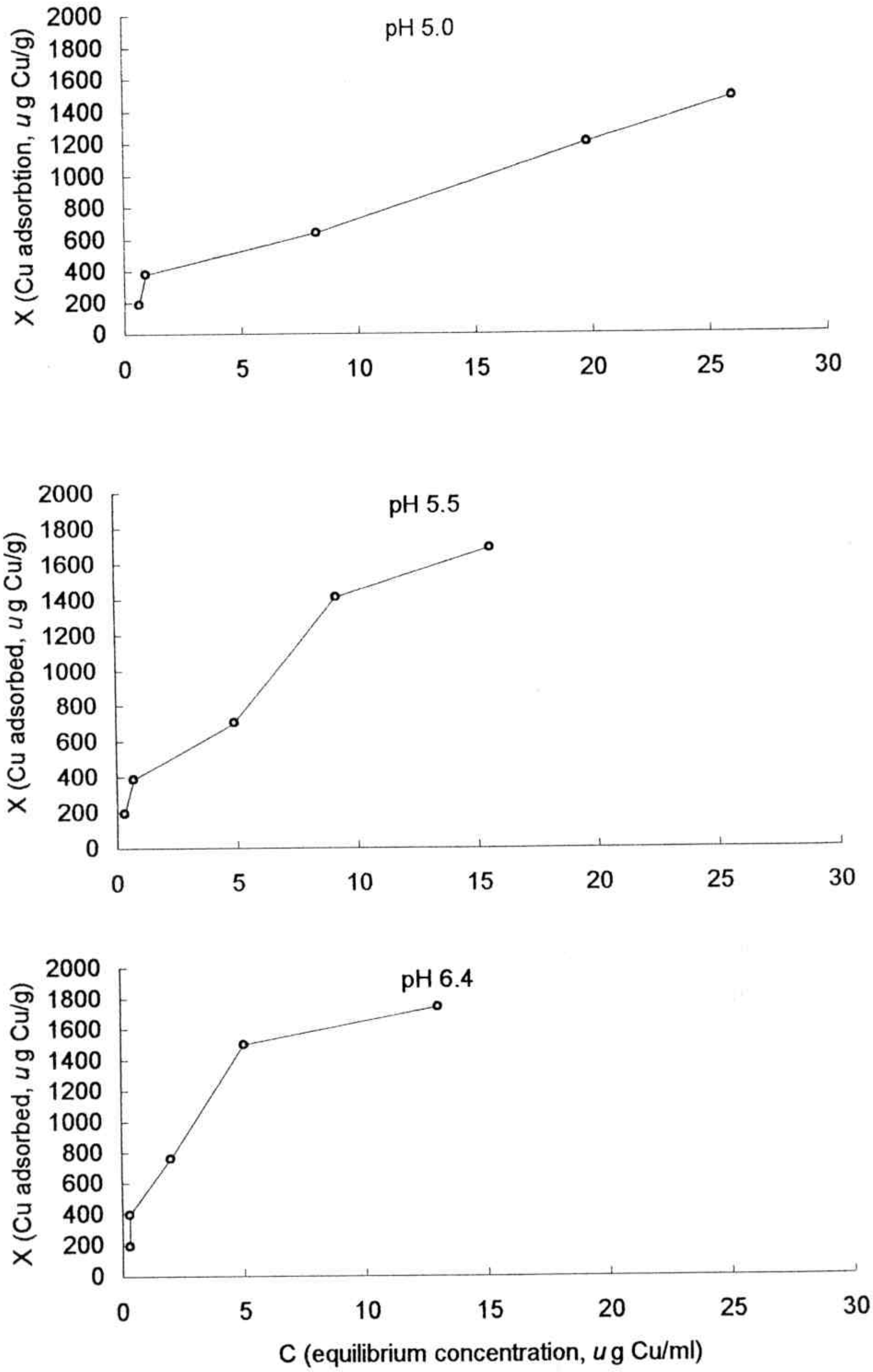


Fig. (2): Copper adsorption isotherms on calcareous soil at various pH va

related to the affinity of Cu for at least two energetically different reactive sites. The first part occurred at low Cu concentrations, where the adsorption isotherms slightly rise. This part represents sites with low affinity for Cu adsorption. The second part of the isotherm occurred at high Cu concentrations. Such response was postulated by **Padmanabham (1983)** who revealed two types of adsorption sites for copper, one of low bonding energy and the other of high bonding energy, correspond with the readily desorbed and less readily desorbed fractions of copper, respectively.

Concerning the effect of pH on Cu adsorption isotherm, data show that increasing pH values from 5.0 up to 6.4 was associated with an increase in Cu adsorption on both the alluvial and calcareous soils. This increase was more pronounced at high concentrations of Cu (80 and 100 μg Cu/mL). This trend was observed for both soils. However, this increase was more obvious in calcareous soil compared with the alluvial one. Similar results were obtained by **Mc Laren and Crawford (1973)** and **Carey et al. (1996)** who found that copper sorption by soils increased substantially with increasing pH values. The increase in Cu adsorption with increasing pH values under condition of this study may be attributed to some factors, i.e., the increase in the pH dependent charge in the soil with increasing pH, and the decrease in H^+ and metallic cation competition for the exchange sites with increasing pH.

4.1.1.1. Application of Langmuir equation:

According to Langmuir equation, data of Cu adsorption on both soils were fitted to the linear form:

$$C/x/m = 1/Kb + C/b$$

Where, x/m = amount of Cu adsobed (μg Cu/g soil), K = constant related to binding energy (mL/μg Cu), b = maximum adsorption capacity (μg Cu/g soil) and C= final equilibrium Cu concentration (μg Cu/mL). All ratios of C/x/m for the different concentrations of Cu to the studied soils were plotted against the corresponding C at various pH values. The obtained results are presented in Figs. (3 & 4) and Tables (2 & 3). The obtained results for alluvial and calcareous soils agreed with the conventional Langmuir isotherm. The correlation coefficients obtained by the regression analysis at pH values 5.0, 5.5 and 6.4 were 0.979**, 0.987** and 0.983**, respectively for alluvial soil. The corresponding values for calcareous soil were 0.936**, 0.918** and 0.988** for the same pH values.

The obtained linear relationships for Cu adsorption reflect the differences between soil properties concerning the ability to adsorb Cu. At pH 5.0, the alluvial soil sorbed about 74 % from the highest applied Cu concentration i.e., 100 μg Cu/mL, also the calcareous soil sorbed about the same percent of the same applied Cu concentration. The corresponding values at pH 5.5 were 77 and 84% for the alluvial and calcareous soils, respectively. At pH 6.4, the percent of Cu adsorbed was 74 and 87 for alluvial and calcareous soils, respectively. In this connection, **Hue et al. (1997)** reported that increasing pH generally increased Cu sorption. The sharpest increase in sorption occurred between pH 6.0 and 7.0, perhaps because most organic molecules and soil minerals change their surface charge from positive or neutral to negative at this pH range; and the retention of Cu mostly as Cu^{2+}, is much stronger by negatively charged surfaces than positively charged ones.

The major advantage of Langmuir equation is that, it is possible to calculate adsorption maximum and the relative binding energy of Cu sorption. From the simple linear relationships obtained (Tables, 4 & 5) between c/x/m vs. C, Cu adsorption maxima (b) were calculated from the slope of the straight line

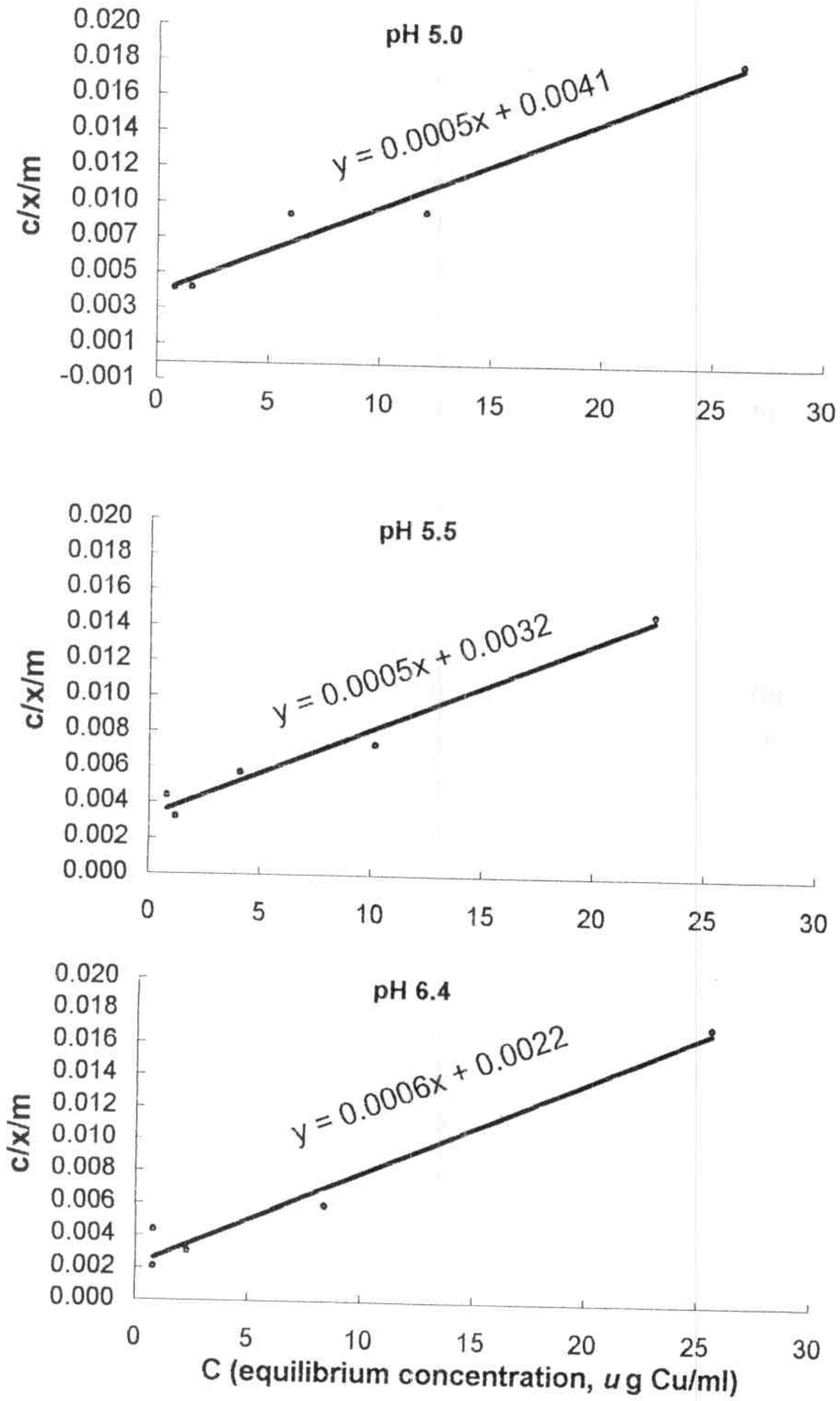


Fig. (3): Copper adsorption isotherms by alluvial soil according to the conventional Langmuir equation at various pH values.

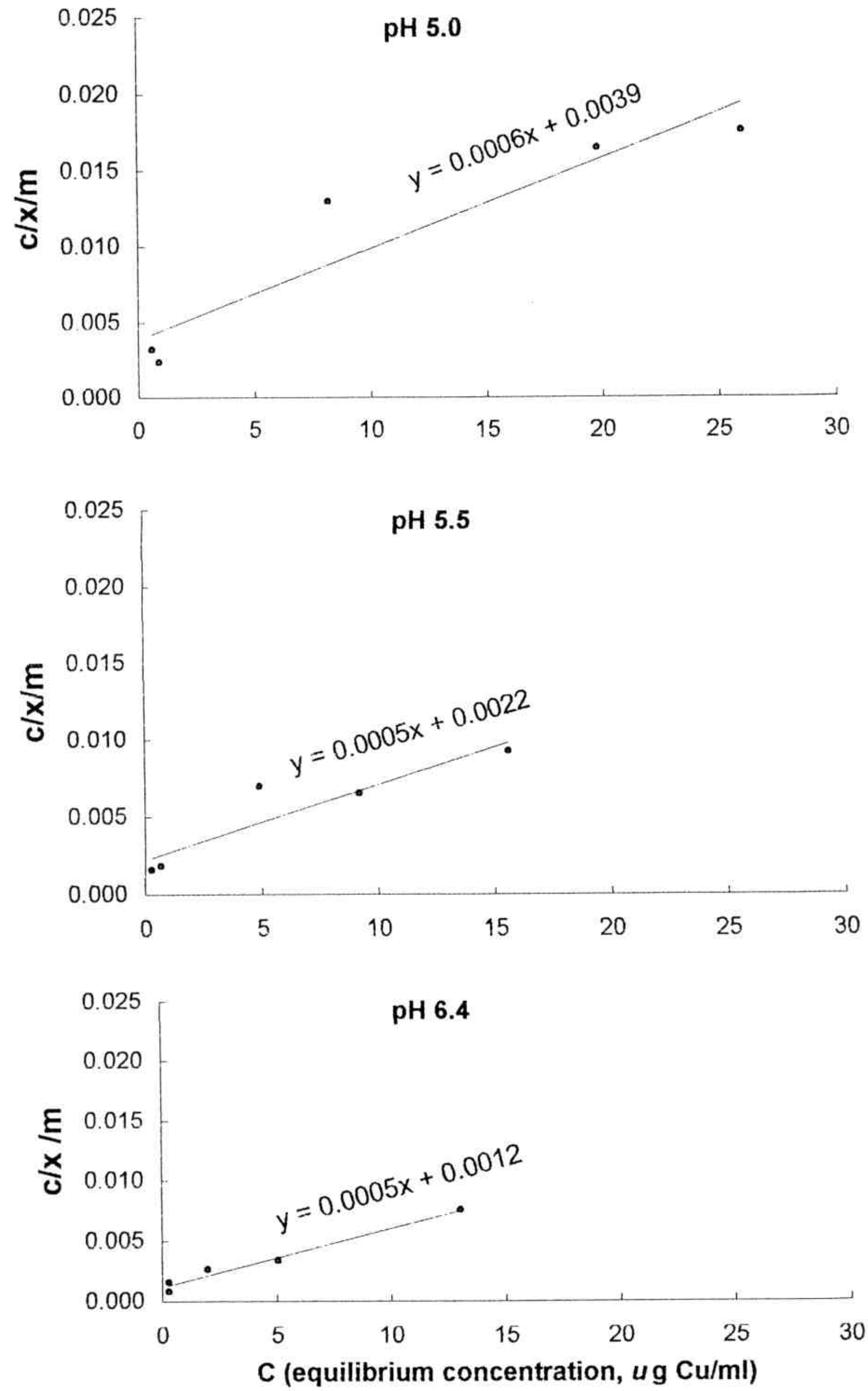


Fig. (4): Copper adsorption isotherms by calcareous soil according to the conventional Langmuir equation at various pH values.

Table (2): Copper adsorption isotherm on alluvial soil according to the Langmuir conventional equation at various pH values.

Initial Cu concentration (μg/ml)	pH 5.0			pH 5.5			pH 6.4		
	C	x/m	C/x/m	C	x/m	C/x/m	C	x/m	C/x/m
10	0.8	184	0.00435	0.8	184	0.00435	0.8	184	0.00435
20	1.6	368	0.00440	1.2	376	0.00319	0.8	384	0.00208
40	6.0	680	0.00882	4.1	718	0.00571	2.3	754	0.00305
80	12.1	1358	0.00891	10.2	1396	0.00731	8.4	1432	0.00587
100	26.3	1474	0.01784	22.8	1544	0.01477	25.6	1488	0.01720

C = final equilibrium concentration (μg Cu/ml).
x/m = adsorbed copper (μg Cu/g soil).

Table (3): Copper adsorption isotherm on calcareous soil according to the Langmuir conventional equation at various pH values.

