

Adsorption – Desorption Behaviors of Cu, Zn, Mn and Fe in Calcareous Soils

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THE adsorption-desorption behavior of Cu^{2+} , Zn^{2+} , Mn^{2+} and Fe^{2+} was studied on the Egyptian calcareous soil surface at two pHs 5.5 and 7.5. A 25 ppm was the initial concentration used for each metal. The experiments were performed using the four elements individually and in a mixture of two elements Cu+Zn, Cu+Mn, Cu+Fe, Zn+Mn, Zn+Fe and Mn+Fe. In addition a mixture of the four elements Cu+Zn+Mn+Fe was studied; with 25 ppm initial concentration for each element either for individual elements or mixtures at two pHs 5.5 and 7.5. The Na_2EDTA salt was used to study the desorption behavior. The adsorption of heavy metals followed the magnitude $\text{Zn} > \text{Fe} > \text{Mn} > \text{Cu}$, while the magnitude of desorption was $\text{Cu} > \text{Zn} > \text{Fe} > \text{Mn}$ at pH 5.5 and 7.5. While the magnitude of selectivity was in the order $\text{Fe} > \text{Mn} > \text{Zn} > \text{Cu}$ at both pHs.

Keywords: Adsorption, Desorption, Heavy metals, Selectivity.

Heavy metals contamination in the environment is of a major concern because of their toxicity and threat to human life and the environment. Much research has been conducted on heavy metal contamination in soils from various anthropogenic sources such as industrial wastes, automobile emissions and agricultural practices.

Based on primary accumulation mechanisms in sediments, heavy metals can be classified into five categories: (i) adsorptive and exchangeable, (ii) bound to carbonate phases, (iii) bound to reducible phases (Fe and Mn oxides), (iv) bound to organic matter and sulfides, and (v) detrital or lattice metals (Salomons & Forstner, 1984). Heavy metals present in these categories have different remobilization behaviors under changing environmental conditions (Forstner, 1985). Therefore, determining total content of heavy metals is insufficient to assess the environmental impact of contaminated soils and sediments (Salomons & Forstner, 1984 and Lena & Gade, 1997).

The general approach is nowadays applied in the description of the adsorption properties of heterogeneous sorbent material through the so-called Generalized Composite (GC) approach (Davis *et al.*, 1998).

The objectives of this work were to study the behavior of some heavy metals in soil through: (i) Obtaining quantitative information on the relation between the amount of heavy metals adsorbed, desorbed, or fixed and the soil properties, and (ii) Studying the competition between heavy metals for adsorption on soil surface, and (iii) the study was carried out at acidic (pH 5.5) and slightly alkaline (pH 7.5) conditions to understand how much the acidity produced from the plant roots in the rhizosphere region could affect the heavy metals solubility under high calcium carbonate content.

Material and Methods

Soil from El-Alamin area, west of Alexandria city has been used in this study, Plate 1. Four soil samples (0-20 cm) were collected to represent the calcareous soils at this area. After air drying soils were finely ground, passed through 20 μ m sieve and the main physical and chemical properties of the soil were determined by the method described by Black (1965) and Page (1982) and the obtained data are given in Table 1. The sulfate salts of ferrous, manganese, copper, and zinc were prepared in water and adjusted to pHs 5.5 or 7.5; also the soil heavy metal suspensions at the same two pHs according to Stumm & Morgan (2002) and Stumm & Wollast (1990) at room temperature (25°). This was carried out to determine to what extent the adsorption or fixation of heavy metals would be affected by soil pH.

