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COPPER AND ZINC DESORPTION FROM SOME IRAQI MARSH SOILS

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ABSTRACT

A laboratory experiment was conducted to study the effect of ionic strength (0.01 and 0.1 M), solution temperature (15 and 30^{o}C) and shaking time (1, 24, and 96 hours) on copper and zinc desorption from five Iraqi soil samples. Results indicated that copper and zinc desorption was increased with increasing time and temperature, while their desorption was decreased with increasing ionic strength. Results proved the suitability of first order equation and power function equation for copper and zinc desorption from some Iraqi soil samples.

INTRODUCTION

Heavy metals are important environmental pollutants threatening the health of human populations and natural ecosystem. Like other inorganic and organic contaminants, the fate of heavy metals in the environment is largely controlled by adsorption and desorption reactions with soil materials (Guzman, *et al.*, 2003).

The three main active soil materials constituents, soil minerals, metal oxides, and organic matter, are important sorbents of heavy metals owing primarily to their cation-exchgange capacity (CEC) and their ability to form inner-sphere complexes through surface reactive groups, such as carboxylic and hydroxyl groups (Weng, 2001).

Soil properties affecting on heavy metals exchange between soil and solid phase such as pH, organic matter (Gu, *et al.*, 1994), and ionic strength (Sparks, 1992). The effect of temperature on heavy metals reaction is well known and important in understanding reaction mechanisms. Savant Arrhenius noted that for most reactions, the increase in rate with increasing temperature is nonlinear. El-Khatib et al (El-khatib *et al.*, 1988) tested Pb-sorption kinetics on three soils and they found the exchange between soil and solution increased with increasing temperature. The objective of this study is to indicate the effect of ionic strength and temperature on cupper and zinc desorption from some Iraqi marsh soil samples at several times by using kinetics models.

MATERIALS AND METHODS

Soil samples (0-15 cm) were collected from five different locations of southern part of Iraqi marshes (AlChabayesh, Um-Al-Naahaj, Al-Maymouna, Hor Al-Hammar, and Um-Al-Ward).

The characteristics of soil samples which are obtained by routine procedures (Black, 1965; Jackson, 1985; Muller, 1979) are given in Table (1). Readily available copper and zinc was extracted by DTPA solution according to the methods of Norvll and Lindsay (1979) which described in Page *et al*. (1985).

Table (1): Physio - chemical characteristics of some Iraqi marsh soil samples.

Soil Samples	pH 1:1	E.Ce dSm^{-1}	O.M gkg^{-1}	$CaCO_3$ gKg^{-1}	Soil particles gkg^{-1}			Soil samples texture
					sand	silt	clay	
AlChabayesh	8.3	2.45	15.50	86.9	95.2	512	392.0	Clayey silt
Um-Al-Naahaj	7.4	2.68	22.45	91.3	38.8	240	721.2	Silty clay
Al-Maymouna	7.5	2.44	17.27	75.3	261.6	96	644.2	Sandy clay
Hor Al-Hammar	7.5	2.16	19.00	66.5	395.6	128	476.4	Silty clay
Um-Al-Ward	7.3	2.87	15.50	95.5	170.4	96	733.6	Sandy clay

Desorption of copper and zinc was studied by using 5.0 gm of air dried soil samples with 50 ml of each solution, (0.01 and 0.1M NaCl), with two temperature degree of solution (15 and 30 ^oC) in, polypropylene centrifuge tubes and equilibrated the suspension for one for 1; 24; and 96 hrs. after equilibration, zinc and copper concentration were determined by using atomic absorption spectrophotometer (SP9).

Copper and zinc desorption was described by using two types of kinetics model, chemical assumption (First order equation) and empirical equation (Power Function equations) which described in Sparks (1992).

SPSS program was used for results analysis.