Initial Cu concentration (µg/ml)	PH 5.0			PH 5.5			PH 6.4		
	C	x/m	C/x/m	C	x/m	C/x/m	C	x/m	C/x/m
10	0.6	188	0.00319	0.3	194	0.00155	0.3	194	0.0015
20	0.9	382	0.00236	0.7	386	0.00181	0.3	394	0.0007
40	8.2	636	0.01289	4.9	702	0.00698	2.0	760	0.0026
80	19.8	1204	0.01645	9.2	1416	0.00650	5.05	1499	0.0033
100	26.0	1480	0.01757	15.6	1688	0.00924	13.0	1740	0.0074

C = final equilibrium concentration (µg Cu/ml).
X = adsorbed copper (µg Cu/g soil).

Table (4): Regression parameters calculated from copper adsorption isotherms on alluvial soil according to the Langmuir equation at various pH values.

pH values	Linear equation	b	K	MBC	r
5.0	C/x/m = 0.0005x + 0.0041	2000	0.12195	243.9	0.979
5.5	C/x/m = 0.0005x + 0.0032	2000	0.15625	312.5	0.987
6.4	C/x/m = 0.0006x + 0.0022	1666.6	0.27322	454.5	0.983

b = adsorption maximum (μg Cu/g soil).
K = binding energy (ml/μg Cu).
MBC = maximum buffering capacity (μg Cu/g soil).
r = correlation coefficient.

Table (5): Regression parameters calculated from copper adsorption isotherms on calcareous soil according to the Langmuir equation at various pH values.

pH values	Linear equation	b_m	K	MBC	r
5.0	$C/X = 0.0006x + 0.0039$	1666.6	0.1538	256.4	0.936
5.5	$C/X = 0.0005x + 0.0022$	2000	0.2273	454.5	0.918
6.4	$C/X = 0.0005x + 0.0012$	2000	0.4167	833.3	0.988

b = adsorption maximum (μg Cu/g soil).
K = binding energy (ml/μg Cu).
MBC = maximum buffering capacity (μg Cu/g soil).
r = correlation coefficient.

(slope =1/b). They expressed the quantity of Cu adsorbed when the adsorbing surfaces are saturated. In addition, the constant K related to the binding energy could be estimated from the intercept (intercept = 1/Kb). The obtained adsorption maxima and the corresponding binding energies for the studied soils are given in Tables (4 & 5). It is noticed that the alluvial soil has the maximum adsorption values of 2000, 2000 and 1666.6 µg Cu/g soil at pH 5.0, 5.5 and 6.4, respectively, while, the calcareous soil has the maximum adsorption values of 1666.6, 2000 and 2000 µg Cu/g soil at the same pH values, respectively. Comparison between the K values (Cu binding energy) at the different soil pH values reveals that in the alluvial soil these values were at pH 6.4 > at pH 5.5 > at pH 5.0 as K values were 0.273, 0.156 and 0.121, respectively. For the calcareous soil, the same order was observed at the same as K values were 0.416, 0.227 and 0.153, respectively.

Data in Tables (4 & 5) also show the maximum buffering capacity (MBC) which is considered a major soil characteristic controlling crop yield response and hence fertilizer requirement. They were calculated as the product of multiplying adsorption maximum by binding energy. The obtained MBC 's for the studied soils showed that the alluvial soil has lower MBC values than the corresponding ones of the calcareous soil. This trend was observed at various pH values. The soil Cu maximum buffering capacity followed a trend similar to that of soil binding energy. So, the Cu fertilizer requirement of the soil-plant system was a function not only of intensity, concentration of Cu in the soil solution or quantity of Cu in the soil, capacity factor, but also of the buffering capacity of the soil itself.

4.1.1.2. Application of Freundlich equation:

According to Freundlich equation ($x/m = ac^n$) or its logarithmic form ($Ln\ x/m = Ln\ a + n\ Ln\ C$), data of Cu adsorption on the alluvial and calcareous soils fitted to the linear form. Where, a and n are constants, x is the amount of adsorbed Cu in µg/g soil and C is the final equilibrium concentration in µg/mL. Data obtained for Ln C and Ln x/m for the studied soils are given in Tables (6 & 7). They were plotted in Figs. (5 & 6). The results reveal that Freundlich equation is suitable to describe Cu adsorption isotherms for alluvial and calcareous soils up to 100 µg Cu/mL (initial concentration). This effect is obvious at the various studied pH values.

The affinity parameter (n) was calculated from the slope of the natural logarithmic regression lines. These results were 0.604 and 0.466 at pH 5.0; 0.624 and 0.521 at pH 5.5 and 0.534 and 0.521 at pH 6.4 for alluvial and calcareous soils, respectively. Comparing the values of the affinity parameter for both soils, data indicated that they were increased with increasing pH values up to 5.5 then decreased and they were higher in alluvial soil than in calcareous one. Also, the results obtained for linear correlation coefficients (Table, 8) proved that Freundlich equation is significantly suitable to represent Cu adsorption isotherms for the studied soils. The values of correlation coefficient " r " were 0.981**, 0.971** and 0.905** for the alluvial soil at pH values 5.0, 5.5 and 6.4, respectively. The corresponding values for the calcareous soil were 0.965**, 0.983** and 0.953** in the same order. The constants given in Table (8) are related to the capacity factor. They were calculated from the simple regression analysis of the logarithmic form of the obtained data. The inverse Ln "a" values are 241, 275 and 347 for alluvial soil at pH values 5.0, 5.5 and 6.4, respectively.

Table (6): Copper adsorption isotherm on alluvial soil according to Freundlich conventional equation at various pH values.

Initial Cu concentration (µg/ml)	PH 5.0		PH 5.5		PH 6.4	
	Ln C	Ln x/m	Ln C	Ln x/m	Ln C	Ln x/m
10	- 0.223	5.215	- 0.223	5.215	- 0.223	5.215
20	0.470	5.908	0.182	5.929	- 0.223	5.951
40	1.792	6.522	1.411	6.576	0.833	6.625
80	2.493	7.214	2.322	7.241	2.128	7.267
100	3.269	7.296	3.127	7.342	3.243	7.305

C = final equilibrium concentration (µg Cu/ml).
x/m = adsorbed copper (µg Cu/g soil).

Table (7): Copper adsorption isotherm on calcareous soil according to Freundlich conventional equation at various pH values.

Initial Cu concentration (µg/ml)	PH 5.0		PH 5.5		PH 6.4	
	Ln C	Ln x/m	Ln C	Ln x/m	Ln C	Ln x/m
10	- 0.511	5.236	- 1.204	5.267	- 1.204	5.267
20	- 0.105	5.945	- 0.357	5.955	- 1.204	5.976
40	2.104	6.455	1.589	6.553	0.693	6.633
80	2.986	7.093	2.219	7.255	1.621	7.312
100	3.258	7.299	2.747	7.431	2.564	7.461

C = final equilibrium concentration (µg Cu/ml).
x/m = adsorbed copper (µg Cu/g soil).

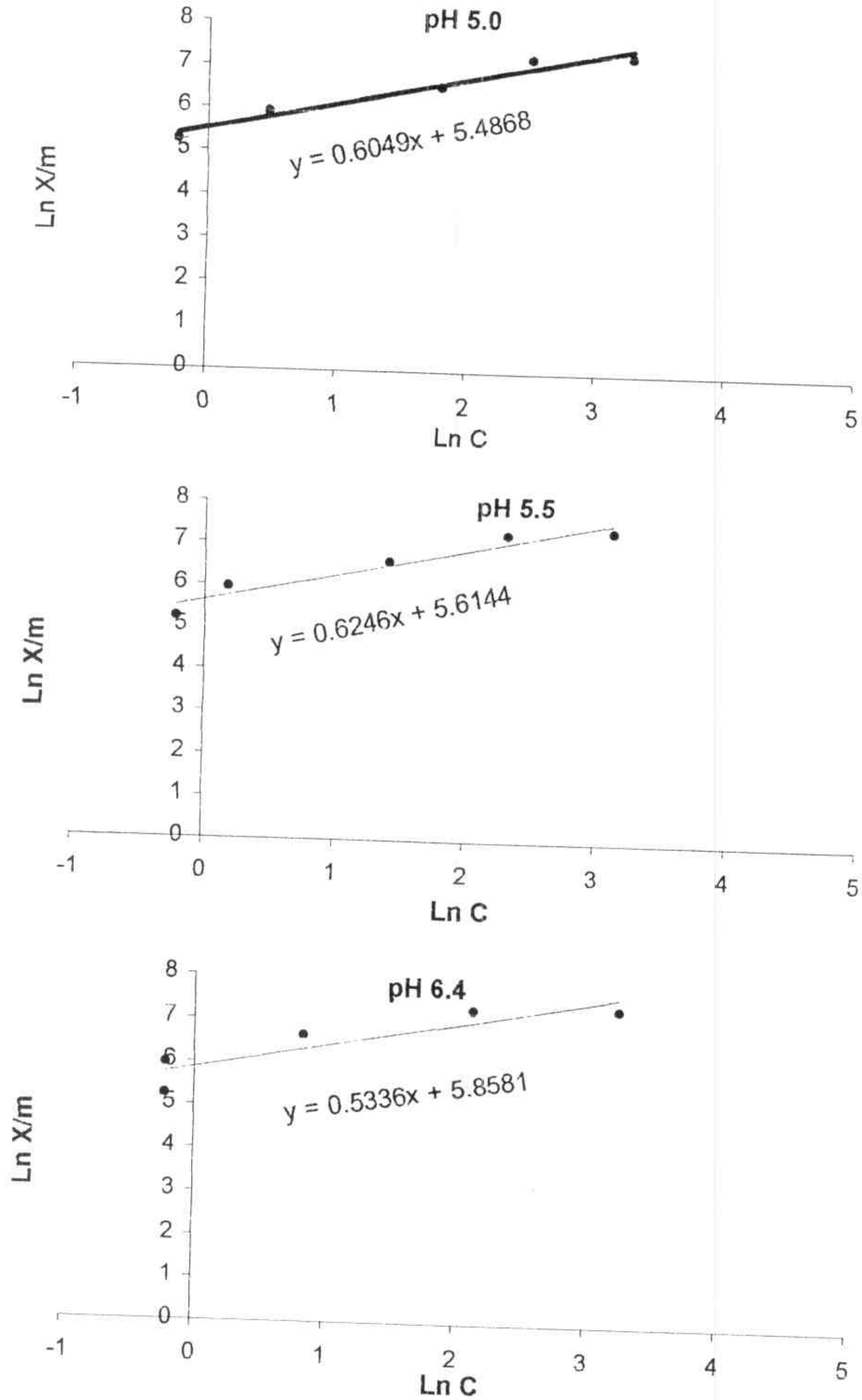


Fig. (5): Copper adsorption isotherms on alluvial soil according to the conventional Freundlich equation at various pH values.

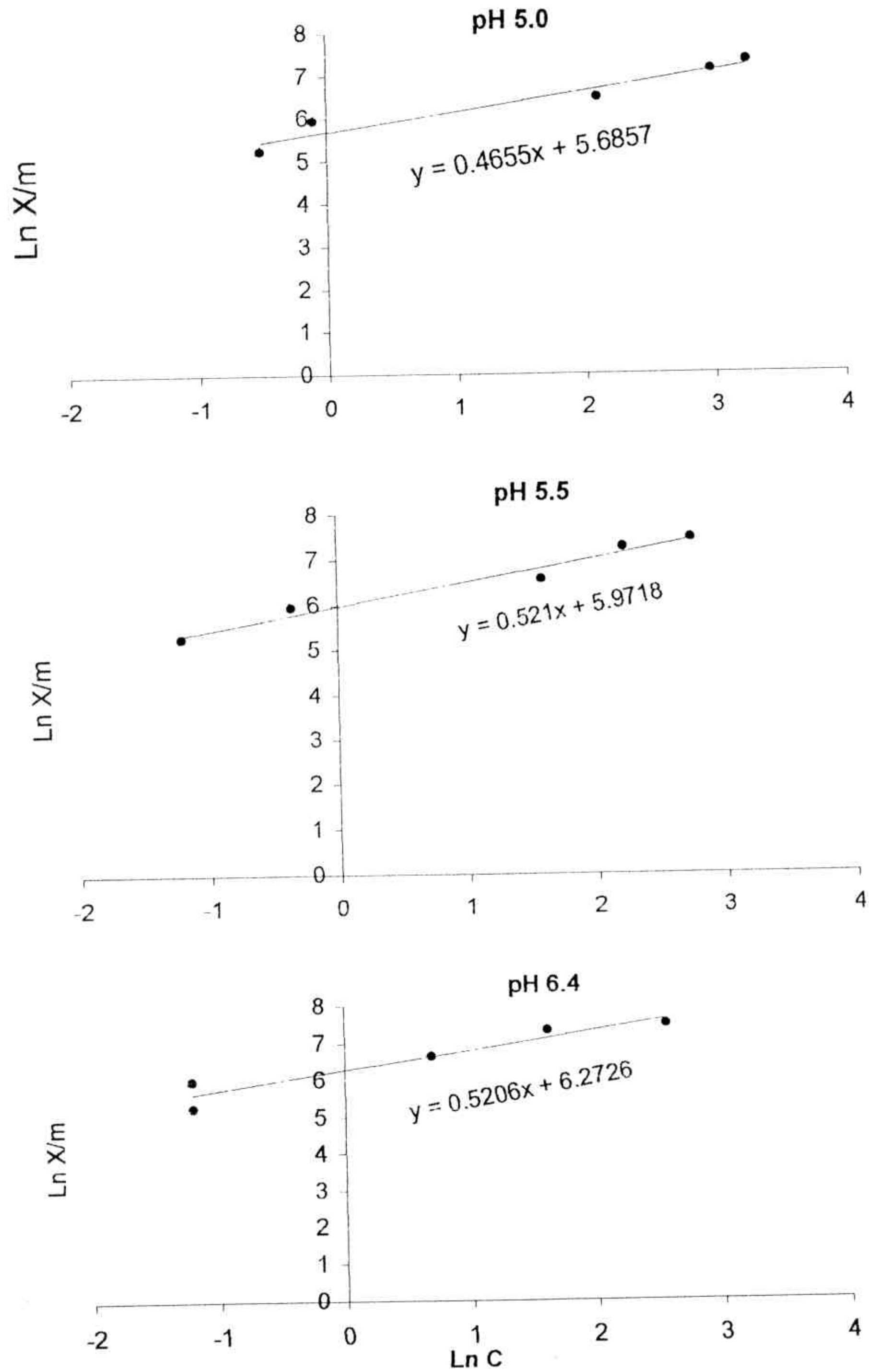


Fig. (6): Copper adsorption isotherms on calcareous soil according to the conventional Freundlich equation at various pH values.

Table (8): Regression parameters calculated from adsorption data for Freundlich isotherms on alluvial and calcareous soils at various pH values.

PH values	Alluvial soil			Calcareous soil		
	Lna	n	r	Lna	n	r
5.0	5.486	0.604	0.981	5.686	0.466	0.965
5.5	5.614	0.625	0.971	5.972	0.521	0.983
6.4	5.858	0.534	0.905	6.273	0.521	0.953

a = intercept
n = slope
r = correlation coefficient

While, the corresponding values for calcareous soil were 295, 390 and 530 in the same order.

4.1.1.3. Application of Temkin equation:

The simplest form of Temkin equation is

$$X = a + b \ Ln \ C$$

Where, a and b are constants, X = the amount of adsorbed + native adsorbed copper, and C is the final Cu equilibrium concentration. A plot of X against Ln C under various pH values was performed for the studied soils (Figs., 7 & 8). Their values are presented in Tables (9 & 10). Such plots gave straight lines.

The model of adsorption from which Temkin equation was derived is one in which the bonding energy (affinity parameter) decreases linearly as the amount of adsorption increases (Table, 11). The correlation coefficients of the studied soils were 0.967**, 0.984** and 0.966** for alluvial soil, while it was 0.939**, 0.937** and 0.973** for calcareous soil at pH values 5.0, 5.5 and 6.4, respectively. These values proved that Temkin isotherm model is quite suitable to be used for describing Cu adsorption on the studied soils.