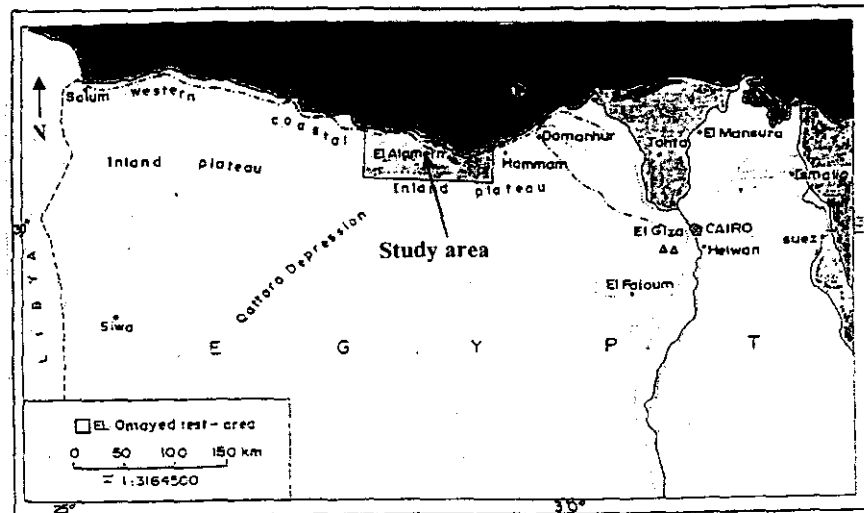


Plate 1. Location of the soil sampling area at the northwestern coast of Egypt .

Soils were prepared to study the behavior of each metal individually. Five grams from each soil was placed in a 100 ml capacity Teflon tube and equilibrated with 50 ml of 25 ppm Cu, Zn, Mn, and Fe at two pHs: 5.5 ± 0.1 and 7.5 ± 0.1 . To examine the competing effect between metals several combinations of 25 ppm for each couple of metals were prepared at two pHs: 5.5 ± 0.1 and 7.5 ± 0.1 as follow: (Cu+Zn), (Cu+Mn), (Cu+Fe), (Zn+Mn), (Zn+Fe) and (Mn+Fe). To study the competition among the four metals in one mixture, a 25 mgL^{-1} from each metal was prepared. The soils suspensions were first adjusted to the required pHs (Stumm & Wollast, 1990) then shaken on a reciprocation shaker, for 30 min/day for a period of 5 days to reach equilibrium, and then centrifuged at 6000 rpm for 30 min. The metals content of the supernatant was measured using atomic absorption spectrometry (AAS) Perkin-Elmer model 5000. The adsorbed amount of metal was calculated from the difference between the initial concentration and the final equilibrating metal concentration. The soil residues were kept for the desorption experiment. These soils were washed twice by 50 ml distilled water. The samples were shaken, after every addition of distilled water for 30 min, only to avoid the metals hydrolysis (Kunze, 1965 & Page, 1982), and the amount of metals in water were measured, there were no detectable amounts of any metal.

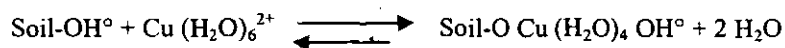
Adsorbed metals were extracted by using 50 ml of 0.1 N NaEDTA to determine to what extent the soil could retain the metal. Extraction was carried out at two pHs 5.5 and 7.5. The soil suspensions were also shaken for 5 days, and then centrifuged at 6000 rpm for 30 min. The metals contents of the supernatant were measured by AAS. The extracted amount was compared with the adsorbed amount to calculate the retained amount on the soil surface under experimental conditions. The reported data are the average of four soil samples.

Results and Discussion

Table 1 showed that the soils are highly calcareous with low organic matter content.

Table 2 represented the adsorption of the metals at two pHs 5.5 and 7.5. The results indicated that adsorption percentage varied among the applied elements. The adsorption percentage increased at the higher pH 7.5 for all elements than at lower pH 5.5.

Several studies concluded that the adsorption mechanisms of Cu onto oxide mineral surfaces principally involve the adsorption of Cu^{2+} and Cu-OH species (Elliott & Huang, 1980; Davis & Leckie, 1978 and Barrow, 1986). This would be represented as follows:



Davis & Leckie (1978) concluded that the models of this equation most likely explain Cu adsorption patterns.

TABLE 1. The main physical and chemical properties of the used soils .

Sample No.	*pH	**EC dS/m	CaCO ₃ (%)	Water soluble Cations meq/l				Water soluble Anions meq/l				O.M (%)	CEC meq/100 g soil	Particle size distribution			Texture	Water soluble Gypsum meq/100 g soil
				Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺	CO ₃ ⁻	HCO ₃ ⁻	Cl ⁻	SO ₄ ⁻			Sand (%)	Silt (%)	Clay (%)		
1	8.57	6.00	39.40	27.80	12.90	31.60	2.10	0.80	3.50	57.50	12.60	0.17	7.40	70.90	18.00	11.10	Sandy Loam	2.52
2	8.31	4.50	66.20	19.50	11.00	20.60	0.75	0.00	2.50	41.30	5.05	0.17	6.40	59.50	30.00	10.50	Sandy Loam	1.01
3	7.50	4.62	55.60	1.00	3.60	2.40	2.50	0.05	2.40	9.50	2.40	0.30	3.40	75.50	18.30	6.20	Loamy Sand	0.20
4	7.92	4.32	42.13	1.00	3.40	1.80	0.60	0.00	3.00	6.00	2.20	0.22	2.80	80.20	12.30	7.50	Sandy Loam	2.32

