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RESEARCH ARTICLE

Influence of pH and Ionic Strength on the Adsorption of Copper and Zinc in Bentonite Clay

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Abstract: This study concerned with the possibility of adsorption of some metal cations such as Cu^{2+} and Zn^{2+} on bentonite ore which were used as an inorganic fertilizer. Maximum adsorption was obtained at pH 5-5.5. The relationship between the amounts of metal cations adsorbed was found to follow the Freundlich adsorption isotherm. Preferential adsorption of both ions on adsorption sites was found to take place; Cu^{2+} is being adsorbed at greater extent than Zn^{2+}. Bentonite samples which allowed adsorbing Cu^{2+} and Zn^{2+} were then subjected to desorption experiments using EDTA/OAc. Sequential leaching of the adsorbed ions revealed that the amounts of desorbed ion are linearly proportional to the amount previously adsorbed.

Keywords: Adsorption, Cations, pH, Bentonite

Introduction

Heavy metals can be introduced into agricultural soils by industrial emissions and by a variety of agricultural treatments, including fertilizers, liming materials, manure, sewage sludge and composts. Several studies on soil chemistry have demonstrated that zinc (Zn) concentration increases in certain agricultural soils as the result of the use of those materials[1]. The phytotoxic threat of Zn and the risk of its contaminating surface or groundwater depend on its concentration in the soil solution, which is related to its adsorption and desorption from soil colloids. Owing to their adsorption capacity, aluminosilicate and mineral oxides are capable of removing many metals over a wide pH range representing an efficient way for the remediation of contaminated soils. Extensive research has assessed the metal adsorption characteristics of natural or modified clays and oxides and has demonstrated that pH variation influences zinc adsorption. Lacin *et al.* has found that the pH has positive effects on zinc adsorption by bentonite clay[2]. Usually, raising the pH increases the capacity for zinc adsorption[3-4]. The increase in adsorption is probably due to cation hydrolysis, since hydroxyl complexes are adsorbed preferentially over uncomplexed cations or to the increase in the negative surface charge of the adsorbent related to the increase in the concentration of hydroxyl ions, leading to an increase in attraction for cation in solution[5]. In the same way, the surface area of the adsorbent can influence in the adsorption process. Bentonite exhibits an enormous surface area when it is hydrated in water. It consists of numerous microscopic platelets, each with negative charges on the flat surfaces and positive charges on the edges. Hydration causes these platelets to separate into a porous structure containing both positive and negative charges. It is well known that the ionic charge and the porous structure give bentonite the ability to adsorb the toxins[6]. Numerous researches have been conducted on natural bentonite to examine its potential for the removal of heavy metal ions. It is found that natural bentonite could be used effectively for the removal of zinc ions from aqueous solutions[7]. Adsorption – desorption processes have a strong influence on the presence of metals in the soil solution. The adsorption of Zn in soils, soil fractions and minerals is well-documented[8-13]. Mineral fertilizers contain elements which are required by plants and those can be classified as macronutrients mainly N, P, K and micronutrients such as Si, Ca, Mg, S, Fe, Cu and Zn[14]. Secondary nutrients exist only in small amounts in ordinary soils and plants. In general all trace elements are toxic to plants if they are present in concentrations above normal. Two of the most important micronutrients are Cu and Zn, occurs in the soil principally as Cu^{2+} and Zn^{2+} ions adsorbed by clay minerals or tied up by organic matter[14], copper play a role in plant growth as an enzyme activator, also it is important in protein metabolism and may be associated with chlorophyll formation[15-19]. Zinc acts either as a metal component of enzymes or as a functional, structural or regulatory cofactor of a large number of enzymes, it is well established that zinc deficiency is associated with an impairment of carbohydrate metabolism and protein synthesis[20]. Micronutrients deficiencies represent a severe problem to the agriculture in Libya[21]. The present work is an attempt to utilize the Libyan bentonite ore as a carrier of plant nutrients as inorganic fertilizer; therefore we try to find the most appropriate conditions for the adsorption of the two micronutrients Cu^{2+} and Zn^{2+} on the surface of bentonite clay. The factors studied are the effect of concentration of the ions and the pH on the process of adsorption. To stimulate the process of plant uptake of micronutrients from the soil, a desorption study is carried out on the previously adsorbed Cu^{2+} and Zn^{2+} ions on bentonite using EDTA as chelating agent.