4.1.2. Adsorption of copper by clay minerals:

Clay minerals used in this study were montmorillonite and palygorskite. Copper adsorption by such clay minerals under the different studied pH values is graphically illustrated in Figs. (9 & 10). Copper adsorbed on the surfaces of montmorillonite and palygorskite increased gradually with increasing the initial Cu concentrations up to 100 µg/mL. This trend was observed at the various pH values. However, this increase was, generally, more pronounced at pH 5.5, where the highest adsorption of Cu was 6820 and 6700 µg/g of montmorillonite and palygorskite, respectively

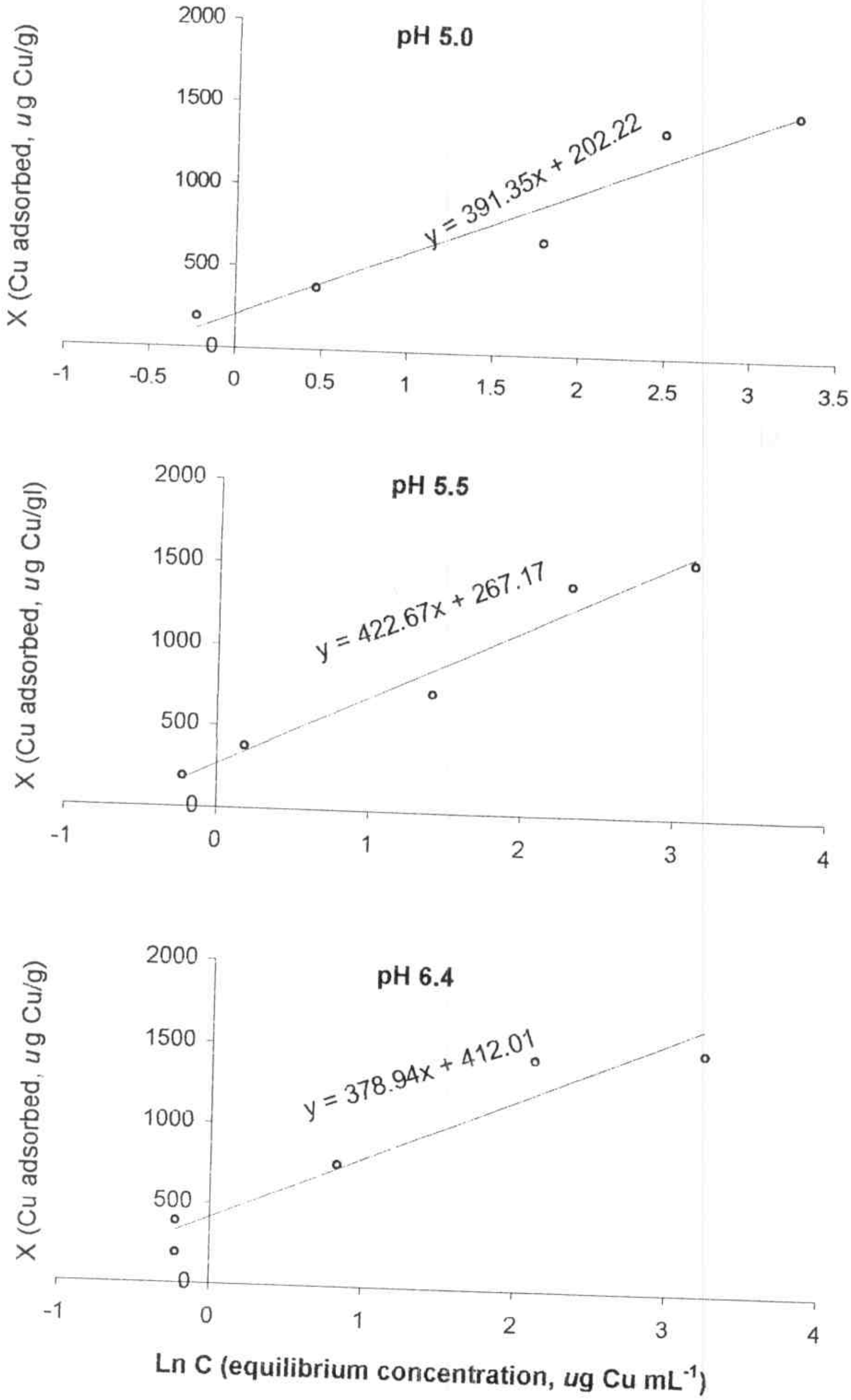


Fig. (7): Copper adsorption isotherms on alluvial soil according to the conventional Temkin equation at various pH values.

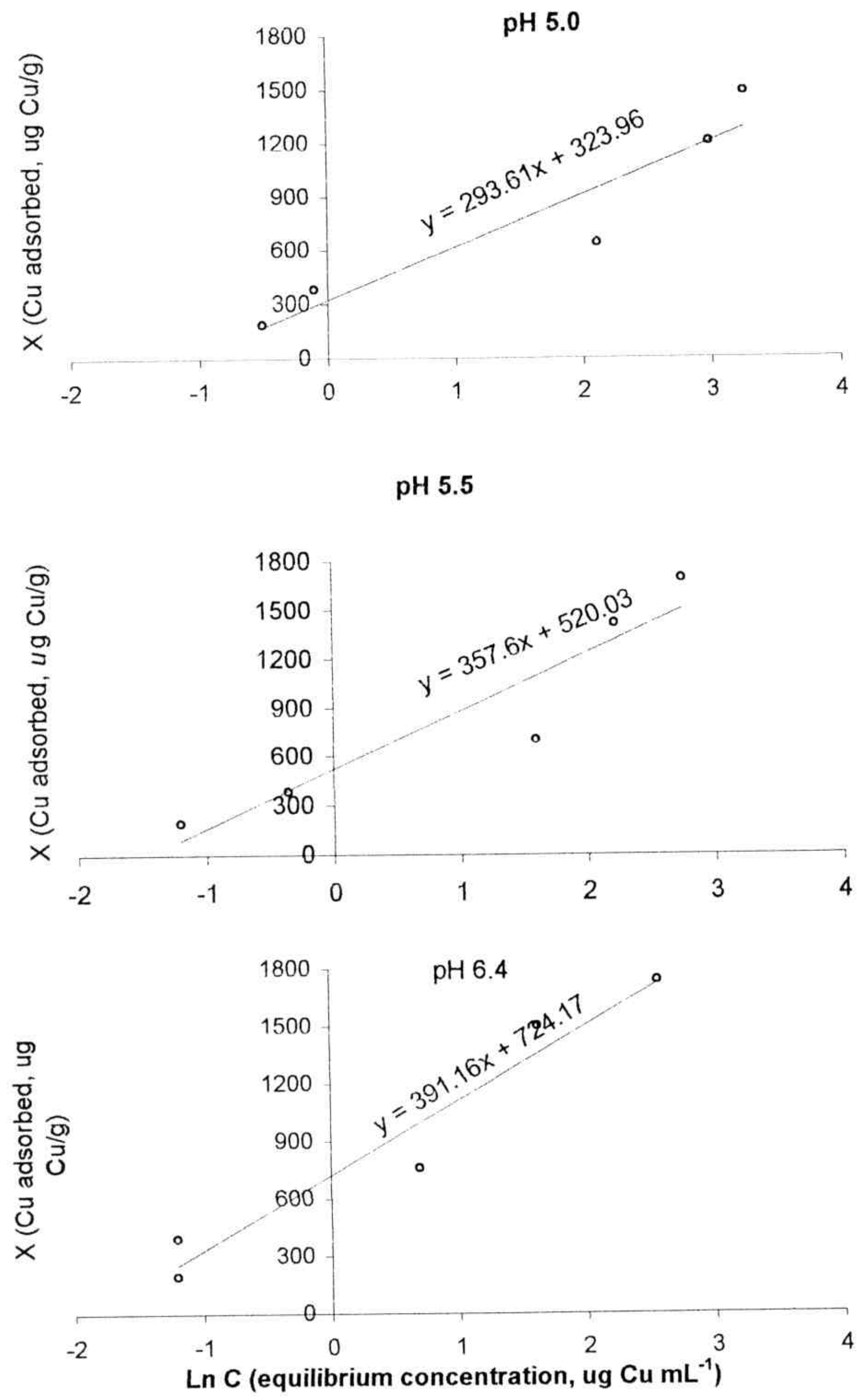


Fig. (8): Copper adsorption isotherms on calcareous soil according to the conventional Temkin equation at various pH values.

Table (9): Copper adsorption isotherm on alluvial soil according to Temkin conventional equation at various pH values.

Initial Cu concentration (µg/ml)	PH 5.0		PH 5.5		PH 6.4	
	Ln C	X	Ln C	X	Ln C	X
10	- 0.223	184	- 0.223	184	- 0.223	184
20	0.470	368	0.182	376	- 0.223	384
40	1.792	680	1.411	718	0.833	754
80	2.493	1358	2.322	1396	2.128	1432
100	3.269	1474	3.127	1544	3.243	1488

C = final equilibrium concentration (µg Cu/ml).
X = adsorbed copper (µg Cu/g soil).

Table (10): Copper adsorption isotherm on calcareous soil according to Temkin conventional equation at various pH values.

I Cu concentration (µg/ml)	PH 5.0		PH 5.5		PH 6.4	
	n C	X	Ln C	X	Ln C	X
10	0.511	188	1.204	194	1.204	194
20	0.105	382	0.357	386	1.204	394
40	2.104	636	1.589	702	0.693	760
80	2.986	204	2.219	416	1.621	499
100	3.258	480	2.747	688	2.564	740

C = final equilibrium concentration (µg Cu/ml).
X = adsorbed copper (µg Cu/g soil).

Table (11): Regression parameters calculated from adsorption data for Temkin isotherms on alluvial and calcareous soils at various pH values.

PH values	Alluvial soil			Calcareous soil		
	a	b	r	a	b	r
5.0	202.22	391.35	0.967	323.96	293.61	0.939
5.5	267.17	422.67	0.984	520.03	357.60	0.937
6.4	412.01	378.94	0.966	724.17	391.16	0.973

a = intercept
b = slope
r = correlation coefficient

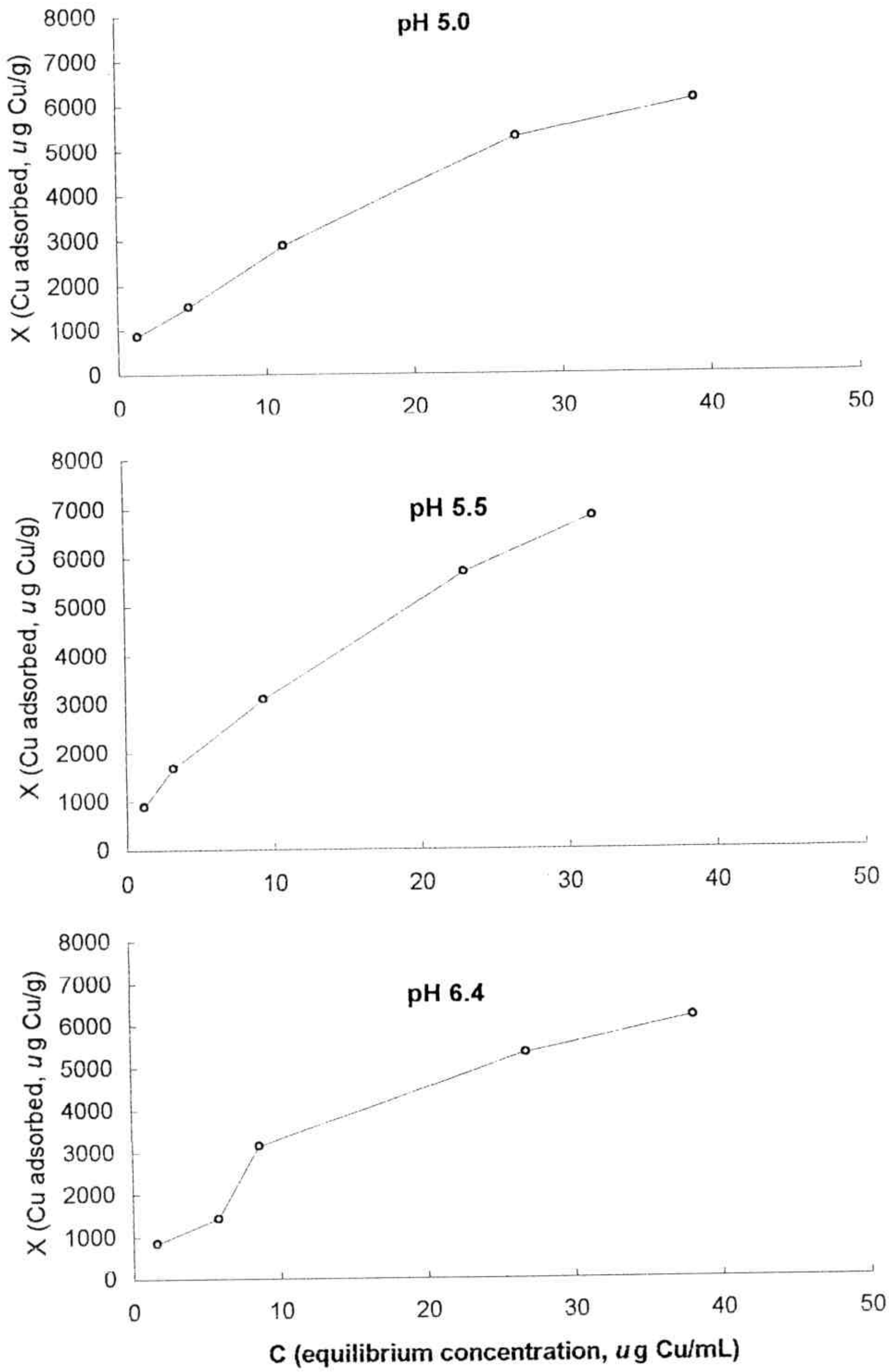


Fig. (9): Copper adsorption isotherms on montmorillonite at various pH values.

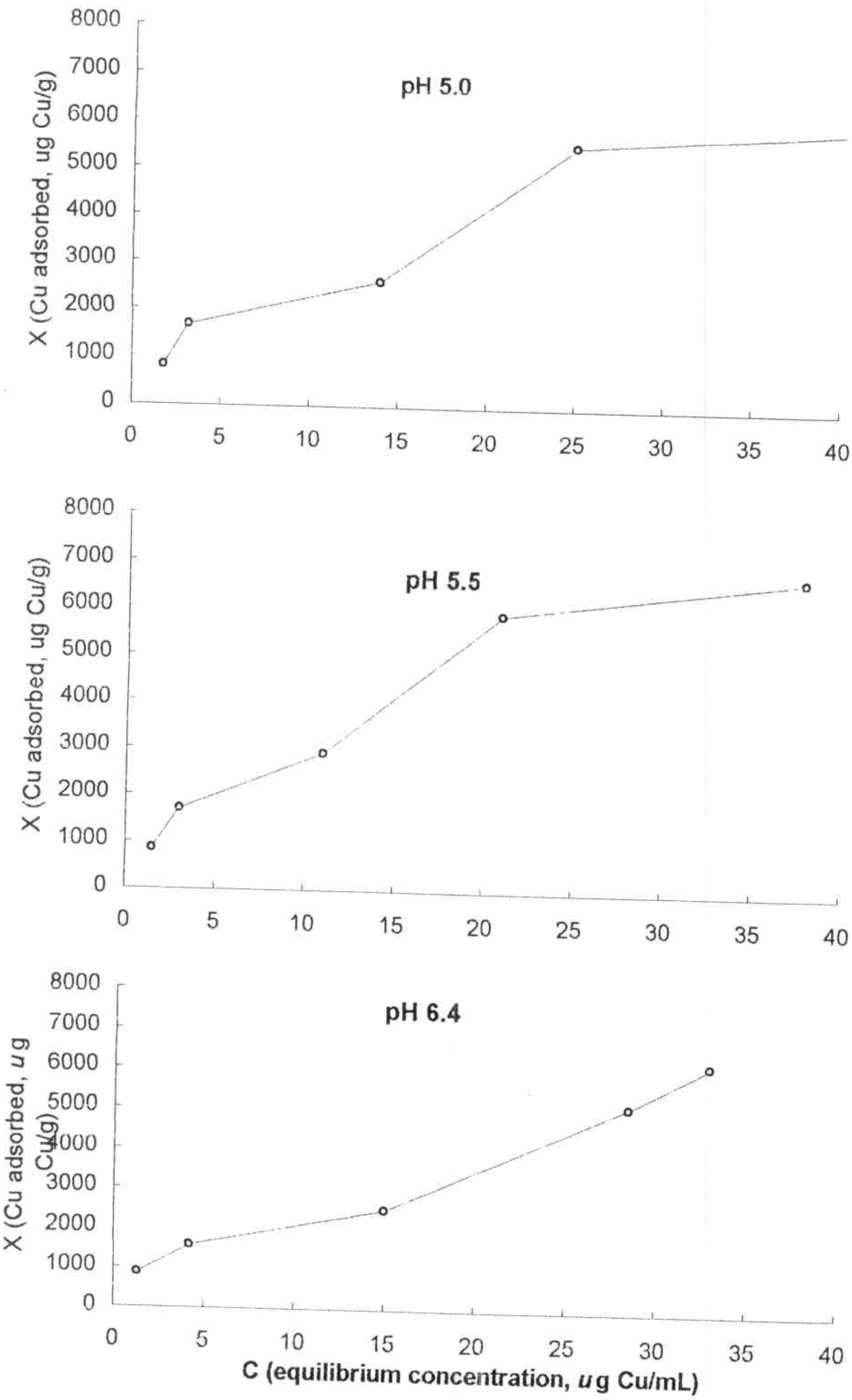


Fig. (10): Copper adsorption isotherms on palygoiskite at various pH valu

when the initial Cu concentration was 100 μg/mL. Generally, adsorption of Cu on montmorillonite under different concentrations of Cu was higher than the corresponding one observed with palygorskite. This increase may be attributed to the higher negative charge found on the surface of montmorillonite mineral. These results are in agreement with those obtained by **Mohamed (2002)**. **Takahashi and Imai (1983)** reported that montmorillonite surface seems to provide the heavy metal cations with three types of adsorption sites. Adsorption onto site I corresponded to the ion exchange reaction where divalent cations are adsorbed up to 70 – 85 % of the adsorption maximum through this reaction. Adsorption into site III which is attributed to the precipitation of the metal hydroxides in the bulk solution. Adsorption into site II also seemed to be closely related to the formation of hydroxy species of the metal cations and exceeded the CEC-value of the montmorillonite.