* measured in 1:2.5 soil-water suspension

** measured in 1:1 soil-water extract

TABLE 2. Selected soil sample represents: adsorbed, extracted and fixed amounts of metals expressed as percent 25 ppm metals concentrations at pH 5.5 ± 0.1 and at pH 7.5 ± 0.1.

Elements	Treatments					
	Adsorbed at pH 5.5	Extracted by EDTA at pH 5.5	Fixed by soil at pH 5.5	Adsorbed at pH 7.5	Extracted by EDTA at pH 7.5	Fixed by soil at pH 7.5
	Percentage					
Fe	91.80	11.57	82.14	90.60	8.46	80.23
Mn	84.16	5.91	78.25	85.23	13.78	71.45
Zn	82.12	12.12	70.00	92.68	27.56	65.12
Cu	76.96	48.71	28.15	80.68	55.20	25.48

In all samples, the extracted Cu percentage at pH 7.5 was higher than at pH 5.5 suggesting that increasing metal ions dissolution at higher pH in the calcareous soil (Martinez & Motto, 2000). During desorption process the Na₂EDTA forms very strong complexes with Cu compared with any other inorganic ligands that might be present in the soil suspensions (Martell & Smith, 1974). Furthermore, Na₂EDTA could also form stronger complexes with Cu than with soil surfaces, thereby competing with the adsorption sites for Cu adsorption (McBride, 1994 and McLean & Bledose, 1992). Vulava *et al.* (1997) concluded that Cu remains complexed with EDTA for all pHs > 4. This could reflect the similarity of binding energy between Cu and surface sites of EDTA.

The results in Table 2 indicated that 82.12 % of the applied Zn (as ZnSO₄.7H₂O) was adsorbed at the pH 5.5 and 92.68% at pH 7.5. This can be attributed to high CaCO₃ content in the soils where Zn solubility in calcareous or alkaline soils was often controlled by solubility of ZnCO₃ or Zn(OH)₂ (Udo *et al.*, 1970; Dhillon *et al.*, 1975 and Saeed & Fox, 1977) beside that the solubility of CaCO₃ increases by decreasing the soil pH, where part of CaCO₃ transformed to bicarbonate (Lindsay, 1979). This produces high Ca²⁺ ions, which in their turn compete strongly with the heavy metal ions on the adsorption sites at this low pH. Moreover, studies of Zn affinity for oxides and hydroxides of Fe and Al (Kinniburgh *et al.*, 1976 and Kalbasi *et al.*, 1978) showed pronounced adsorption even under acidic conditions and a strong dependence of adsorption on pH. From this study it can be concluded that Zn adsorption at pH 5.5 and 7.5 on soils, which are low in organic matter content, seems to be determined by specific adsorption process. So, the highly pH-dependent retention of Zn in a non-exchangeable form (65 to 70 % of the applied Zn, Table 2) in the soil attributed to the existence of oxide surfaces, which are known to have a high affinity for Zn²⁺ (John & Latifatu, 2004).

Contribution of MgCO₃ and CaCO₃

Jurinak & Bauer (1956) concluded that, by increasing the percentage of MgCO₃ in the soil, the total adsorption of zinc is increased and the reaction is endothermic. Specific adsorption of zinc could be attributed to the existence of MgCO₃. The similarity of the ionic radii of magnesium and zinc ions (0.78 Å and 0.83 Å) makes Zn²⁺ to fit well into the MgCO₃ lattice. This idea is supported by the fact that the unit cell lengths of ZnCO₃ (5.67 Å) and MgCO₃ (5.63 Å) are nearly equal. Also, due to the greater polarizability and polarizing power of Zn²⁺ relative to Mg²⁺, one would expect Zn²⁺ to compete favorably with Mg²⁺ for lattice sites (Fig.1).