Experimental

The bentonite ore was obtained from Umm-Ar-Razam area at north east of Libya; the upper layers of the earth crust in this area are mostly limestone, while the lower layers consist mainly of bentonite.

The bentonite samples collected at depth 3-9 meters and from six different drilling sites, the samples were allowed to dry in air. The ore lumps obtained were fragmented to smaller pieces by a steel hammer and then crushed to below 10mm particles using a Jaw-Crusher. A representation sample was obtained from the six crushed ore samples by the method of quartering[22]. Then these samples (about 5 kg) were further dried at 105-110 °C, then grounded further to obtain grain size ~200 mesh (74 µ), this particle size was needed for complete chemical and x-ray analysis as well as for adsorption experiments.

Chemical analysis of ore

One gram of the ore sample was mixed with one gram of Na_2CO_3 and the mixture was fused at 1000 °C using platinum crucible, the fusion product was extracted with HCl solution (100 mL, 1:1), then filtered and washed. The filtrate and washing were completed to 500 mL measuring flask. Such solution was used for determination of Al_2O_3, CaO, MgO, Fe_2O_3, Mn, Cu and Zn using standard methods[23]. Moisture content was determined using moisture balance. The chemical analysis results of bentonite ore are given in Table 1.

Table 1. Chemical analysis of Umm-Ar-Razam bentonite ore

Component	Wt %
Al_2O_3	19.00
SiO_2	34.70
Fe_2O_3	7.35
CaO	7.98
MgO	2.35
SO_4^{2-}	0.765
P	1.5 ppm
Moisture	10.23
L.O.I	13.59
Organic Matter	0.279
Organic Carbon	0.162
K_2O	1.34
Na_2O	1.44
Cu	0.45 ppm
Zn	0.66 ppm
N	0.02

X-Ray analysis of the ore

X-ray diffraction analysis of powdered bentonite sample showed the presence of the following minerals: Montmorillonite [$Na_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2.XH_2O$],Kaolinite [$Al_2Si_2O_5(OH)_4$], Quartz ($SiO_2$), Gypsum ($CaSO_4.2H_2O$), Calcite ($CaCO_3$). According to the above results Umm-Ar-Razam ore may be classified as low grade bentonite.

Adsorption experiments

Adsorption experiments were conducted by mixing 1 g bentonite sample 74 µ with standard solutions of Cu^{2+} and Zn^{2+}.

Preparation of standard solutions

Standard Cu^{2+} and Zn^{2+} solutions were prepared using Analar grade reagents, pure Zinc metal and Copper metal were used.

1 g Metal was dissolved in a mixture of concentrated H_2SO_4 (30 mL) and concentrated HNO_3 (20 mL) then made upto 1 liter using double distilled water in a measuring flask to give a standard solution of 1000 ppm of the metal ion, from this solution concentration 200, 400, 600 and 800 ppm were prepared. Determination of Cu^{2+} and Zn^{2+} concentrations were done by atomic absorption spectrometer (AAS). Measurements showed that best sensitivity and accuracy of the spectrophotometer was in the range up to 5 ppm and hence all solutions were diluted to be within that range.