First Order Equation

Rate= -dC/dt = Kd(Cu₀-Cuₜ) …………………………..(1)

Rearranging the equation

$$-\frac{dCu_o}{(Cu_o - Cu_t)} = Kd\, dt \quad \ldots\ldots (2)$$

Taking the natural log of both side of eq (2) one obtains:-

$$\mathbf{Ln\ (Cu_o - Cu_t) = Ln\ Cu_o - Kdt} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Cu_o= Copper concentration at equilibrium (mg/kg)
Cu_t = Copper desorbed after (t) time (mg/kg)
T= time (hours)
Kd= Copper desorption coefficient (1/hr.)

Power Function Equation

$$\mathbf{Cu_t = Cu_o\ t^{kd}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Taking the natural log of both sides of eq. (4) 0ne obtains-

$$\mathbf{Ln\ Cu_t = Ln\ Cu_o + Kd\ Ln\ t}$$

By plotting $LnCu_t$ vs. Lnt, a linear relationship is obtained and one can determined Kd from the slope and $LnCu_o$ from the intercept.

The same equations were used for proving zinc desorption from the studied marshes soil samples.

RESULTS AND DISCUSSION

Results listed in Table (2) shows the concentration of copper and zinc extracted with DTPA solution. Copper concentration was higher than zinc concentration in the studied marshes locations. These values mean copper and zinc are found incorporated in clay minerals and organic matter and may be desorbed to water (Masond, 2005). Al-Manssory *et al*. (2004) found that the concentration($mg.kg^{-1}$) of cupper and zinc in the surface sediments of five station along 17km of northern part of Shatt Al-Arab River during 1997-1998 were as, Cu(19.38to 39.22), and Zn(11.07 to 131.79), and they remembered that sediment were moderately polluted with these heavy metals.

Table (2): Copper and zinc concentrations for some Iraqi marsh soil samples extracted with DTPA solution ($mg.kg^{-1}$).

Soil samples	Copper	Zinc
Al-Chabayesh	1.58	0.85
Um-Al-Naahaj	4.38	1.42
Al-Maymouna	2.88	1.53
Hor Al-Hammar	1.46	0.64
Um-Al-Ward	2.44	0.90

From the results of Tables (3 and 4), which indicate copper and zinc desorption from Al-Chabayesh, Um-Al-Naahaj, Al-Maymouna, Hor Al-Hammar, and Um-Al-Ward soil samples with, highest level of copper and zinc desorption at 96 hrs. equal to (36.03, 27.25, 27.78, 34.08 and 24.58)% of Cu-DTPA, and (21.25, 56.81, 65.28, 47.58, and 74.78)% of Zn-DTPA respectively, that's mean the studied soil samples, have the ability to desorbed copper and zinc to solution phase (water) with the time and polluted it with heavy metals.

Locations appeared a significant effect on copper and zinc desorption, and they take the following order for Cu-desorption: (Um-Al-Naahaj > Al-Maymouna > Um-Al-Ward > Al-Chabayesh > Hor Al-Hammar) and (Al-Maymouna > Um-Al-Naahaj > Um-Al-Ward > Al-Chabayesh > Hor Al-Hammar) for Zn-desorption, this may be due to the physical and chemical properties of studied soil samples. Results in Table (5) indicate the correlation coefficient between soil properties and copper and zinc desorbed from the studied soils, which appear the effects of clay content and soil organic matter on the amount of copper and zinc desorbed from some Iraqi marsh soil samples. While ionic strength and solution temperature did not appear a significant effects on copper and zinc desorption.

Results of zinc and copper desorption from the studied marshes soil samples indicate a high simple regression coefficients (R) were obtained by using these equations for all the treatments employed in present study (Ionic strength, temperature degree) and for both heavy metals (copper and zinc). Muller (1979) showed that heavy metals found in solid phase as carbonate or chelates with organic matter, which may be released to liquid phase by changing the environmental factors such as salinity or pH, organic acids, and the distribution coefficients of copper and zinc was changed with changing of environment factors.