The results revealed that Na₂EDTA extracted 12.12% of Zn ions from soil at pH 5.5 and 27.56% at pH 7.5. It is impossible to interpret the reactions of EDTA chelates in soils without considering Ca²⁺ competition for the EDTA ligand. However, any EDTA in solution, which is not present as chelates of transition metals, can be safely assumed to complex Ca²⁺ because Ca²⁺ forms a more stable complex with EDTA than do any other relatively abundant cations in soil solutions (Norvel & Lindsay 1969). So, in this study the soil is calcareous and EDTA chelated or extracted low Zn amounts due to the competition of Ca²⁺ with Zn ions for EDTA ligand. CaEDTA is undoubtedly the dominant species formed initially, but many other complexes are also formed and may become increasingly important with time (Norvel & Lindsay 1969).

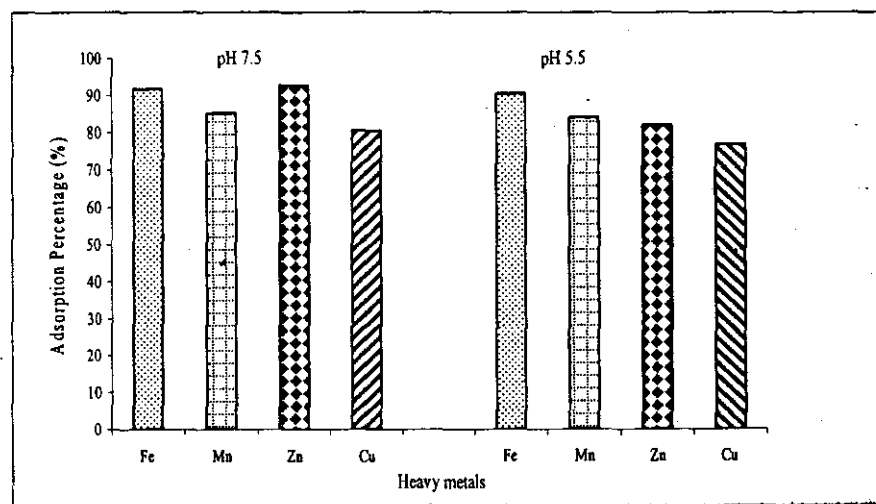


Fig. 1. The adsorption percentage of 25 ppm of each metal at pH 5.5 and at pH 7.5 (This results are an average value of the four metals).

The results indicated that there is no significant difference between the adsorbed amounts of Mn^{2+} at the two-pHs (5.5 and 7.5). It has been found that ions such as Mn^{2+} are strongly adsorbed by $CaCO_3$ and even more strongly by $MgCO_3$ (McBride, 1979). In many cases the solubility product for metal hydroxide, $Mn(OH)_2$; $pK_{sp} = 15.19$, or carbonate, $MnCO_3$; $pK_{sp} = 8.08$, was too low to control the equilibrium concentration of Mn^{2+} in solution (Lindsay, 1979). In this study Mn^{2+} ions were strongly adsorbed by $CaCO_3$ surface this result is completely in agreement with the later opinions. The presence of $CaCO_3$ in soil might immobilize Mn by chemisorption on its surfaces consequently the solubility of Mn will be decreased. Furthermore, under the conditions where $CaCO_3$ is a major soil constituent, Mn is expected to be primarily in insoluble forms, *i.e.*, precipitated (Fahad, 1987). On the other hand, the extracted amounts of Mn^{2+} by EDTA were low at the two-pHs (5.91% and 13.78%) respectively. This can be in turn attributed not only to the immobilization of Mn^{2+} on the $CaCO_3$ surface, but also the precipitation of $MnCO_3$ as a separate phase (Carol & John, 1993). Fahad (1987) concluded that addition of EDTA to the calcareous soils might increase the release of insoluble Mn. This increase was explained by the transformation of the solid phase soil Mn into soluble MnEDTA complexes. The results of this study concluded that the reaction of Mn^{2+} with $CaCO_3$ is leading, not only to the precipitation of $MnCO_3$, but also the release of Ca^{2+} should be considered. So, the released Ca^{2+} will compete Mn^{2+} for EDTA complex formation (McBride, 1979) concluded that most of the soluble manganese in the calcareous soils was in the $Mn(H_2O)_6^{2+}$ form.