Data also show that Cu adsorption did not reach a maximum even at the highest concentration of Cu (100 μg/mL) for both of the two minerals. However, at all Cu concentrations, both minerals appeared to have the same magnitude of adsorbed Cu.

4.1.2.1. Application of Langmuir equation:

Values of C/x/m for the different concentrations of Cu adsorbed on montmorillonite and Palygorskite were plotted against the corresponding C ones at the different pH values. These results are illustrated in Figs. (11 & 12) and presented in Tables (12 & 13). The obtained results for montmorillonite and palygroskite minerals fit the conventional Langmuir isotherm. The correlation coefficients obtained by the regression analysis at pH 5.0, 5.5 and 6.4 were 0.959**, 0.973** and 0.916** for montmorillonite and 0.909**, 0.949** and 0.812** for Palygorskite, respectively. At pH 5.0, the samples of montmorillonite and palygroskite sorbed 61 and

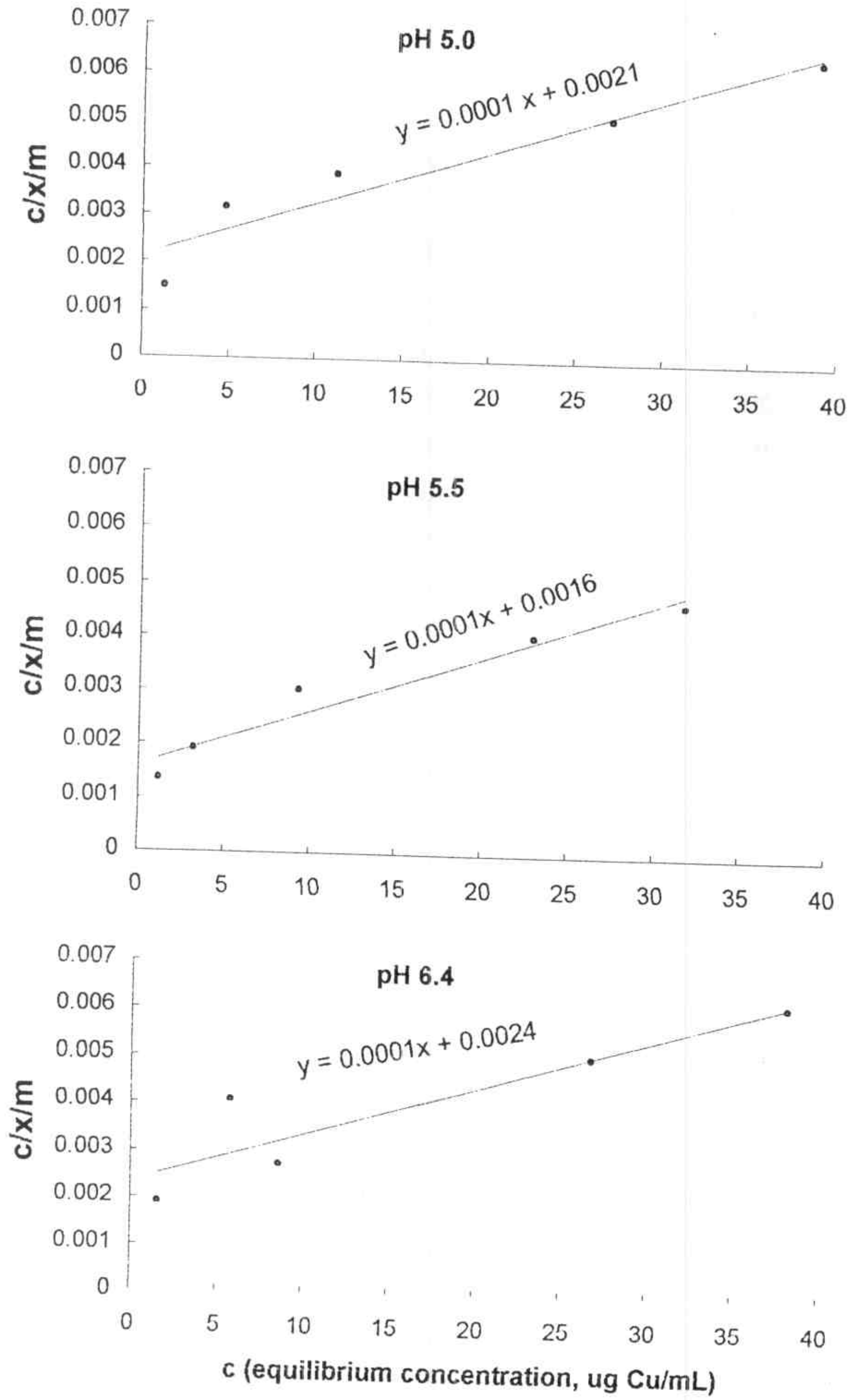


Fig. (11): Copper adsorption isotherms by Mont. mineral according to the conventional Langmuir equation.

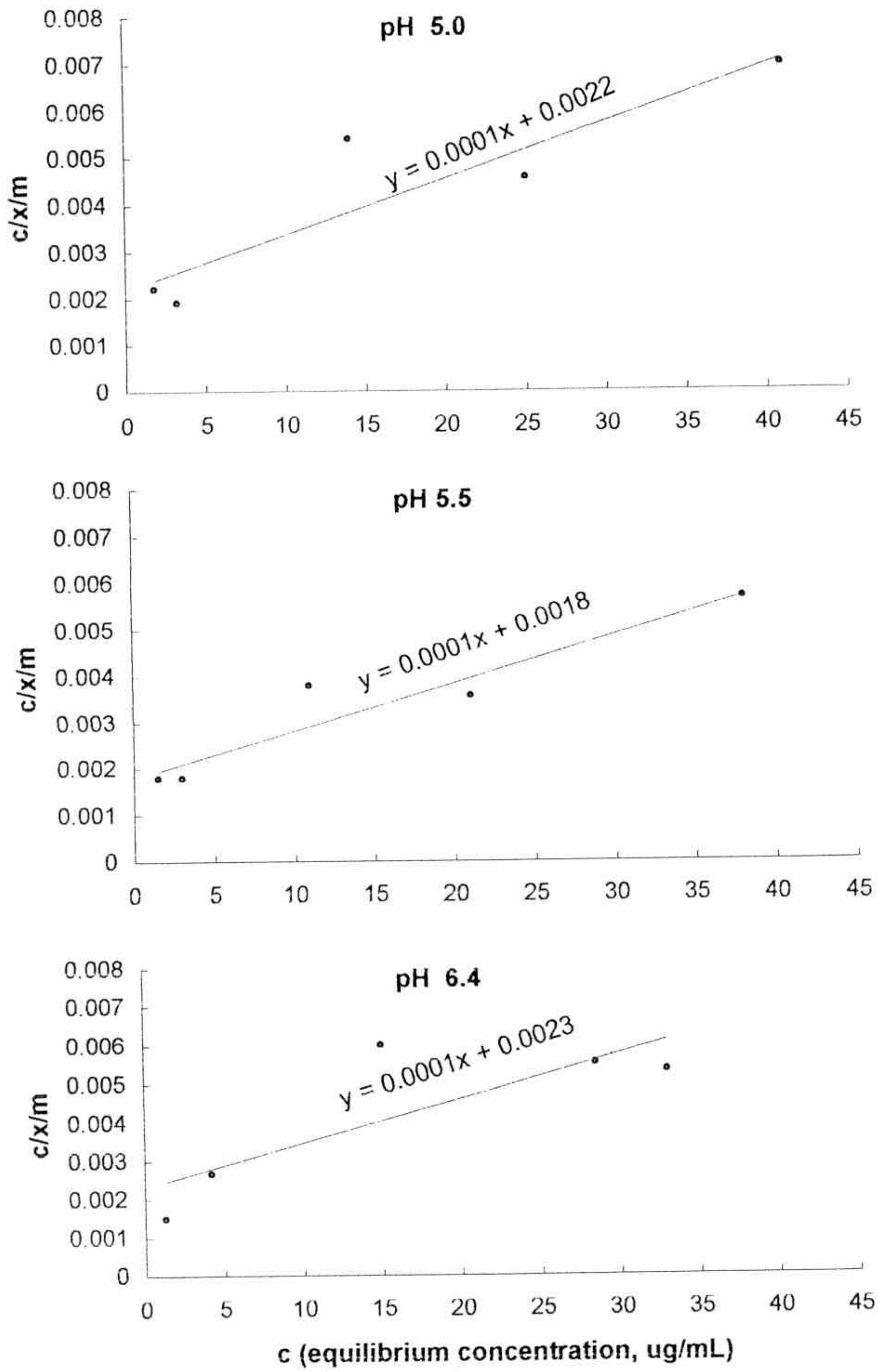


Fig. (12): Copper adsorption isotherms by Palygoiskite mineral according to the conventional Langmuir equation.

Table (12): Copper adsorption isotherm on montmorillonite according to the Langmuir conventional equation at various pH values.

Initial Cu concentration (µg/ml)	PH 5.0			PH 5.5			PH 6.4		
	C	x/m	C/x/m	C	x/m	C/x/m	C	x	C/x/m
10	1.3	870	0.00149	1.2	880	0.00136	1.6	840	0.00191
20	4.8	1520	0.00316	3.2	1680	0.00191	5.8	1420	0.00408
40	11.2	2880	0.00389	9.3	3070	0.00303	8.6	3140	0.00274
80	27	5300	0.00509	23.0	5700	0.00404	26.8	5320	0.00504
100	39	6100	0.00639	31.8	6820	0.00466	38.2	6180	0.00618

C = final equilibrium concentration (µg Cu/ml).
x/m = adsorbed copper (µg Cu/g soil).

Table (13): Copper adsorption isotherm on palgyorskite according to the Langmuir conventional equation at various pH values.

Initial Cu concentration (µg/ml)	PH 5.0			PH 5.5			PH 6.4		
	C	x/m	C/x/m	C	x/m	C/x/m	C	x/m	C/x/m
10	1.8	820	0.00220	1.5	850	0.00177	1.3	870	0.00149
20	3.2	1680	0.00190	3.0	1700	0.00177	4.2	1580	0.00266
40	14.0	2600	0.00538	11.0	2900	0.00379	15.0	2500	0.00600
80	25.0	5500	0.00455	21.0	5900	0.00356	28.5	5150	0.00553
100	41.0	5900	0.00695	38.0	6700	0.00567	33.0	6200	0.00532

C = final equilibrium concentration (µg Cu/ml).
x/m = adsorbed copper (µg Cu/g soil).

59 %, respectively from the initial Cu concentration, i.e. 100 μg/mL. The corresponding values at pH 5.5 were 68.2 and 62 % for montmorillonite and Palygorskite, respectively, while, at pH 6.4, the percentages of Cu adsorbed on montmorillonite and Palygorskite were 61.8 and 67 %, respectively.

From the simple linear relationships between C/x/m vs. C (Figs. 11 & 12), Cu adsorption maxima (b) were calculated from the slope of the straight line. They explained the maximum quantities of adsorbed Cu when the surface of mineral are saturated. Also, the constant K related to the binding energy could be estimated from the intercept. Their values for montmorillonite and Palygorskite minerals are given in Tables (14 & 15), respectively. It is obvious that the two minerals have almost the same maximum adsorption values of 10000 μg Cu/g mineral at the different studied pH values. On the other hand, the differences in the constant K (binding energy) between the minerals were widened as the pH increased. The montmorillonite had the order of pH 5.5 > pH 5.0 > pH 6.4. The K values were 0.0625, 0.0476 and 0.0416, for montmorillonite at pH 5, 5.5 and 6.4. The corresponding K values for Palygorskite were 0.0555, 0.0455 and 0.0434, at pH 5, 5.5 and 6.4, respectively.

4.1.2.2. Application of Freundlich equation:

Data obtained for Ln C and Ln x/m for the studied clay minerals are shown in Tables (16 & 17) and were plotted in Figs. (13 & 14). Data reveal that Freundlich equation is suitable to describe Cu adsorption isotherms for montmorillonite and Palygorskite minerals up to 100 μg Cu/mL (initial concentration). This response being obvious at different pH values. Values of the affinity parameter (n) were 0.598 and 0.590 at pH 5.0; 0.623 and 0.633 at pH 5.5 and 0.658 and 0.579 at pH 6.4 for montmorillonite

Table (14): Regression parameters calculated from copper adsorption isotherms by montmorillonite according to the Langmuir equation at different pH values.

pH values	Linear equation	b	K	MBC	r
5.0	C/x/m = 0.0001x + 0.0021	10000	0.0476	476.2	0.959
5.5	C/x/m = 0.0001x + 0.0016	10000	0.0625	625.0	0.973
6.4	C/x/m = 0.0001x + 0.0024	10000	0.0416	416.7	0.916

b = adsorption maximum (µg Cu/g soil).
K = binding energy (ml/µg Cu).
MBC = maximum buffering capacity (µg Cu/g soil).
r = correlation coefficient.

Table (15): Regression parameters calculated from copper adsorption isotherms by palygorskite according to the Langmuir equation at different pH values.

pH values	Linear equation	b	K	MBC	r
5.0	C/x/m = 0.0001x + 0.0022	10000	0.0455	454.5	0.909
5.5	C/x/m = 0.0001x + 0.0017	10000	0.0588	588.2	0.957
6.4	C/x/m = 0.0001x + 0.0024	10000	0.0416	416.7	0.773

b = adsorption maximum (µg Cu/g soil).
K = binding energy (ml/µg Cu).
MBC = maximum buffering capacity (µg Cu/g soil).
r = correlation coefficient.

Table (16): Copper adsorption isotherm on montmorillonite according to Freundlich conventional equation at various pH values.

Initial Cu concentration (µg/ml)	PH 5.0		PH 5.5		PH 6.4	
	Ln C	Ln x/m	Ln C	Ln x/m	Ln C	Ln x/m
10	0.262	6.768	0.182	6.779	0.470	6.733
20	1.568	7.326	1.163	7.426	1.757	7.258
40	2.415	7.965	2.230	8.029	2.151	8.051
80	3.295	8.575	3.135	8.648	3.288	8.579
100	3.663	8.716	3.459	8.827	3.642	8.729

C = final equilibrium concentration (µg Cu/ml).
x/m = adsorbed copper (µg Cu/g soil).