Table (3): Effect of ionic strength, temperature, time of extraction on copper desorption from some Iraqi marsh soil samples

Sediments locations	Ionic Strength (M.L^{-1})	Temp. (^{o}C)	Cu-desorbed (mg.kg^{-1})		
			1hr	24hrs.	96hrs.
Al-Chabayesh	0.01	15	0.217	0.325	0.542
		30	0.235	0.420	0.655
	0.1	15	0.195	0.280	0.475
		30	0.210	0.395	0.605
Um-Al-Naahaj	0.01	15	0.420	0.800	1.220
		30	0.465	0.885	1.350
	0.1	15	0.380	0.645	1.025
		30	0.420	0.760	1.180
Al-Maymouna	0.01	15	0.285	0.525	0.810
		30	0.320	0.600	0.920
	0.1	15	0.240	0.425	0.665
		30	0.280	0.525	0.805
Hor Al-Hammar	0.01	15	0.180	0.320	0.500
		30	0.210	0.385	0.595
	0.1	15	0.150	0.260	0.410
		30	0.175	0.310	0.485
Um Al-Ward	0.01	15	0.217	0.397	0.614
		30	0.240	0.450	0.690
	0.1	15	0.180	0.320	0.500
		30	0.210	0.395	0.605

Table (4): Effect of ionic strength, temperature, time of extraction on zinc desorption from some Iraqi marsh soil samples

Sediments locations	Ionic Strength ($M.L^{-1}$)	Temp. (^oC)	Zn-desorbed ($mg.kg^{-1}$) 1hr	24hrs.	96hrs.
Al-Chabayesh	0.01	15	0.146	0.219	0.365
		30	0.220	0.380	0.600
	0.1	15	0.130	0.195	0.325
		30	0.148	0.270	0.418
Um-Al-Naahaj	0.01	15	0.292	0.509	0.801
		30	0.318	0.558	0.876
	0.1	15	0.276	0.458	0.734
		30	0.298	0.518	0.816
Al-Maymouna	0.01	15	0.340	0.632	0.972
		30	0.370	0.698	1.068
	0.1	15	0.320	0.605	0.925
		30	0.365	0.665	1.030
Hor Al-Hammar	0.01	15	0.120	0.185	0.305
		30	0.146	0.219	0.365
	0.1	15	0.100	0.148	0.248
		30	0.120	0.180	0.300
Um Al-Ward	0.01	15	0.240	0.438	0.678
		30	0.260	0.480	0.740
	0.1	15	0.222	0.402	0.624
		30	0.230	0.420	0.650

Table (5): Correlation coefficient values between soil properties and copper and zinc desorbed from some Iraqi marsh soil samples.

Metal desorbed	Correlation coefficient(r)						
	pH	E.C	$CaCO_3$	O.M	Sand	Silt	Clay
Cu-desorbed	-0.335	0.392	-0.365	0.907*	-0.609	-0.046	0.887*
Zn-desorbed	-0.434	0.481	-0.542	0.932*	-0.334	-0.138	0.902*

Table (6): First order equation for Copper desorption form some Iraqi Marshes soil samples