Dahiya & Sing (1977) concluded that all forms of manganese decreased with increasing $CaCO_3$ upto 16% and that increase the time of incubation decreased the extracted manganese with all forms of extractants due to oxidation and hydration of manganese to high insoluble oxides and hydroxides.

The results of Fe^{2+} adsorption showed the same behavior as Mn^{2+} where there was no significant difference between adsorption of Fe^{2+} at the two pHs. Wallace (1963) concluded that in aerated soils Fe^{2+} , is so readily oxidized to Fe^{3+} , which is extremely insoluble this is due to that the free energy of formation for Fe^{2+} (-84.94 KJ/mol) while for Fe^{3+} it is (-10.59 KJ/mol) (Stumm and Morgan, 2002). So, the results agree with the last conclusion where the experiments were carried out in aerobic conditions and the added Fe as (ferrous sulfate) is oxidized to ferric which then precipitated (Brennan & Lindsay, 1998).

The presence of chelating agents is one of several possible explanations of how plants are able to obtain Fe, which ordinarily is very insoluble in soil (Wallace, 1963). In the presence of EDTA the results indicated clear differences between the desorbed Fe at the two pHs (5.5 and 7.5). At pH 5.5, the desorbed amount of Fe was higher than at pH 7.5 in all soil samples. This can be attributed to the difference in the solubility products among Fe species as pH changes. Lindsay (1979) concluded that, below pH 6.75, Fe^{2+} is the major iron species in solution and between pH 6.75 and

9.3, FeOH^+ is the predominant species while above pH 9.3, Fe(OH)_2 is the major solution species. The hydrolysis species (Fe(OH)_3) are quite insignificant in the pH range of soils *i.e.*, precipitated. Then, from the present results it can be concluded that at pH 5.5 the solubility of iron was higher than at pH 7.5. For that reason, EDTA would chelate higher amount of iron at pH 5.5 than at pH 7.5. In general, the desorbed amounts of Fe at the two pHs are low and this can be explained through the instantaneous reactions of EDTA with soluble and readily exchangeable cations and to simultaneous slower reactions of chelating ligands with the labile forms of competing cations. Dyanand & Sinha (1979) also found that in calcareous soils, CaEDTA was initially the dominant chelate species formed in competing with iron species for chelating ligands.

Competition among heavy metals

The magnitudes of adsorption of metals on soils were $\text{Zn} > \text{Fe} > \text{Mn} > \text{Cu}$ at pHs 5.5 and 7.5. While the magnitudes of metals desorption were $\text{Cu} > \text{Zn} > \text{Fe} > \text{Mn}$ at pH 5.5 and 7.5. The magnitudes of selectivity were $\text{Fe} > \text{Mn} > \text{Zn} > \text{Cu}$ at both pHs. The comparison between desorption and selectivity at the two pHs, for each heavy metal indicated that for Cu^{2+} the desorbed amount was greater than the selected amount indicating the low selectivity for Cu^{2+} (Biddappa *et al.*, 1981). On the other hand, the rest of heavy metals had an opposite behavior, where the desorbed amount was smaller than the selected amount providing high selectivity for Cu, Zn, Fe and Mn (McBride, 1991).

Figures 2 and 3 showed the behavior of heavy metal mixtures at two pHs. For Fe+Zn the results indicated that the selectivity of Fe was higher than that of Zn, while Zn adsorption was higher than Fe at pH 5.5 and 7.5. This behavior could be due to the chemical nature of zinc in alkaline soils, which depends on the properties of zinc. This explains the strong adsorption of zinc on clay and also its tendency to form numerous complexes (Jurinak & Bauer, 1956 and Assaad & Nielsen, 1985).

The results concerning Fe+Cu exhibited that Fe was more selective than Cu at the two-pH values, but Fe was more selective at the higher pH (7.5). This behavior could be due to two factors: a) pH 7.5 is close to the isoelectric point of different types of oxides and hydroxides of iron and b) the precipitation of iron oxides and hydroxides at high pH values (Sposito, 1984). Also as the pH increases, the number of the negative sites at CaCO_3 and MgCO_3 increases (Vulava *et al.*, 1997). So the tendency of Fe ions for producing negative sites was higher at pH 7.5.