Table (17): Copper adsorption isotherm on palgyorskite according to Freundlich conventional equation at various pH values

Initial Cu concentration (μg/ml)	PH 5.0		PH 5.5		PH 6.4	
	Ln C	Ln x/m	Ln C	Ln x/m	Ln C	Ln x/m
10	0.587	6.709	0.405	6.745	0.262	6.768
20	1.163	7.426	1.098	7.438	1.435	7.365
40	2.639	7.863	2.397	7.972	2.708	7.824
80	3.218	8.612	3.044	8.682	3.349	8.546
100	3.713	8.628	3.637	8.809	3.496	8.732

C = final equilibrium concentration (μg Cu/ml).
x/m = adsorbed copper (μg Cu/g soil).

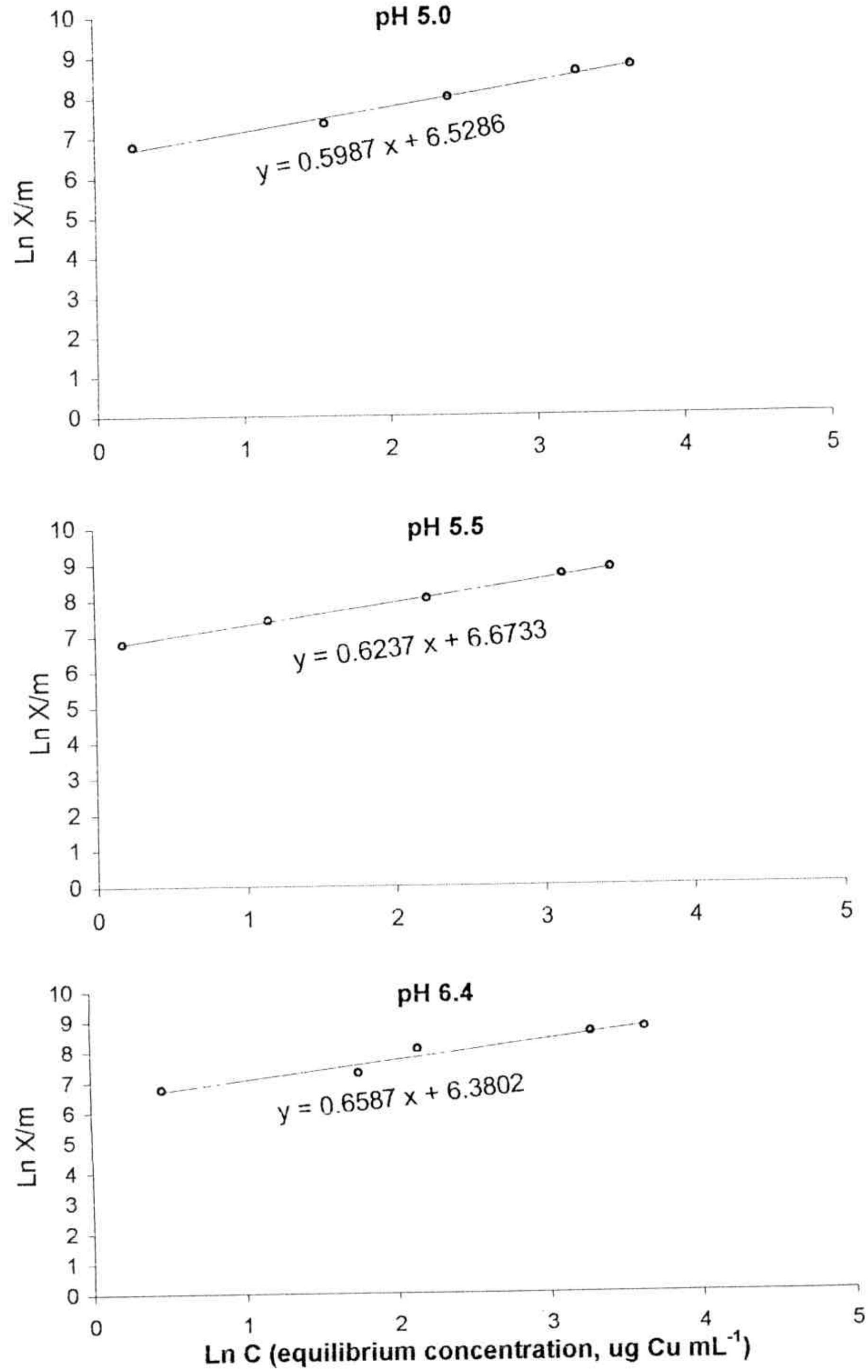


Fig. (13): Copper adsorption isotherms on montmorillonite according to t conventional Freundlich equation at various pH values.

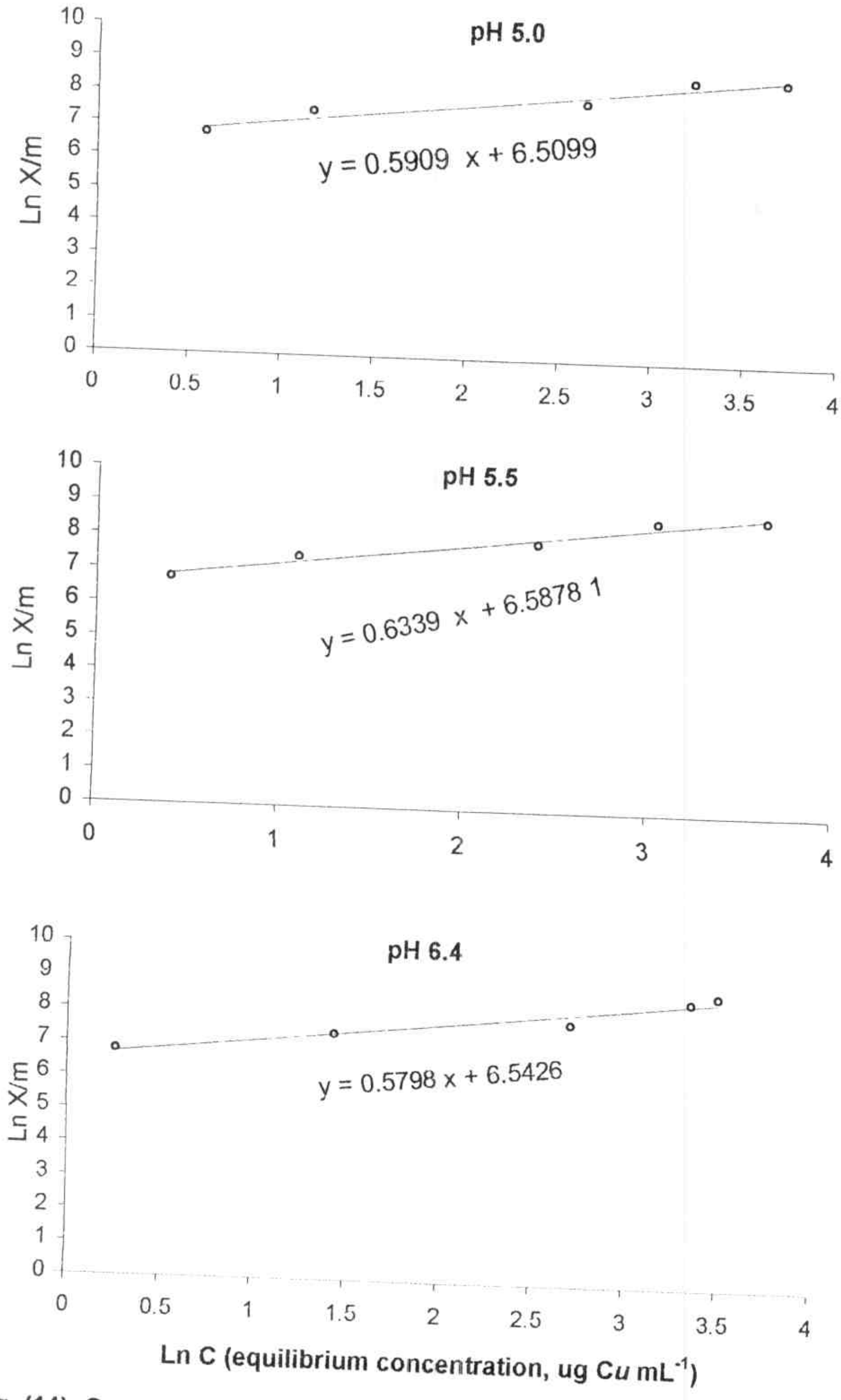


Fig. (14): Copper adsorption isotherms on palygoiskite according to the conventional Freundlich equation at various pH values.

and Palygorskite, respectively. Comparing values of the affinity parameter for both minerals, revealed an increase with increasing pH values up to 6.4 for montmorillonite and only up to 5.5 for Palygorskite. Also, values of the affinity parameter were, generally, higher for montmorillonite, than for Palygorskite.

The results obtained for the linear correlation coefficients (Table, 18) prove that Freundlich equation is significantly suitable to represent Cu adsorption on the studied montmorillonite and Palygorskite minerals. The "r" values were 0.994**, 0.999** and 0.974** for montmorillonite at pH values 5.0, 5.5 and 6.4, respectively. The corresponding values for Palygorskite were 0.969**, 0.985** and 0.977** at the same order. The constants given in Table (18) were calculated from the simple regression equation of the logarithmic form of the obtained data. The inverse Ln a values were 684, 790 and 590 for montmorillonite at pH values 5.0, 5.5 and 6.4, respectively. While, the corresponding values for palygorskite were 670, 720 and 695 in the same order.

4.1.2.3. Application of Temkin equation:

A plot of X values against Ln C ones at the different studied pH values were performed for the studied clay minerals (Figs., 15 & 16). The results of Tables (19 & 20) proved that increasing pH values from 5.0 to 6.4 was associated with an increase in Cu adsorption on the surfaces of montmorillonite and palygroskite minerals. The correlation coefficients (Table, 21) were 0.954**, 0.966** and 0.960** for montmorillonite, while they were 0.943**, 0.960** and 0.905** for Palygorskite at pH values 5.0, 5.5 and 6.4, respectively. These results indicate that Temkin isotherm model is suitable to be applied for the studied minerals as shown in the cases of Langmuir and Freundlich equations.

Table (18): Regression parameters calculated from adsorption data for Freundlich isotherms on clay minerals at various pH values.

PH	Montmorillonite			Palgyorskite		
values	Lna	n	r	Lna	n	r
5.0	6.528	0.598	0.994	6.509	0.590	0.969
5.5	6.673	0.623	0.999	6.587	0.633	0.985
6.4	6.380	0.658	0.974	6.542	0.579	0.977

a = intercept
n = slope
r = correlation coefficient

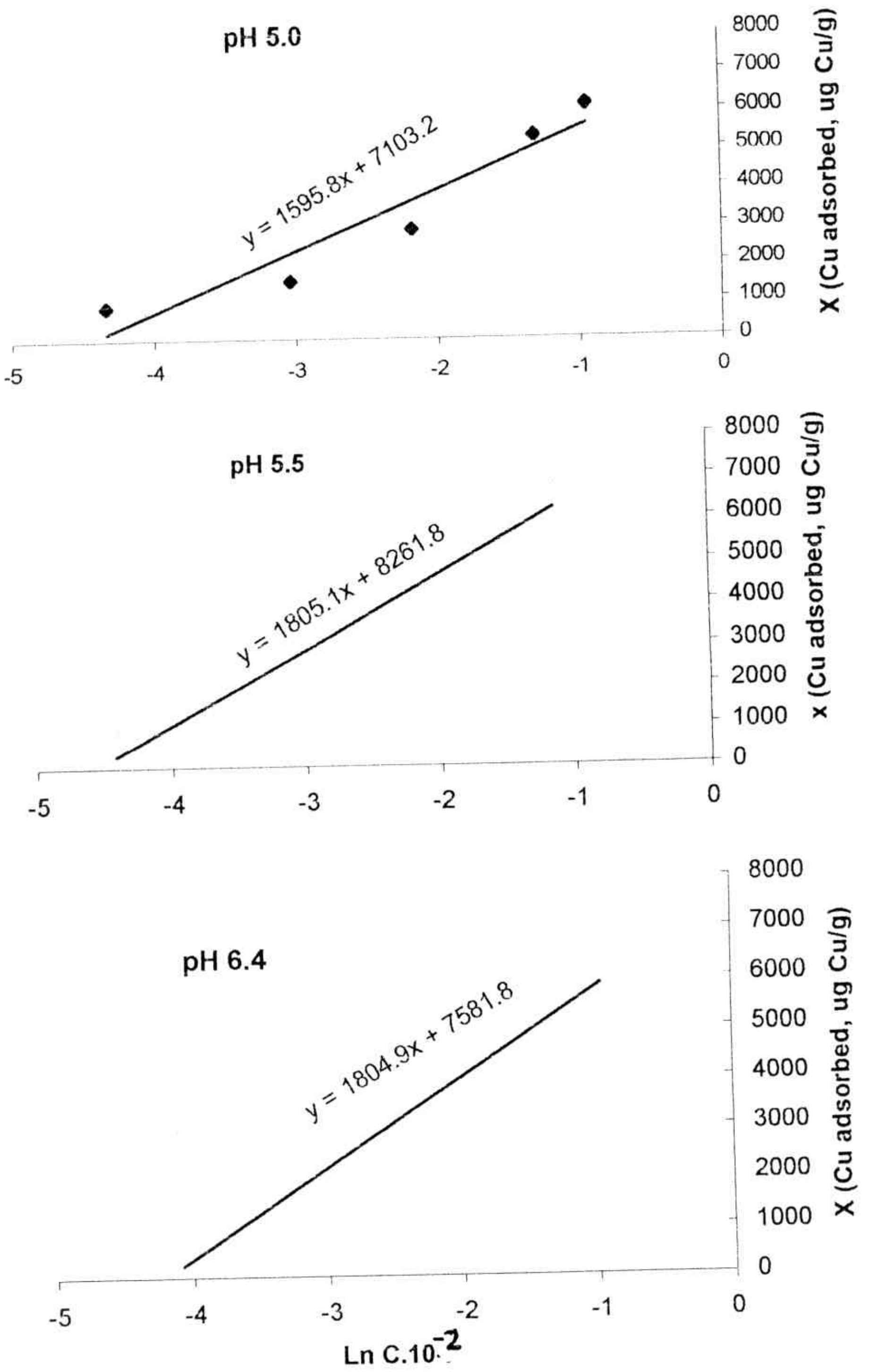


Fig. (15): Copper adsorption isotherms on montmorillonite according to the conventional Temkin equation at various pH values.