Technique of adsorption experiments

Duplicate 1 g samples of bentonite (74 µ) were equilibrated for 24 h including an initial conditioning for 2 h on a reciprocating shaker at 25 °C with 20 mL of different metal cation solutions. The metal cation concentrations of Cu^{2+} and Zn^{2+} were 200, 400, 600 and 800 ppm, as sulphates. The samples were then centrifuged and the centrifugates were analyzed for the respective cation concentration by atomic absorption spectrophotometer, the adsorption densities for each cation were calculated.

pH adjustment

When 1 g bentonite is well mixed with double distilled water (20 mL), the pH of the emulsion is 7.9-8.1, that may be due to the presence of some alkaline cations such as K^+, Na^+, Ca^{2+} and Mg^{2+}. When adding the metal cation solution of pH 2.5 to bentonite the pH of the mixture becomes ~6. To adjust the pH of the mixture to the required value few drops of either 5 M KOH or H_2SO_4 were added.

Desorption experiments

Desorption tests were conducted by sequential extraction of the respective metal cation-equilibrated bentonite with four consecutive portions of 10 mL each of mixed solution of 1 M ammonium acetate and 0.01 M EDTA solution. The bentonite –metal cation system from parallel adsorption tests were shaken for one hr intervals at 25 °C with the leach solutions and centrifuged. The centrifugates of each test were collected in 50 mL volumetric flasks and were analyzed for the respective metal cation concentration on an atomic absorption spectrophotometer; the quantities desorbed of each metal cation were calculated.

Results and Discussion

Adsorption of Cu^{2+} ion and Zn^{2+} ion on the bentonite

Effect of pH of the medium on adsorption

The process of cation exchange between solid surface and the solution containing the heavy metal cations is highly dependent on the pH value of the medium. Accordingly, the adsorption of Cu^{2+} and Zn^{2+} was studied at different pH values ranging from highly acidic (pH= 0.5-1.0) to neutral (pH=6.5-7.0). When 1 g of bentonite ore is mixed with 20 mL of double distilled water, the pH of the emulsion is 7.9-8.1. The alkalinity of the emulsion is most probably due to the predominance of the cations Ca, Mg, Na and K on the surface of clay crystals which gives rise to the formation of the corresponding hydroxides. On the other hand when 1 g of the bentonite ore is mixed with 20 mL of the metal cation solution (pH=2.5) the pH of the mixture becomes about 6. The pH value is varied by adding few drops of 5 M KOH or H_2SO_4. The results of adsorption experiments are given in Tables 2 and 3.

Table 2. Adsorption of Cu^{2+} ions on bentonite at different pH values

Original Conc. of Cu^{2+}, ppm	pH	Cu^{2+} remaining in solution, ppm	Cu^{2+} adsorbed, ppm	Remarks
(20 mL water)	7.0	Traces	-	Blank
200	1.0	179.72	20.28	Normal samples
200	1.0	183.60	16.40	Normal samples
200	2.8	137.28	62.72	Normal samples
200	2.9	130.59	69.41	Normal samples
200	4.9	75.76	124.24	Normal samples
200	5.0	63.00	137.00	Normal samples
200	5.6	59.92	140.08	Normal samples
200	6.5	2.85	→	Precipitation
200	3.6	164.04	35.96	Samples treated
200	5.0	130.59	69.41	with
200	5.5	112.40	87.60	1:1 HNO_3
400	0.6	383.38	16.62	Normal samples

Contd…

400	0.6	375.40	24.60	Normal samples
400	2.9	317.50	82.50	Normal samples
400	4.5	170.34	129.66	Normal samples
400	4.9	124.20	175.80	Normal samples
400	5.0	123.00	234.00	Normal samples
400	5.5	114.77	285.23	Normal samples
400	6.1	16.14	→	Precipitation
400	6.5	17.25	→	Precipitation
400	2.8	363.76	36.04	Samples treated with 1:1 HNO_3
400	4.9	277.91	122.09	
400	5.6	260.80	139.20	
600	0.5	575.73	24.27	Normal samples
600	0.5	580.44	19.56	Normal samples
600	4.1	419.40	180.60	Normal samples
600	5.0	268.34	327.00	Normal samples
600	5.5	203.19	396.81	Normal samples
800	0.4	785.20	14.80	Normal samples
800	3.0	620.79	179.21	Normal samples
800	5.0	353.00	417.00	Normal samples
800	5.0	353.34	446.66	Normal samples
800	5.5	321.72	478.28	Normal samples
800	6.0	29.74	→	Precipitation