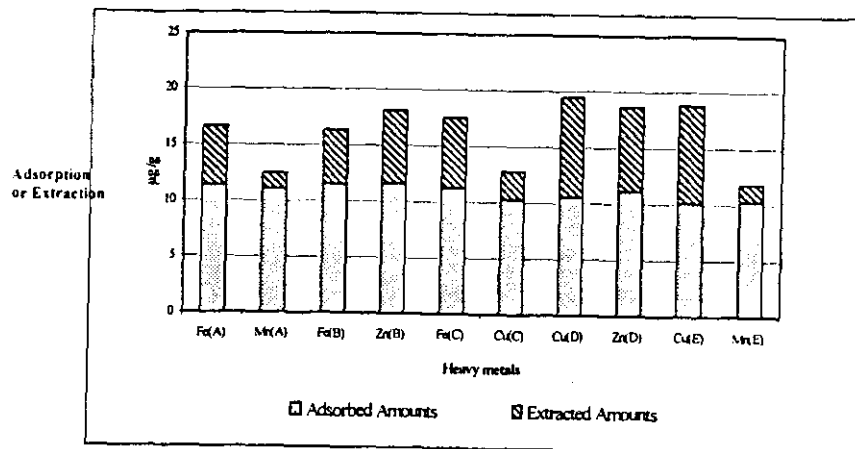


Fig.2. The adsorbed and the extracted amounts, from applied total concentration (25 ppm) of equal heavy metals ratio at pH 5.5 (A=Fe+Mn, B=Fe+Zn, C=Fe+Cu, D=Cu+Zn and E=Cu+Mn).

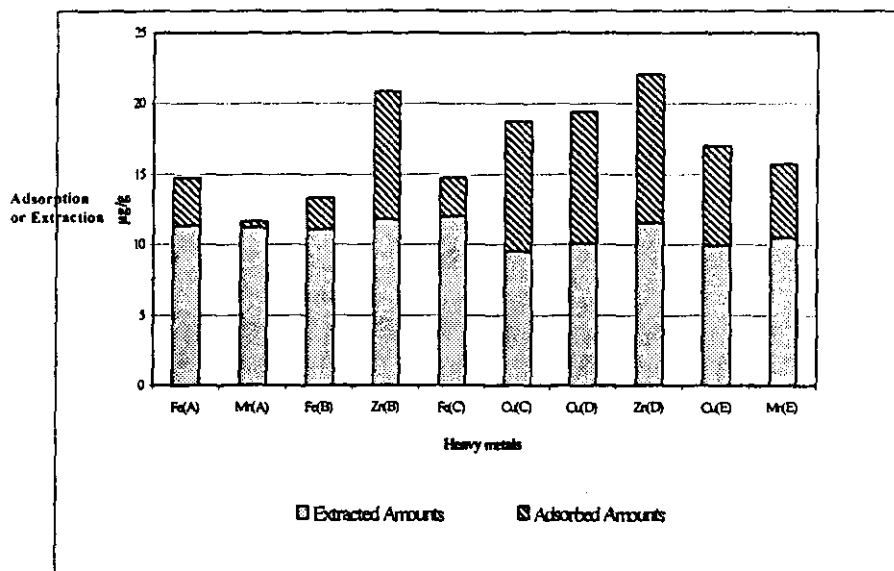


Fig. 3. The adsorbed and the extracted amounts, from applied total concentration (25 ppm) of equal heavy metals ratio at pH 7.5 (A=Fe+Mn, B=Fe+Zn, C=Fe+Cu, D=Cu+Zn and E=Cu+Mn).

For Fe+Mn, the results indicated that Mn was slightly more selective than Fe especially at pH 7.5. These results revealed the same behavior for competition between heavy metals in all soils. Kuo & Baker (1980) found similar results for Cu, Zn and Cd competitive sorption in soils in the absence of Ca^{2+} ions. This implies that calcium is not effective in preventing competition between ions for low affinity sites in soil clays. Also, Atanassova (1999) gave similar conclusion through a study on the competitive effect of Cu, Zn, Cd and Ni on adsorption and desorption by soil clays. Regarding other heavy metal couples, the present results revealed that for Zn+Cu, Zn was much more selective than Cu at pH 5.5 and 7.5. Also Zn was more selective than Mn at the two-pH values. In addition, Mn was much more selective than Cu at the two-pH values. The final conclusion for this study was that; Cu^{2+} had the lowest selectivity among other studied elements, while Zn^{2+} had the highest selectivity.