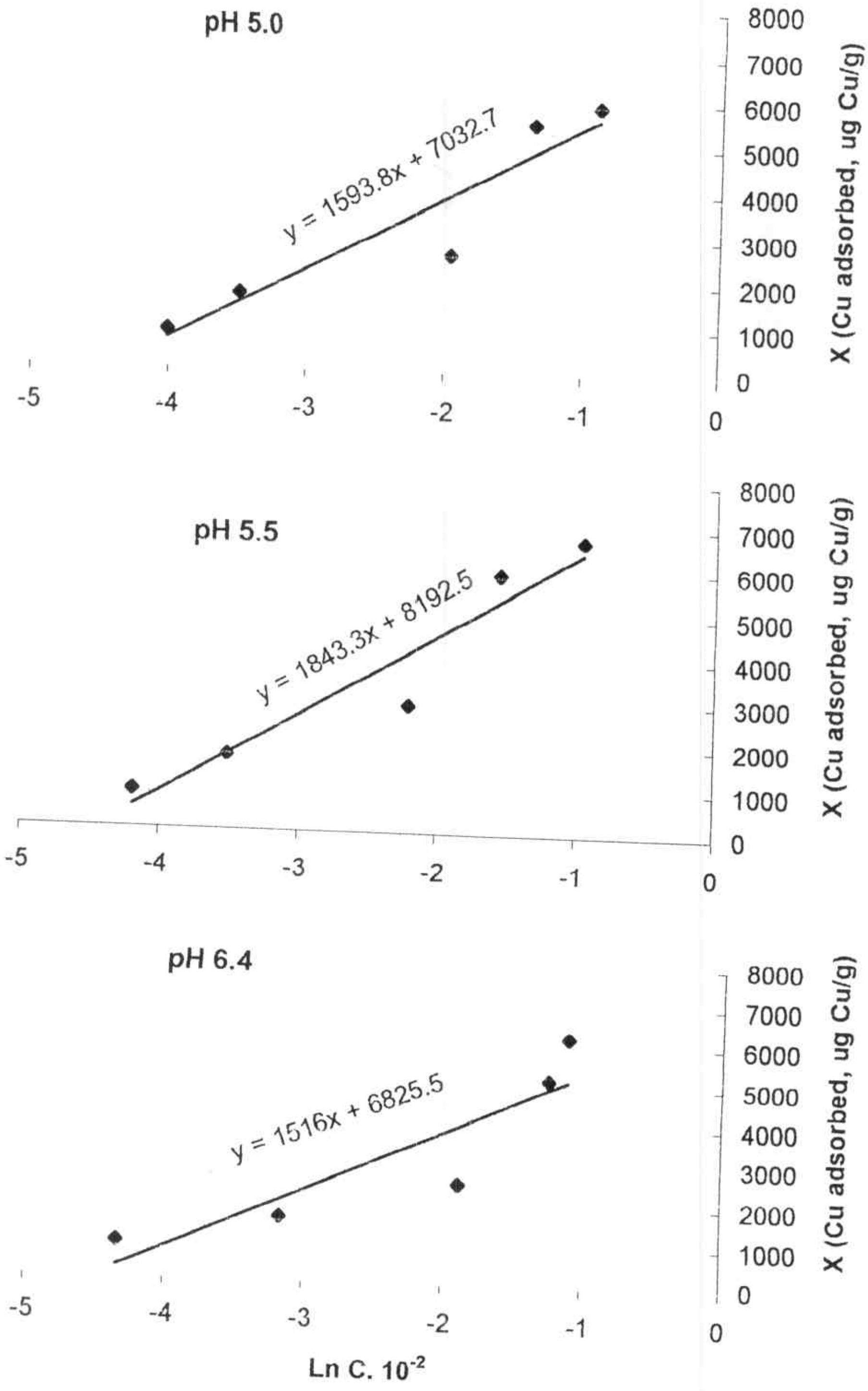


Fig. (16): Copper adsorption isotherms on palygorskite according to the conventional Temkin equation at various pH values.

Table (19): Copper adsorption isotherm on montmorillonite according to Temkin conventional equation at various pH values.

Initial Cu concentration (µg/ml)	PH 5.0		PH 5.5		PH 6.4	
	Ln C. 10^{-2}	X	Ln C. 10^{-2}	X	Ln C. 10^{-2}	X
10	-4.34	870	-4.42	880	-4.08	840
20	-3.04	1520	-3.44	1680	-2.84	1420
40	-2.18	2880	-2.37	3070	-2.45	3140
80	-1.31	5300	-1.46	5700	-1.31	5320
100	-0.94	6100	-1.14	6820	-0.96	6180

C = final equilibrium concentration (µg Cu/ml).
X = adsorbed copper (µg Cu/g soil).

Table (20): Copper adsorption isotherm on palgyorskite according to Temkin conventional equation at various pH values

Initial Cu concentration (µg/ml)	PH 5.0		PH 5.5		PH 6.4	
	Ln C. 10^{-2}	X	Ln C. 10^{-2}	X	Ln C. 10^{-2}	X
10	-4.01	820	-4.19	850	-4.34	870
20	-3.49	1680	-3.51	1700	-3.17	1580
40	-1.96	2600	-2.21	2900	-1.89	2500
80	-1.36	5500	-1.56	5900	-1.25	5150
100	-0.89	5900	-0.96	6700	-1.11	6200

C = final equilibrium concentration (µg Cu/ml).
X = adsorbed copper (µg Cu/g soil).

Table (21): Regression parameters calculated from adsorption data for Temkin isotherms on clay minerals at various pH values.

PH values	Montmorillonite			Palgyorskite		
	a	b	r	a	b	r
5.0	7103.2	1596.2	0.954	7032.7	1609.3	0.943
5.5	8261.8	1808.2	0.966	8192.5	1841.7	0.960
6.4	7581.8	1774.9	0.960	6825.5	1517.5	0.905

a = intercept
b = slope
r = correlation coefficient

4.1.3. Adsorption of copper on humic acid:

Adsorption of Cu on humic acid as organic material at different pH values is graphically illustrated in Fig. (17). Increasing the initial Cu concentrations from 0 to 100 µg/mL was associated with an increase in Cu adsorbed on humic acid. This trend was observed at various pH values. Also, increasing pH values from 5.0 to 6.4 was associated with an increase of Cu adsorbed on humic. This increase was much pronounced at pH 5.5, where the highest adsorption of Cu was 8440 µg/g humic at initial Cu concentration of 100 µg/mL, probably due to increasing the positive charge. In this connection, **Murphy et al. (1990)** reported that, upon low pH values (pH < 6), the humic substances favor the copper adsorption centers, while upon higher pH values, they inhibit this process by the formation of non adsorbed aquacomplexes.

Moreover, Cu adsorption on humic acid did not reach its maximum even at the highest concentration of Cu (100 µg/mL), where the percent of Cu adsorbed on humic reached 34.6, 42.2 and 30.8 % from the highest initial concentration (100 µg/mL) at pH 5.0, 5.5 and 6.4, respectively. **Bansal (1993)** showed that, in the presence of humic acid, the added copper was slowly inactivated.

4.1.3.1. Application of Langmuir equation:

Values of the ratio C/x/m for the different concentrations of Cu in equilibration with the humic acid were plotted against the corresponding C ones at the various pH values (Fig. 18) and presented in Table (22). The adsorption confirmed to the conventional Langmuir isotherm, where the correlation coefficients (Table, 23) were 0.875**, 0.937** and 0.970** at pH 5.0, 5.5 and 6.4, respectively. The highest Cu adsorbed on humic acid was observed at pH 5.5, where 42.2 % from initial Cu concentration (100 µg/mL) was adsorbed.

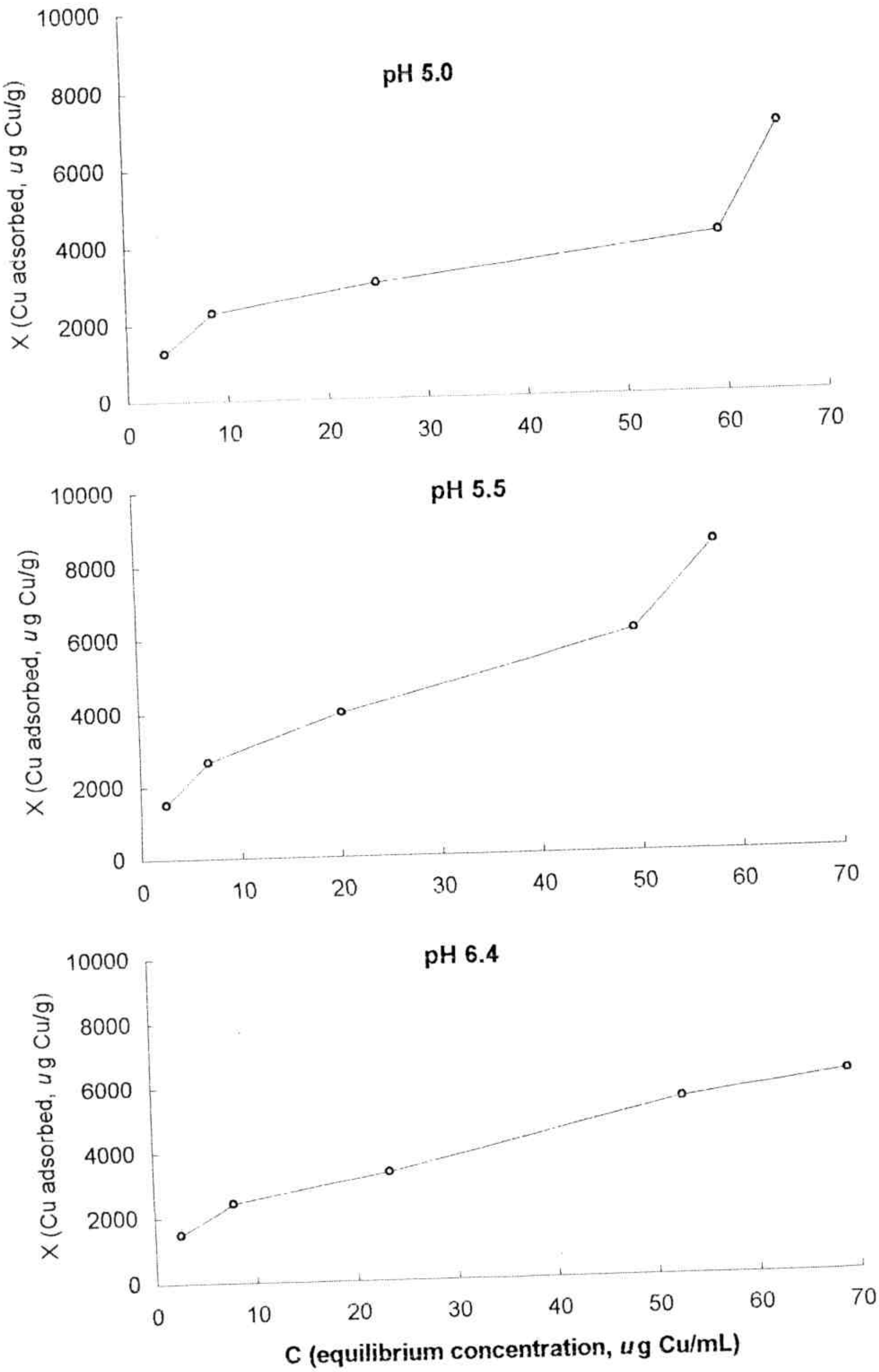
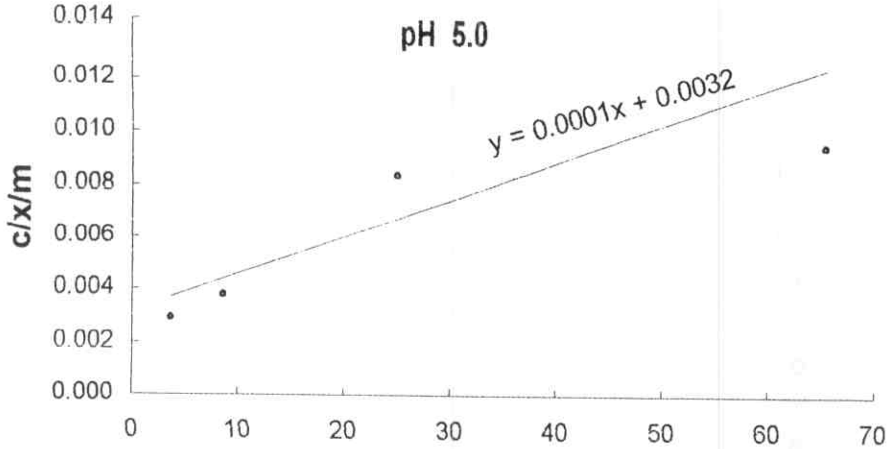
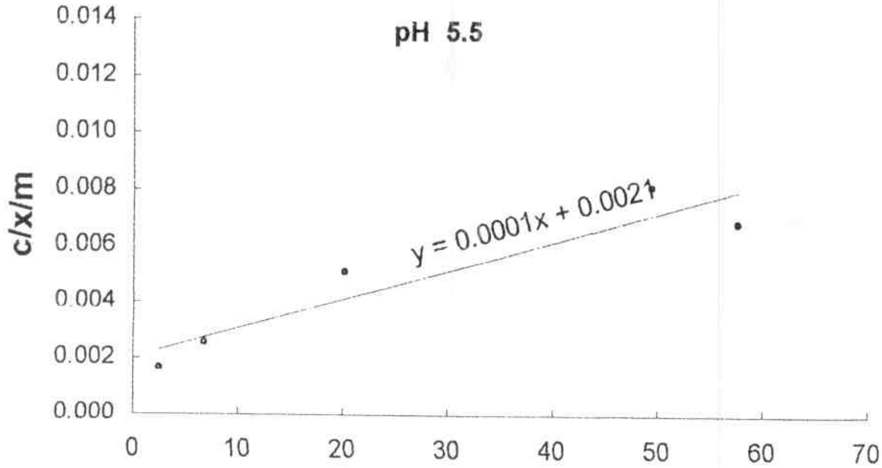


Fig. (17): Copper adsorption isotherms on humic acid at various pH value





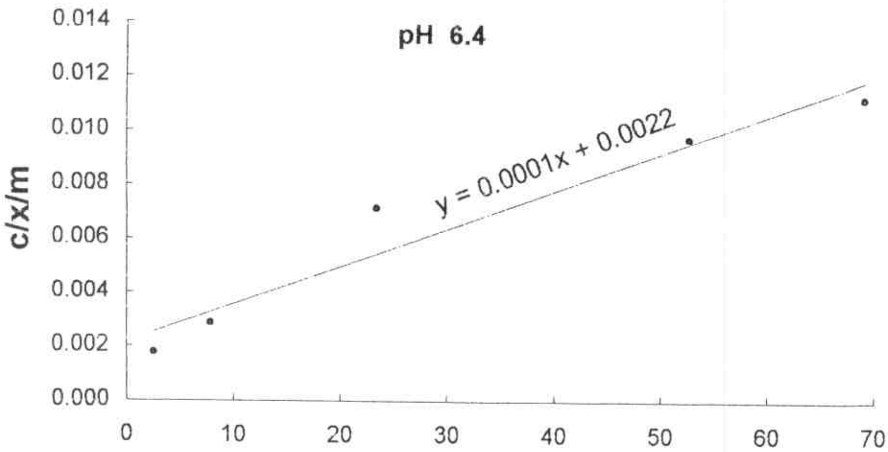


Fig. (18): Copper adsorption isotherms by Humic acid according to the conventional Langmuir equation.

Table (22): Copper adsorption isotherm on humic acid according to the Langmuir conventional equation at various pH values.

Initial Cu concentration (µg/ml)	PH 5.0			PH 5.5			PH 6.4		
	C	x	C/x/m	C	x	C/x/m	C	x/m	C/x/m
10	3.7	1260	0.00294	2.5	1500	0.00167	2.6	1480	0.00176
20	8.6	2280	0.00377	6.8	2640	0.00258	7.9	2420	0.00285
40	25.0	3000	0.00833	20.2	3960	0.00510	23.5	3300	0.00712
80	59.3	4140	0.01430	49.6	6080	0.00816	52.8	5440	0.00971
100	65.4	6920	0.00945	57.8	8440	0.00685	69.2	6160	0.01120

C = final equilibrium concentration (µg Cu/ml).
x/m = adsorbed copper (µg Cu/g soil).

Table (23): Regression parameters calculated from copper adsorption isotherms by Humic acid according to the Langmuir equation at different pH values.

pH values	Linear equation	b	K	MBC	r
5.0	C/x/m = 0.0001x + 0.0041	10000	0.0313	312.5	0.875
5.5	C/x/m = 0.0001x + 0.0032	10000	0.0476	476.2	0.937
6.4	C/x/m = 0.0001x + 0.0022	10000	0.0455	454.5	0.970

b = adsorption maximum (ug Cu/g soil).
K = binding energy (ml/ug Cu).
MBC = maximum buffering capacity (ug Cu/g soil).
r = correlation coefficient.

4.1.3.2. Application of Freundlich equation:

Values of Ln C and Ln x/m for the humic acid in equilibrium with the different concentrations of Cu are given in Table (24) and illustrated graphically in Fig. (19). It is obvious that Freundlich equation is suitable to describe Cu adsorption on humic acid upon application of Cu at concentrations up to 100 µg /mL. This suitability was observed at the different pH values. Values of the affinity parameter (n) which express the adsorption maxima of Cu at pH 5.0, 5.5 and 6.4 were 0.490, 0.503 and 0.426, respectively. The values of correlation coefficients (Table, 25) prove that Freundlich equation is significantly suitable to represent Cu adsorption isotherms. The values were 0.955**, 0.988** and 0.993** at pH 5.0, 5.5 and 6.4, respectively. The inverse Ln a values which express the binding energy were 695, 950 and 980 at pH 5.0, 5.5 and 6.4, respectively.