Table 3. Adsorption of Zn^{2+} ions on bentonite at different pH values

Original Conc. of Zn^{2+}, ppm	pH	Zn^{2+} remaining in solution, ppm	Zn^{2+} adsorbed, ppm	Remarks
(20 mL water)	7.00	Traces	-	Blank
200	1.0	184.84	15.16	Normal samples
200	2.8	145.22	54.78	Normal samples
200	2.9	153.08	46.92	Normal samples
200	5.0	60.00	140.00	Normal samples
200	5.4	47.00	153.00	Normal samples
600	1.6	514.54	85.46	Normal samples
600	3.2	446.76	153.24	Normal samples
600	5.0	297.00	303.00	Normal samples
600	5.5	238.73	361.27	Normal samples
600	6.1	224.11	375.89	Normal samples

The results showed that adsorption of the heavy metal cations on bentonite are very sensitive to the pH value of the medium. Adsorption takes place slightly at lower pH values (up to pH= 3.5-4.0), above this value adsorption becomes significant and maximized at pH= 5 for both ions (Cu^{2+} and Zn^{2+}).

At higher pH the metal cations begin to hydrolyze and precipitate and hence become not available for adsorption. Precipitation of Cu^{2+} ion and Zn^{2+} ion in their solutions as hydroxides were found to occur at pH= 5.95 and pH= 6.90 respectively.

Generally, the specific adsorption of these metals at low concentrations ($< 10^{-3}$ M) was found to increase with pH and was virtually complete at pH values less than the corresponding pK (the first hydrolysis constant of the metal, thus the cation which is most readily hydrolyzed in solution also has the highest affinity to be adsorbed[23]. However, the present results agree with such conclusions.

Adsorption studies

The relationship between the equilibrium concentrations (C) of the metal cations Cu^{2+} and Zn^{2+} and the amounts of cations adsorbed on bentonite surface (x/m) was studied at pH= 5. The results are given in Tables 4 and 5.

Table 4. Amounts of Cu^{2+} ions adsorbed onto bentonite at pH= 5

Equilibrium Conc. of Cu^{2+}(C)			Amounts of Cu^{2+} adsorbed per 1 g bentonite (x/m)		
ppm	meq/L	log C	ppm	meq/g	log x/m
200	3.150	0.4983	137	2.157	0.3339
400	6.300	0.7993	234	3.685	0.567
600	9.450	0.9750	327	5.149	0.7118
800	12.600	1.1004	417	6.567	0.8174

Each reading is the average of four measurements.

Table 5. Amount of Zn^{2+} ions adsorbed onto bentonite at pH= 5

Equilibrium Conc. of Zn^{2+}(C)			Amount of Zn^{2+} adsorbed per 1 g bentonite (x/m)		
ppm	meq/L	log C	ppm	meq/g	log x/m
200	3.059	0.4856	140	2.141	0.3306
400	6.118	0.7866	229	3.502	0.5443
600	9.177	0.9627	303	4.634	0.6660
800	12.236	1.0879	376	5.751	0.7597

It is obvious that the amount of Cu^{2+} and Zn^{2+} ions adsorbed increase with increase in the equilibrium concentration of the cation in the bulk solution, but the increase becomes less for higher concentrations. However adsorption seems to reach a maximum value when all adsorption sites are occupied with ions.

Applying the Freundlich adsorption isotherm equation shown below to the experimental data, it satisfactorily fits and give a straight line relationship between log x/m and log C for both Cu^{2+} and Zn^{2+} (Figure 1 & 2).