Figure 4 showed the selectivity of heavy metals in the mixture of the four elements (Fe+Mn+Zn+Cu). The results indicated that Fe was the highest selective element among the studied heavy metals and Cu was the lowest selective element. From this study, the magnitude of selectivity can be introduced as $\text{Fe} > \text{Mn} > \text{Zn} > \text{Cu}$. This order of selectivity showed that the lower the concentration in the soil solution the higher the selectivity of the metal.

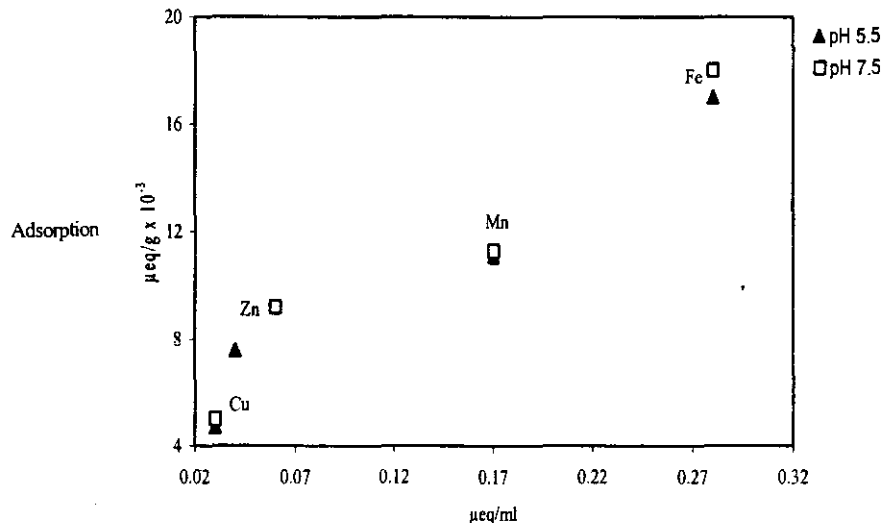


Fig.4. The relation between equilibrium concentrations and adsorbed amounts of heavy metals at equal ratios ($\text{Fe}+\text{Mn}+\text{Zn}+\text{Cu}=25\text{mgL}^{-1}$).

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سلوك إدمصاص وإستخلاص لعناصر النحاس و الزنك و المنجنيز والحديد فى الأراضى الجيرية

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تم دراسة سلوك الإدمصاص والإستخلاص للنحاس و الزنك و المنجنيز و الحديد فى الأراضى الجيرية المصرية تحت درجتى حموضة ٥,٥ و ٧,٥. و كان التركيز الأساسى المستخدم فى الدراسة لكل العناصر هو ٢٥ جزء فى المليون. تم إجراء التجارب باستخدام الأربعة عناصر سابقة الذكر فى صورة منفردة أو فى صورة مخلوط بين عنصرين مثل (الحديد+الزنك)، (الحديد+المنجنيز)، (الحديد+النحاس)، (النحاس+المنجنيز) ، (الزنك+المنجنيز) و (النحاس + الزنك) و ذلك لدراسة التفاضل بين العناصر على مواقع الإدمصاص. و كانت المحاليل متساوية التركيز (٢٥ جزء فى المليون) من كل عنصر أضيفت إلى الأراضى عند رقمى الحموضة ٥,٥ و ٧,٥. كما تم إضافة محلول يحتوى على تركيزات متساوية من الأربعة عناصر (٢٥ جزء فى المليون) مخلوطة سوياً (حديد+منجنيز+زنك+نحاس) و ذلك لمعرفة أفضلية كل عنصر الأخر. من واقع نتائج إدمصاص و إستخلاص و تثبيت العناصر كل على حدى أمكن وضع ترتيب يقارن بين هذه العناصر من حيث الخواص موضع الدراسة كما يلي:

الإدمصاص أخذ الترتيب، الزنك < الحديد < المنجنيز < النحاس، بينما أخذ الإستخلاص الترتيب، النحاس < الزنك < الحديد < المنجنيز، أما التثبيت فقد كان ترتيبه، الحديد < المنجنيز < الزنك < النحاس و ذلك عند رقمى الحموضة موضع الدراسة.