Soil samples	First Order Equation-Copper	R
For all ionic strength(I) and temperature		
Al_Chabayesh	Y= -0.298 – 0.00305 Ln time	0.991
Um-Al-Naahaj	Y= 1.359- 0.00215 Ln time	0.979
Al-Maymouna	Y = 0.938 – 0.00221 Ln time	0.978
Hor Al-Hammar	Y= 0.229 – 0.00286 ln time	0.984
Um Al-Ward	Y = 0.800 – 0.00232 Ln time	0.991
At 0.01 $mM.l^{-1}$		
Al_Chabayesh	Y = 0.290 -0.00327 Ln time	0.993
Um-Al-Naahaj	Y= 1.353 – 0.0024 Ln time	0.971
Al-Maymouna	Y 0.927 -0.00243 Ln time	0.977
Hor Al-Hammar	Y= 0.213 – 0.00326 ln time	0.983
Um Al-Ward	Y= 0.772 – 0.00199 ln time	0.929
Al_Chabayesh	Y = 0.307 – 0.00284 ln time	0.991
Um-Al-Naahaj	Y= 1.368 – 0.00194 ln time	0.983
Al-Maymouna	Y= 0.943 – 0.00193 ln time	0.984
Hor Al-Hammar	Y= 0.245 – 0.00248 ln time	0.986
Um Al-Ward	Y = 0.804 – 0.00170 ln time	0.977
Al_Chabayesh	Y= 0.315 – 0.00258 ln time	0.998
Um-Al-Naahaj	Y= 1.366 0.00199 ln time	0.981
Al-Maymouna	Y = 0. 947 – 0.00199 ln time	0.981
Hor Al-Hammar	Y= 0.243 – 0.00254 ln time	0.985
Um Al-Ward	Y= 0.788 – 0.00161 ln time	0.916
Al_Chabayesh	Y= 0.281 – 0.00355 ln time	0.982
Um-Al-Naahaj	Y= 1.352 – 0.00232 ln time	0.977
Al-Maymouna	Y= 0.928 – 0.00243 ln time	0.976
Hor Al-Hammar	Y = 0.216 – 0.00319 ln time	0.984
Um Al-Ward	Y= 0.787 – 0.00206 ln time	0.976

Where Y = Ln Copper desorption value

Table (7): First order equation for zinc desorption form some Iraqi marshes soil samples.

Soil samples	First Order Equation-Zinc	R
For all ionic strength(I) and temperature		
Al_Chabayesh	Y= -0.389– 0.00499Ln time	0.993
Um-Al-Naahaj	Y= 0.0953- 0.00619 Ln time	0.994
Al-Maymouna	Y = 0.126 – 0.00804 Ln time	0.990
Hor Al-Hammar	Y= -0.663– 0.00448ln time	0.999
Um Al-Ward	Y = -0.433 – 0.0111 Ln time	0.993
Al_Chabayesh	Y = -0.361-0.00654 Ln time	0.991
Um-Al-Naahaj	Y = 0.0943– 0.0079Ln time	0.998
Al-Maymouna	Y= 0.121-0.00843 Ln time	0.991
Hor Al-Hammar	Y= -0.758– 0.00438 ln time	0.988
Um Al-Ward	Y=- 0.461– 0.0126 ln time	0.997
Al_Chabayesh	Y= - 0.368 – 0.00302 ln time	0.973
Um-Al-Naahaj	Y= -.1030.00573 ln time	0.994
Al-Maymouna	Y = 0. 133– 0.00772 ln time	0.991
Hor Al-Hammar	Y= - 0.639 – 0.00384 ln time	0.999
Um Al-Ward	Y=- 0.428– 0.00960 ln time	0.994
Al_Chabayesh	Y= - 0.345– 0.00355 ln time	0.998
Um-Al-Naahaj	Y= -0.106.00563 ln time	0.993
Al-Maymouna	Y = 0. 215– 0.00139 ln time	0.999
Hor Al-Hammar	Y= - 0.719 – 0.00425 ln time	0.998
Um Al-Ward	Y=- 0.435– 0.0101 ln time	0.995
Al_Chabayesh	Y=- 0.424 – 0.00773 ln time	0.991
Um-Al-Naahaj	Y=0.08025– 0.00673 ln time	0.993
Al-Maymouna	Y= 0.112– 0.00895ln time	0.992
Hor Al-Hammar	Y = 0.764– 0.00583ln time	0.999
Um Al-Ward	Y=- 0.455– 0.0119 ln time	0.996

Where Y = Ln Zinc desorption value

Table (8): Power Function equation for Copper desorption form some Iraqi marshes soil samples.