4.1.3.3. Application of Temkin equation:

A plot of X against Ln C at the various pH values is illustrated in Fig. (20) and presented in Table (26). Increasing the initial Cu concentration up to 100 µg/ml was associated with an increase in its adsorption on the humic acid. Also, a similar trend was found at the pH values of 5.0 and 6.4. The correlation coefficients (Table, 25) were 0.874**, 0.935** and 0.961** at pH 5.0, 5.5 and 6.4, respectively, indicating that Temkin isotherm model is also suitable to be used for describing Cu adsorption on the humic acid.

4.2. Copper desorption:

4.2.1. Copper desorption from the soils:

The results obtained for copper desorption from the previously adsorbed Cu by both the alluvial and calcareous soils are

Table (24): Copper adsorption isotherm on humic acid according to Freundlich conventional equation at various pH values.

Initial Cu concentration (µg/ml)	PH 5.0		PH 5.5		PH 6.4	
	Ln C	Ln x/m	Ln C	Ln x/m	Ln C	Ln x/m
10	1.308	7.138	0.916	7.313	0.955	7.299
20	2.151	7.731	1.916	7.878	2.066	7.791
40	3.218	8.006	3.005	8.283	3.157	8.101
80	4.082	8.328	3.903	8.712	3.966	8.601
100	4.180	8.842	4.056	9.040	4.237	8.725

C = final equilibrium concentration (µg Cu/ml).
x/m = adsorbed copper (µg Cu/g soil).

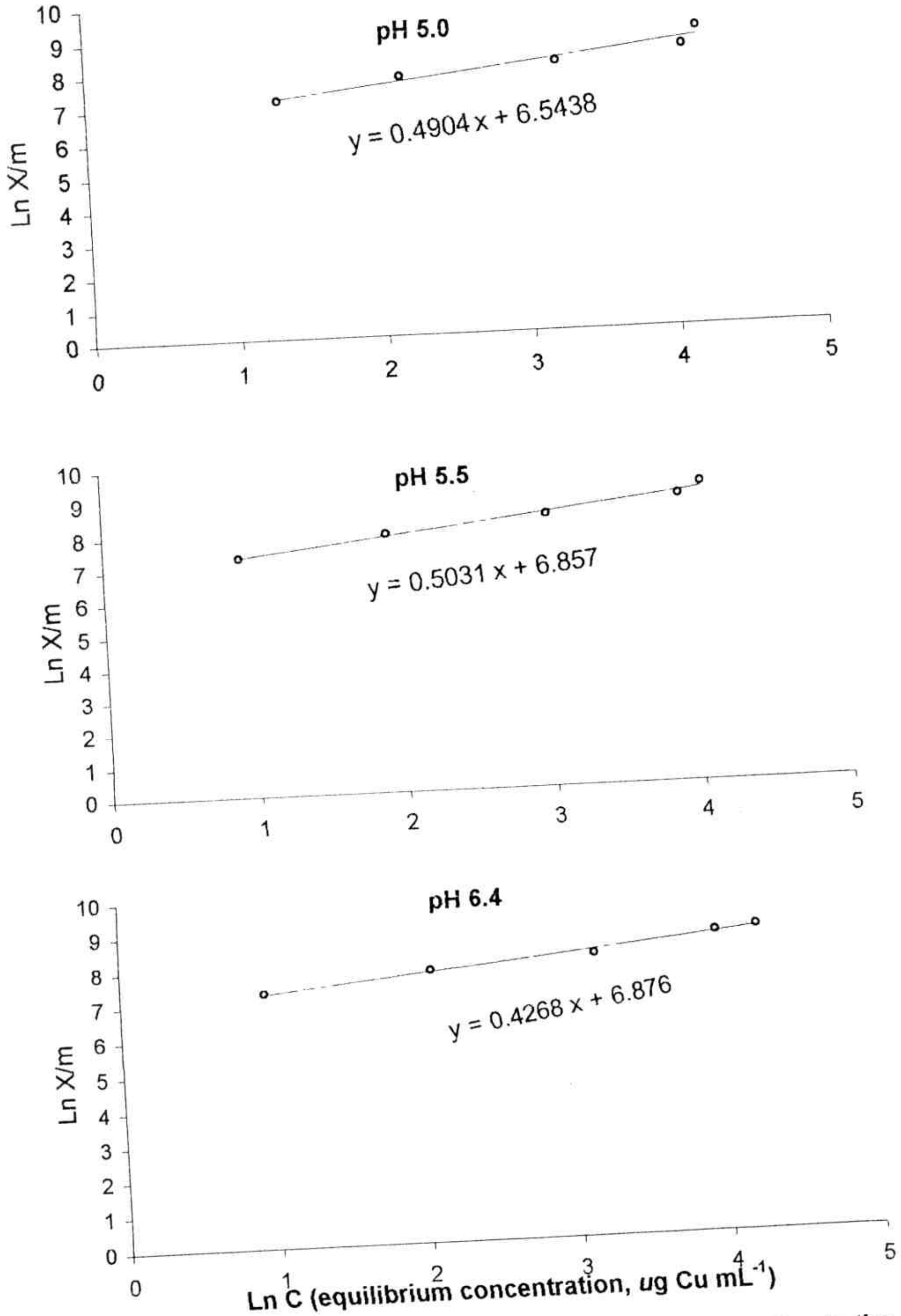


Fig. (19): Copper adsorption isotherms on humic acid according to the conventional Freundlich equation at various pH values.

Table (25): Regression parameters calculated from adsorption data for Freundlich and Temkin isotherms on humic acid at various pH values.

PH values	Freundlich			Temkin		
	Lna	n	r	a	b	r
5.0	6.543	0.490	0.955	7032.7	1525.2	0.874
5.5	6.857	0.503	0.988	8192.5	1939.1	0.935
6.4	6.876	0.426	0.993	6825.5	1397.5	0.961

a = intercept
n = slope
r = correlation coefficient

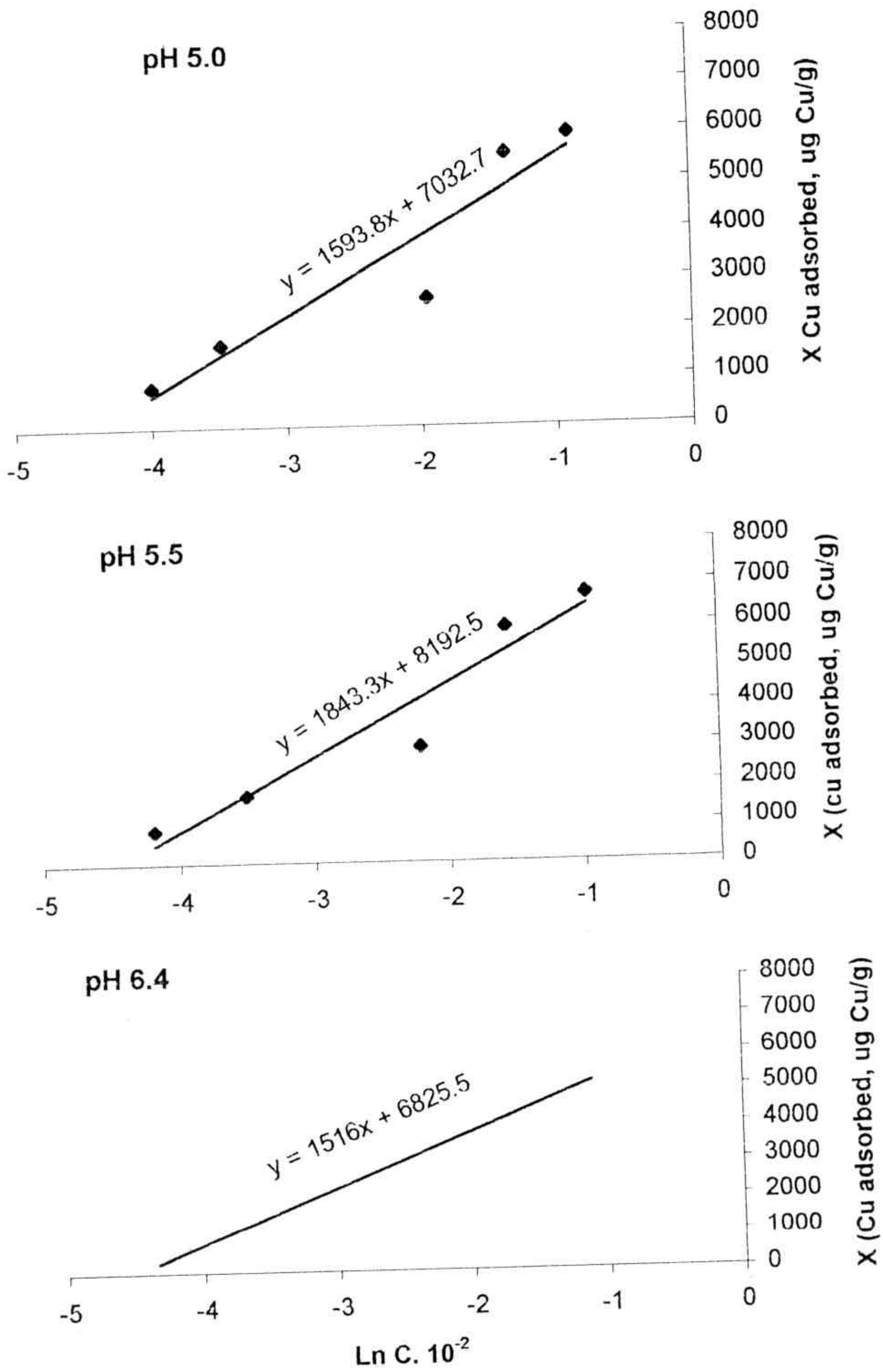


Fig. (20): Copper adsorption isotherms on humic acid according to the conventional Temkin equation at various pH values.

Table (26): Copper adsorption isotherm on humic acid according to Temkin conventional equation at various pH values

Initial Cu concentration (µg/ml)	PH 5.0		PH 5.5		PH 6.4	
	Ln C. 10^{-2}	X	Ln C. 10^{-2}	X	Ln C. 10^{-2}	X
10	-3.29	1260	-3.68	1500	-3.65	1480
20	-2.45	2280	-2.68	2640	-2.54	2420
40	-1.38	3000	-1.59	3960	-1.45	3300
80	-0.52	4140	-0.70	6080	-0.63	5440
100	-0.42	6920	-0.55	8440	-0.37	6160

C = final equilibrium concentration (µg Cu/ml).
X = adsorbed copper (µg Cu/g soil).

presented in Tables (27 & 28). The amounts of Cu adsorbed and desorbed increased with increasing concentration of the added Cu. These increases varied widely between the soils according to values of their maximum adsorption, maximum buffering capacity and other soil properties.

The amounts of Cu desorbed from the alluvial soil exhibited higher values compared to the calcareous soil. The percentages of desorbed Cu to its corresponding adsorbed ones ranged between 43 and 76%; 43 and 69%, and 60 and 79 at pH values 5.0, 5.5 and 6.4, respectively. As for calcareous soil, these percentages were 32 – 62 %; 29 – 52 % and 56 – 71 % at the same abovementioned pH values, respectively. In this connection, **McBride et al. (1984)** found that sorption of Cu by soil components has been shown to be largely irreversible or only slowly reversible. **Barrow (1985)** concluded that initial sorption reactions may be followed by slower reaction that would render a fraction of sorbed Cu unavailable.

It was also noticed that the amounts of desorbed Cu from alluvial soil were, generally, higher than the retained ones, especially at pH 6.4, while, the opposite trend was observed for the calcareous soil, where the amounts of desorbed Cu were generally lower than the retained ones (except at pH 6.4). probably due to the high $CaCO_3$ content. In this concern, **Hogg et al. (1993)** reported that the amount of Cu desorbed from soil depends not only on total amount of labile Cu in soils but also on soil pH. At pH 6.4, the amounts of desorbed Cu from the calcareous soil were higher than the corresponding retained ones.

Copper desorption curves obtained via plotting the amount of desorbed Cu against the amounts adsorbed exhibited straight lines for the studied soils (Fig., 21). The calculated correlation coefficients at pH 5.0 were 0.994** and 0.985** for the alluvial and calcareous soils, respectively. The corresponding correlation

Table (27): Adsorbed, desorbed and retained copper expressed as ug/g soil and percentages for alluvial soil at various pH values

Added	Adsorbed		Desorbed		Retained	
µg Cu/g soil	µg Cu/g soil	Cu adsorbed %*	µg Cu/g soil	Cu desorbed %*	µg Cu/g soil	Cu retained %*
			PH 5.0			
200	184	92	80	43	104	57
400	368	92	160	43	208	57
800	680	85	400	59	280	41
1600	1358	85	920	68	438	32
2000	1474	74	1120	76	354	24
			PH 5.5			
200	184	92	80	43	104	57
400	376	94	180	48	196	52
800	718	90	380	53	338	47
1600	1396	87	820	59	576	41
2000	1544	77	1060	69	484	31
			PH 6.4			
200	184	92	110	60	74	40
400	384	96	250	65	134	35
800	754	94	500	66	254	34
1600	1432	90	1040	73	392	27
2000	1488	74	1180	79	308	21

* Cu desorbed, % was calculated by dividing Cu desorbed, $\mu g\ g^{-1}$, on Cu adsorbed, $\mu g\ g^{-1}$, and multiplied by 100.

Table (28): Adsorbed, desorbed and retained copper expressed as µg/g soil and percentages for calcareous soil at various pH values

Added	Adsorbed		Desorbed		Retained	
µg Cu/g soil	µg Cu/g soil	Cu adsorbed, %*	µg Cu/g soil	Cu desorbed, %*	µg Cu/g soil	Cu retained, %*
			PH 5.0			
200	188	94	60	32	128	68
400	382	96	160	42	222	58
800	636	80	300	47	336	53
1600	1204	75	588	49	616	51
2000	1480	74	924	62	556	38
			PH 5.5			
200	194	97	56	29	138	71
400	386	97	150	39	236	61
800	702	88	310	44	392	56
1600	1416	88	646	46	770	54
2000	1688	84	876	52	812	48
			PH 6.4			
200	194	97	108	56	86	44
400	394	99	228	58	166	42
800	760	95	480	63	280	37
1600	1499	94	988	66	511	34
2000	1740	87	1228	71	512	29

* Cu desorbed, % was calculated by dividing Cu desorbed, µg g^{-1}, on Cu adsorbed, µg g^{-1}, and multiplied by 100.