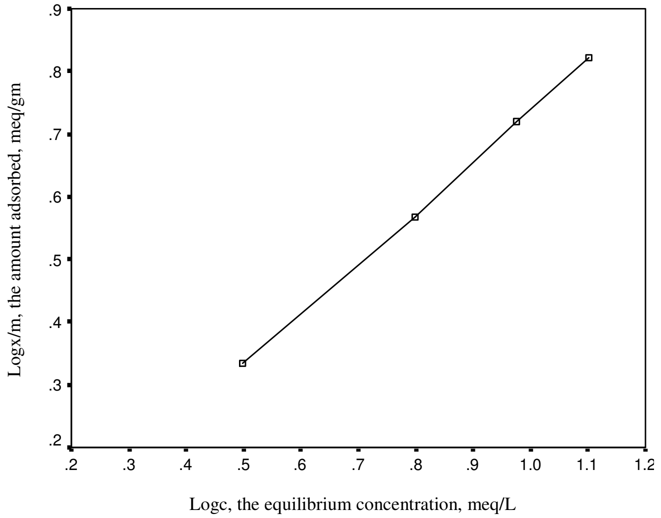

Figure 1. Freundlich adsorption isotherms for Cu^{+2} at pH 5

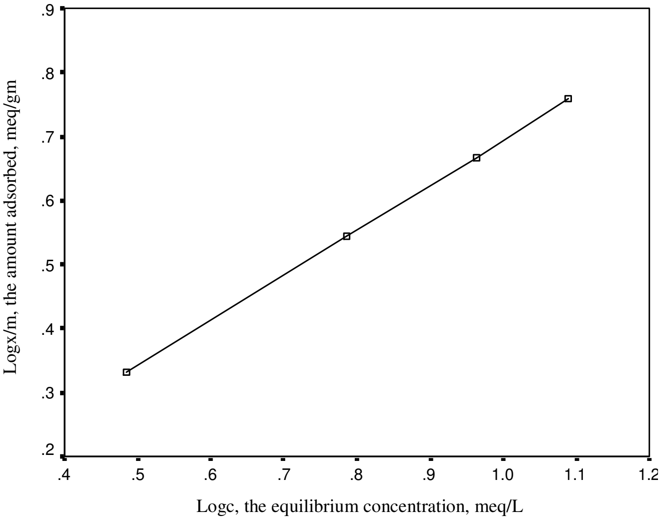

Figure 2. Freundlich adsorption isotherms for Zn^{+2} at pH 5

log x/m = l/n log C + log K

Where x = the amount of heavy metal cation absorbed
m = weight of adsorbate

Thus x/m = amount absorbed per unit weight
l/n = constant
C = equilibrium concentration of metal cation
K = constant

On the other hand the present data does not fit with Langmuir isotherms, however it has been reported that copper is absorbed by clay minerals and by quartz according to Freundlich adsorption isotherm[24]. Other researchers have reported that Cu^{2+} and Zn^{2+} cations are adsorbed both specifically and non-specifically by the soil[25].

Kuo and Mikkelson[26] found that at extremely low concentrations (0.1 µg/g), zinc adsorption by soil could be described by Langmuir isotherm, whereas at higher concentrations only Freundlich equation could describe the adsorption. On the other hand, some other workers reported that copper adsorption could be described by Freundlich isotherm when its concentration was initially 200 µg or greater which agrees with the present results[27].

Adsorption of a mixture of Cu^{2+} and Zn^{2+}

To find the effect of both cations on their adsorption experiments were also conducted using mixtures of both metal cations at pH= 5, the results are given in Table 6.

Table 6. Adsorption of a mixture of Cu^{2+} and Zn^{2+} at pH= 5

Concentration of ions in original solution, ppm	Amounts adsorbed from the mixture		Amounts adsorbed from single ion solution	
	Cu^{2+} ppm	Zn^{2+} ppm	Cu^{2+} ppm	Zn^{2+} ppm
200 Cu^{2+}+200 Zn^{2+}	107.6	88.2	137.0	140.0
400 Cu^{2+}+400 Zn^{2+}	159.2	115.6	234.0	229.0