Soil samples	Power Function Equation-Copper	R
For all ionic strength(I) and temperature		
Al_Chabayesh	Y= -1.576 + 0.20 Ln time	0.979
Um-Al-Naahaj	Y=- 0.888+ 0222 Ln time	0.992
Al-Maymouna	Y = -1.292 + 0.223 Ln time	0.992
Hor Al-Hammar	Y= -1.747 + 0.217 ln time	0.989
Um Al-Ward	Y = -0.269- 0.104 Ln time	0.628
At 0.01 $mM.l^{-1}$		
Al_Chabayesh	Y = - 1.521 + 0.204 Ln time	0.979
Um-Al-Naahaj	Y= -0.833+ 0.228 Ln time	0.995
Al-Maymouna	Y = -1.217 + 0.224 Ln time	0.993
Hor Al-Hammar	Y= -1.659 +0.220 ln time	0.991
Um Al-Ward	Y= - 1.496 + 0.223 ln time	0.993
At 0.1$mM.L^{-1}$		
Al_Chabayesh	Y = -1.628 + 0.205 ln time	0.980
Um-Al-Naahaj	Y= -0.943+ 0.214 ln time	0.988
Al-Maymouna	Y= -1.370 + 0.221 ln time	0.992
Hor Al-Hammar	Y= -1.842 + 0.214 ln time	0.987
Um Al-Ward	Y = -1.658 + 0.222 ln time	0.992
At 15 ^oC		
Al_Chabayesh	Y= -1.627 + 0.185 ln time	0.952
Um-Al-Naahaj	Y= -0.941 + 0.219 ln time	0.990
Al-Maymouna	Y = -0.228 – 0.0062 Ln time	0.477
Hor Al-Hammar	Y= -1.829 + 0.215 ln time	0.987
Um Al-Ward	Y= -1.642 + 0.219 ln time	0.990
At 30 ^oC		
Al_Chabayesh	Y= -1.524 + 0.221 ln time	0.992
Um-Al-Naahaj	Y= 0.0822+ 0.0352 ln time	0.382
Al-Maymouna	Y= -1.224 + 0.226 ln time	0.994
Hor Al-Hammar	Y = -1.673 + 0.219 ln time	0.990
Um Al-Ward	Y= -1.512 + 0.226 ln time	0.994

Where Y = Ln Copper desorption value

Table (9): Power Function equation for zinc desorption form some Iraqi marshes soil samples

Soil Samples	Power Function Equation-zinc	R
For all ionic strength(I) and temperature		
Al_Chabayesh	**Y= -1.849+ 0.20 Ln time**	**0.977**
Um-Al-Naahaj	**Y=- 1.246+ 0211 Ln time**	**0.985**
Al-Maymouna	**Y = -1.077 + 0.224 Ln time**	**0.991**
Hor Al-Hammar	**Y= -1.886 + 0.265 ln time**	**0.690**
Um Al-Ward	**Y = -1.458- 0.221 Ln time**	**0.992**
At 0.01 $mM.l^{-1}$		
Al_Chabayesh	**Y = - 1.733 + 0.202 Ln time**	**0.977**
Um-Al-Naahaj	**Y= -1.215+ 0.213 Ln time**	**0.987**
Al-Maymouna	**Y = -1.057 + 0.225 Ln time**	**0.994**
Hor Al-Hammar	**Y= -2.060 +0.190 ln time**	**0.962**
Um Al-Ward	**Y= - 1.409 + 0.222 ln time**	**0.992**
At 0.1$mM.L^{-1}$		
Al_Chabayesh	**Y = -1.645 + 0.116 ln time**	**0.861**
Um-Al-Naahaj	**Y= -1.279+ 0.209 ln time**	**0.983**
Al-Maymouna	**Y= -1.092+ 0.0.223 ln time**	**0.993**
Hor Al-Hammar	**Y= -2.252 + 0.187 ln time**	**0.957**
Um Al-Ward	**Y = -1.511 + 0.220 ln time**	**0.991**
At 15 ^{o}C		
Al_Chabayesh	**Y= -2.026+ 0.188 ln time**	**0.959**
Um-Al-Naahaj	**Y= -1.290 + 0.209 ln time**	**0.984**
Al-Maymouna	**Y = -1.130+ 0.226 Ln time**	**0.994**
Hor Al-Hammar	**Y= -2.252 + 0.190 ln time**	**0.959**
Um Al-Ward	**Y= -1.489 + 0.220 ln time**	**0.991**
At 30 ^{o}C		
Al_Chabayesh	**Y= -1.720 + 0.215 ln time**	**0.988**
Um-Al-Naahaj	**Y= -1.206+ 0.214 ln time**	**0.987**
Al-Maymouna	**Y= -1.008 + 0.206 ln time**	**0.999**
Hor Al-Hammar	**Y = -2.062 + 0.188 ln time**	**0.957**
Um Al-Ward	**Y= -1.429 + 0.222 ln time**	**0.992**