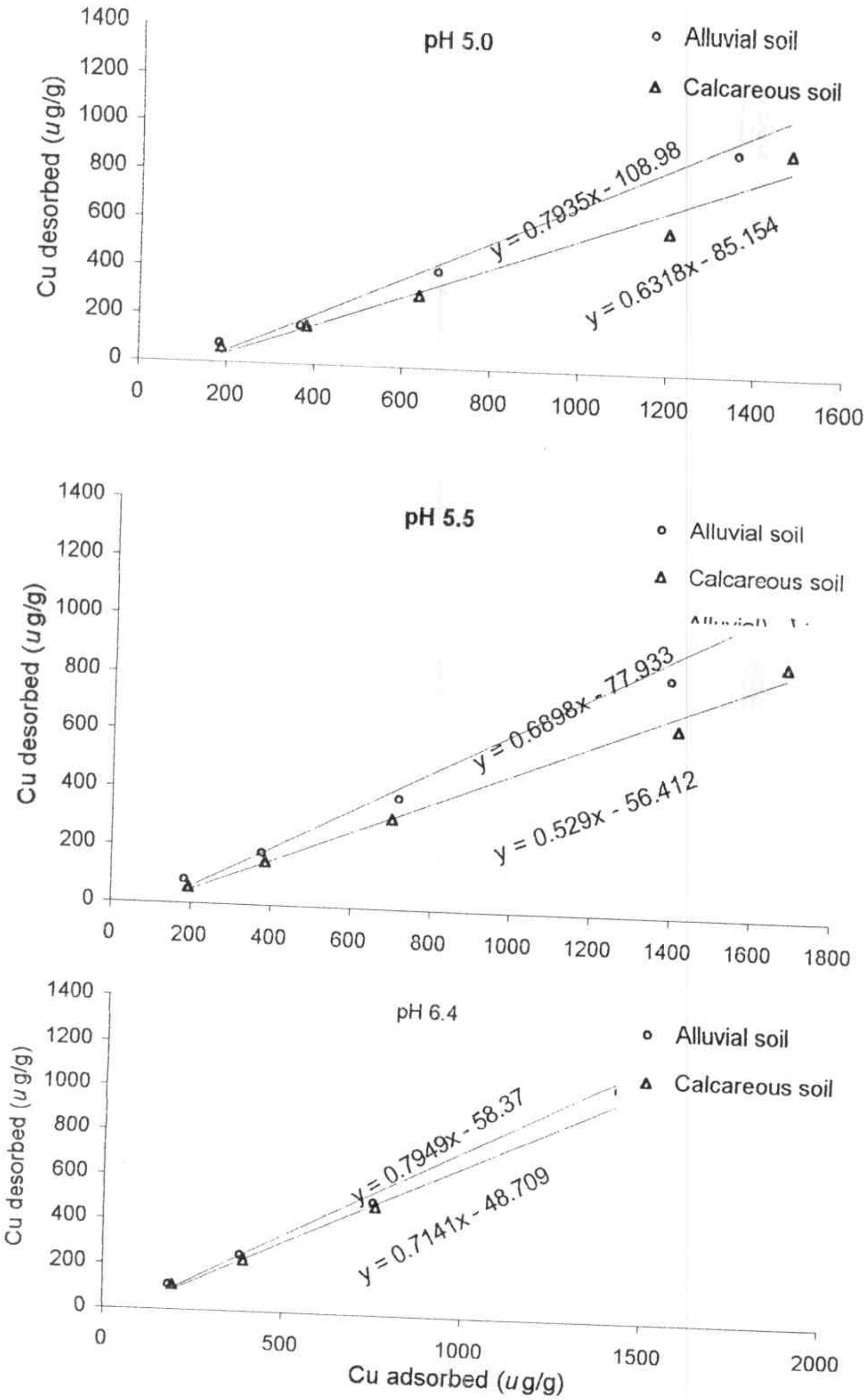


Fig. (21): Copper desorption isotherms from two different soils.

coefficients at pH 5.5 were 0.991** and 0.995**; while at pH 6.4, they were 0.996** and 0.998** at the same order. Different slopes and intercepts were observed, indicating the existence of different desorption buffering capacities of these soils. Generally, the alluvial soil showed the highest desorption buffering capacity at various pH values compared to calcareous one.

4.2.2. Copper desorption from the clay minerals:

Desorption of Cu from the studied clay minerals is shown in Tables (29 & 30). Values of the desorbed Cu at all pH values for both montmorillonite and palygroskite minerals seemed to be increased as the initial concentration of the applied Cu increased. However, such increases varied widely between the two studied minerals according to their maximum adsorption and maximum buffering capacity values. The highest increase was observed at pH 5.5, where Cu desorbed increased from 650 to 6520 µg/g for montmorillonite and from 220 to 2380 µg/g for palygroskite with increasing added Cu from 1000 to 10000 µg/g, respectively. However, the lowest values of desorbed Cu by both minerals were obtained at the high pH (6.4). These results are in agreement with those reported by **Cavallaro and McBride (1984)** who found that desorption of Cu from clays decreases with increasing pH.

Moreover, the amount of desorbed Cu from montmorillonite mineral exhibited higher values than those desorbed from palygroskite. The relative percentages of desorbed Cu as percentages of the adsorbed amount ranged from 68 to 90; 74 to 96 and 35 to 82 % at pH 5.0, 5.5 and 6.4, respectively.

On the contrary, the amounts of desorbed Cu on montmorillonite were higher than the retained ones, while the opposite trend was observed for palygroskite.

Table (29): Adsorbed, desorbed and retained copper expressed as µg/g mineral and percentages for montmorillonite at various pH values

Added	Adsorbed		Desorbed		Retained	
µg Cu/g mineral	µg Cu/g soil	Cu adsorbed, %*	µg Cu/g soil	Cu desorbed, %*	µg Cu/g soil	Cu retained, %*
			PH 5.0			
1000	870	87	590	68	280	32
2000	1520	76	1080	71	440	29
4000	2880	72	2500	87	380	13
8000	5300	66	4750	90	550	10
10000	6100	61	5690	93	410	7
			PH 5.5			
1000	880	88	650	74	230	26
2000	1680	84	1290	77	390	23
4000	3070	77	2800	91	270	9
8000	5700	71	5270	92	430	8
10000	6820	68	6520	96	300	4
			PH 6.4			
1000	840	84	460	55	380	45
2000	1420	71	1000	70	420	30
4000	3140	79	2386	76	754	24
8000	5320	65	4160	78	1160	22
10000	6180	62	5068	82	1112	18

* Cu desorbed, % was calculated by dividing Cu desorbed, µg g^{-1}, on Cu adsorbed, µg g^{-1}, and multiplied by 100.

Table (30): Adsorbed, desorbed and retained copper expressed as µg/g mineral and percentages for palgyorskite at various pH values

Added	Adsorbed		Desorbed		Retained	
µg Cu/g mineral	µg Cu/g soil	Cu adsorbed, %*	µg Cu/g soil	Cu adsorbed, %*	µg Cu/g soil	Cu retained, %*
			PH 5.0			
1000	820	82	150	18	670	82
2000	1680	84	370	22	1310	78
4000	2600	65	702	27	1898	73
8000	5500	69	1705	31	3795	69
10000	5900	59	2120	36	3780	64
			PH 5.5			
1000	850	85	212	25	638	75
2000	1700	85	560	33	1140	67
4000	2900	73	950	33	1950	67
8000	5900	74	2124	36	3776	64
10000	6700	67	2546	38	4154	62
			PH 6.4			
1000	870	87	140	16	730	84
2000	1580	79	325	21	1255	79
4000	2500	63	525	21	1975	79
8000	5150	64	1560	30	3590	70
10000	6200	62	2170	35	4030	65

* Cu desorbed, % was calculated by dividing Cu desorbed, µg g^{-1}, on Cu adsorbed, µg g^{-1}, and multiplied by 100.

Copper desorption curves obtained via plotting the amount of desorbed Cu against the amounts of adsorbed Cu are shown in Fig. (22). The calculated correlation coefficients at pH 5.0 were 0.999** and 0.994** for montmorillonite and palygroskite minerals, respectively. The corresponding correlation coefficients at pH 5.5 were 0.999** and 0.998**; while at pH 6.4, they were 0.999** and 0.969** at the same order.

4.2.3. Humic acid:

Desorption of Cu from humic acid is shown in Table (31). Increasing the added amounts of Cu slightly increased the desorbed Cu at all pH values. The highest increase was observed at pH 5.5, where Cu desorbed increased from 880 to 5420 μg/g with increasing added Cu from 2000 to 20000 μg/g, respectively. However, the lowest values of desorbed Cu were obtained at the lowest pH (5.0).

Moreover, the amounts of desorbed Cu from humic acid as percentage of the adsorbed ones ranged between 46 and 58; 59 and 64 and 50 and 50 % at pH 5.0, 5.5 and 6.4, respectively.

Also, data revealed that the amounts of desorbed Cu from humic acid were slightly higher than the retained ones at pH 5.5, while, at pH 5.0 and 6.4 the amounts of desorbed Cu were almost equal to those of the retained Cu.

Copper desorption curves obtained via plotting the amount of desorbed Cu against the amount of adsorbed are shown in Fig. (23). The calculated correlation coefficients were 0.999**; 0.999** and 0.999** at pH 5.0, 5.5 and 6.4, respectively.

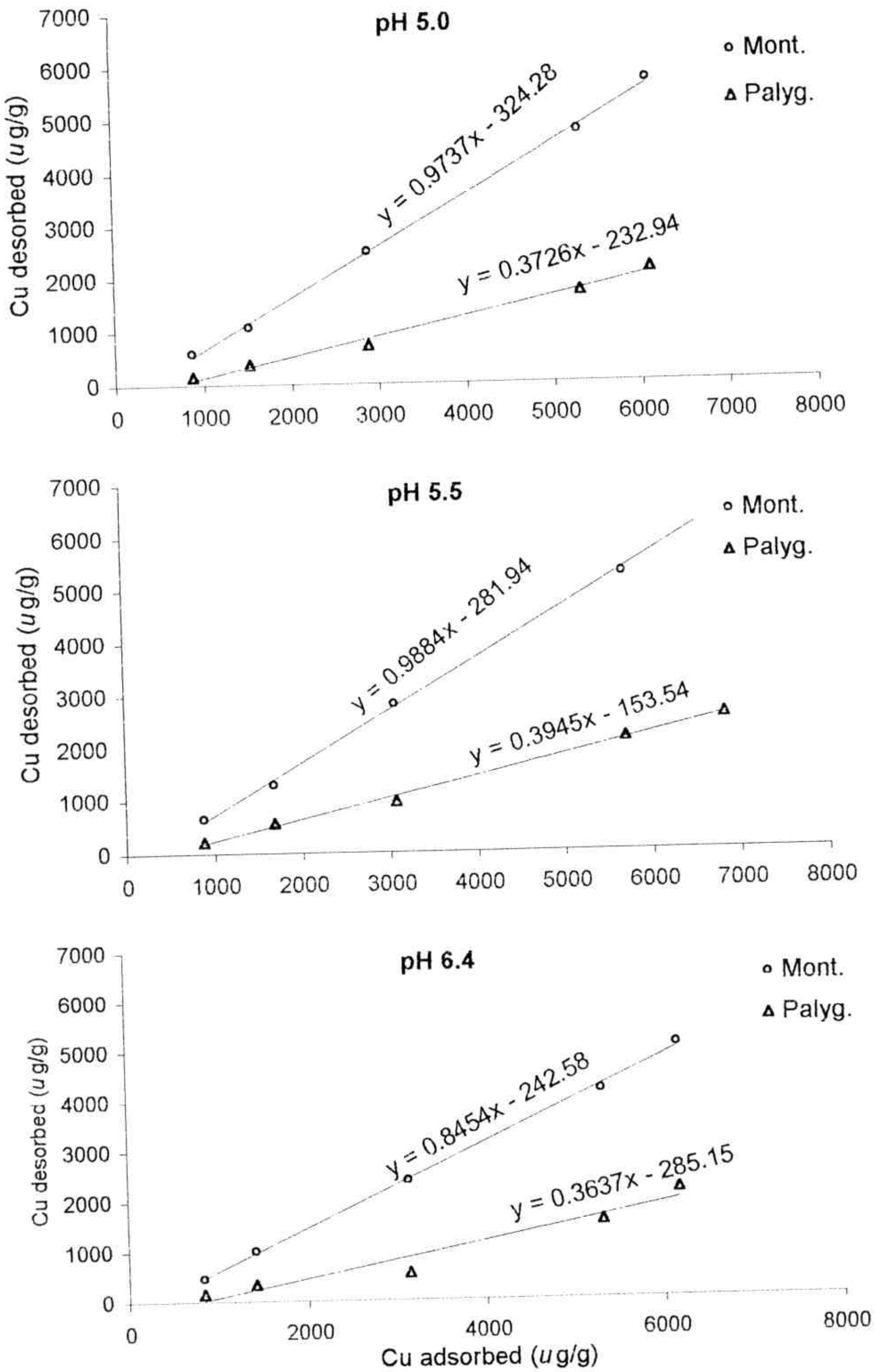


Fig. (22): Copper desorption isotherms from two different clay minerals.

Table (31): Adsorbed, desorbed and retained copper expressed as µg/g material and percentages for humic acid at various pH values

Added	Adsorbed		Desorbed		Retained	
µg Cu/g mineral	µg Cu/g soil	Cu adsorbed, %*	µg Cu/g soil	Cu desorbed, %*	µg Cu/g soil	Cu retained, %*
PH 5.0						
2000	1260	63	580	46	680	54
4000	2280	57	1100	48	1180	52
8000	3000	38	1500	50	1500	50
16000	4140	26	2010	49	2130	51
20000	6920	35	3320	48	3600	52
PH 5.5						
2000	1500	75	880	59	620	41
4000	2640	66	1620	61	1020	39
8000	3960	50	2550	64	1410	36
16000	6080	38	3820	63	2260	37
20000	8440	42	5420	64	3020	36
PH 6.4						
2000	1480	74	740	50	740	50
4000	2420	61	1360	56	1060	44
8000	3300	41	1910	58	1390	42
16000	5440	34	3260	60	2180	40
20000	6160	31	3690	60	2470	40

* Cu desorbed, % was calculated by dividing Cu desorbed, µg g^{-1}, on Cu adsorbed, µg g^{-1}, and multiplied by 100.

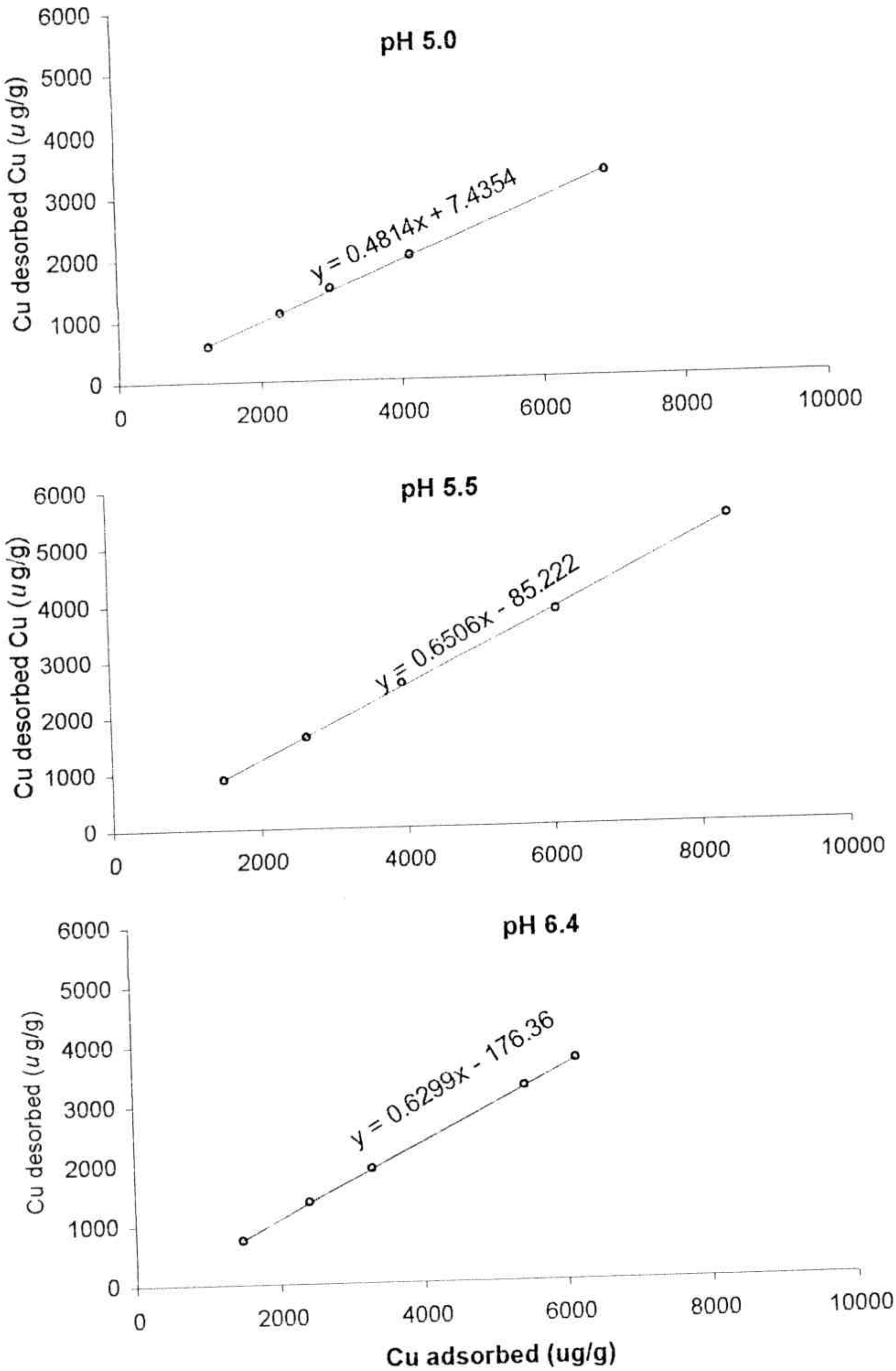


Fig. (23): Copper desorption isotherms from humic acid.