Where Y = Ln zinc desorption value

REFERENCES

AL-Manssory, F.A., Abdul Kareem, M.A. and Yassen, M.M. 2004. An Assessment of environmental pollution by some trace metals in the northern part of shatt AL-Arab sediments, Southern Iraq. Iraqi Jour. Earth Sci.,: 11-22.

Ajil, S.Z. 1999. Use of mathematical models on prediction phosphate availability index and the fertilizer requirement for corn grown in calcareous soils. Thesis in Soil Sci College of Agric. Univ. of Basrah, Iraq.

Black, C.A. 1965. Methods of soil analysis. Physical properties. Am. Soc. Agron. Inc. Publisher.

EL-Khatib, E.A., and Hern, J.L. 1988. Kinetics of phosphate from appakhian soils. soil Sci 145: 222-229.

Gu, B.J, Schmit, Z. Liang, C.L. and McCarthy, J.F. 1994. adsrption and desorption of natural organic matter on iron oxide-mechanisms and models. Environ. Sci. Technol. 28: 38-46.

Guzman, M.C., Celis, R. Hermosin, M.C. Leone, P. Negre, M. and Cornjo, J. 2003. Sorption-Desorption of Lead (11) by model association of soil colloids. soil Sci .Soc. Am. J. 67: 1378-1387.

Jackson, M.L. 1958. Soil chemical analysis prentice Hall, Ino, Englewood Cliffs, N. J.

Lindsay, W.L. 1979. Chemical equilibria in Soils. John Wiley and Sons, New York.

Masoud, M.S., elewa, A.A. Ali, A.E. and Mohamd, E.M. 2005. Distribution of some metal concentration in water and sediments of lake Edku, Egypt. Bulletin of the chemists and Technologists of Maccedonia 24: 21-34.

Muller, G. 1979. Schwermetalle in den sedimenten des Rheas-Verenderungen Seit. Umschav, 79: 133-149. (in Audry, S.; J. Schafer, G. Blanc; J.M. Jouanneaua, 2004b. Fifty-year sedimentary record of heavy metal pollution (Cd, Zn, CuPb) in Lot River reservios (France). Environ. Poll., 132: 413-426.

Page, A.L., Miller, R.H. and Kenney, D.R. 1982. Methods of Soil Analysis. Part 2 Chemical and Biological Properties. Amer. Soc. Agron. Inc. publisher, Madison. Wisconsin.

Sparks, D.L. 1992. Kinetics of soil chemicals processes. Academic Press Inc., (England).

Weng, L., Temminghoff, E.J.M. and Van Riemsdjk, W.H. 2001. Contribution of individual sorbents to the control of heavy metal activity in sandy soil. Environs. Technol., 35: 4436-4443.

انطلاق النحاس والزنك من بعض نماذج ترب أهوار العراق

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المستخلص

نفذت تجربة مختبريه لدراسة تأثير القوة الأيونية (1.01 و0.1 مولاري) ودرجة حرارة المحلول (15 و30م) والزمن (1 و24 و96 ساعة) على انطلاق النحاس والزنك من خمسة ترب من اهوار العراق. أوضحت النتائج بأن انطلاق النحاس والزنك يزداد مع زيادة درجة الحرارة والزمن، في حين يقل انطلاقهما مع زيادة القوة الأيونية وإمكانية استخدام معادلة الرتبة الأولى ودالة القوة لوصف انطلاق النحاس والزنك من بعض ترب اهوار جنوبي العراق.