The above data indicate that the amounts of Cu^{2+} and Zn^{2+} simultaneously adsorbed onto bentonite surface from a solution containing a mixture of both ions are lower as compared with the amounts adsorbed if each cation is alone. But the amount of Cu^{2+} adsorbed appears to be relatively higher than those of Zn^{2+}. Considering the total amounts of Cu^{2+} and Zn^{2+} ions adsorbed from a mixture solution of 200 ppm Cu^{2+} + 200 ppm Zn^{2+} it equals to (107.6 + 88.2 = 195.8). This value when compared with the value of the amounts adsorbed from an original solutions of concentration 400 ppm of a single ion it reveals that adsorption of each cation is lowered in the presence of other cation. The available adsorption sites are preferentially distributed between both cations depending on the strength of link of each cation.

Results of Kurdi and Doner[28] indicated that the amounts of Cu adsorbed by clay loam only slightly affected by Zn addition. Increasing the Zn concentration up to 250 µg/mL (10 times the concentration of Cu) brought about 9% decreases in Cu adsorbed. This demonstrates the instability of Zn to compete with Cu or to remove adsorbed Cu from adsorption sites. On the other hand they found that Zn adsorption was greatly affected by Cu additions. Thus the amounts of Zn adsorbed decrease by 28 to 68% by Cu additions depending on the type of clay.

Desorption with EDTA / ammonium acetate

The slow release of micronutrients from bentonite surface to plants is simulated by the chelating reaction between EDTA and the adsorbed cation. The bentonite samples previously allowed adsorbing Cu^{2+} ions and Zn^{2+} ions are then subjected to desorption of such ions by sequential treatment with EDTA/ Ammonium acetate solution. The results obtained for four successive leaching of each sample are given in Tables 7 and 8.

Table 7. Desorption of Cu^{2+} previously adsorbed onto bentonite

Original equilibrium Conc. of Cu^{2+} in adsorption solution, ppm	Amount of Cu^{2+} adsorbed at pH= 5, ppm	Amount of Cu^{2+} leached		
		Leach No.	ppm Cu^{2+} leached	Total amount of Cu^{2+} leached, ppm
200	137	1	48.20	70.61
200		2	15.61	
200		3	4.85	
200		4	1.95	
400	234	1	77.50	136.14
400		2	45.71	
400		3	9.49	
400		4	3.44	
600	327	1	109.45	196.34
600		2	63.57	
600		3	17.11	
600		4	6.21	
800	417	1	154.57	260.35
800		2	70.79	
800		3	24.67	
800		4	10.32	

Table 8. Desorption of Zn^{2+} previously adsorbed onto bentonite

Original equilibrium Conc. of Zn^{2+} in adsorption solution, ppm	Amount of Zn^{2+} adsorbed at pH= 5, ppm	Amount of Zn^{2+} leached		
		Leach No.	ppm Zn^{2+} leached	Total amount of Zn^{2+} leached, ppm
200	140	1	34.48	94.53
200		2	25.63	
200		3	22.05	
200		4	12.37	
400	229	1	48.07	125.51
400		2	30.40	
400		3	26.72	
400		4	20.32	
600	303	1	52.10	151.00
600		2	40.78	
600		3	30.48	
600		4	27.64	
800	376	1	58.44	177.15
800		2	49.05	
800		3	38.99	
800		4	30.67	

The above results showed that the greater amount of cation is removed in the first leach and decreases as the remaining cation concentration decrease. This may also reveal that the metal cations are adsorbed at different adsorption sites, either on surface of the crystals or in the intra layer positions and hence their availability for chelation with EDTA is different. However, the amounts of the metal cations adsorbed onto bentonite and those desorbed by EDTA are given in meq/g in Table 9 and 10.

Table 9. Desorption of Cu^{2+} by EDTA

Amount of Cu^{2+} adsorbed		Amount of Cu^{2+} desorbed	
ppm	meq/g	ppm	meq/g
137	2.157	70.61	1.112
234	3.685	136.14	2.144
327	5.149	196.34	3.092
417	6.567	260.35	4.100

Table 10. Desorption of Zn^{2+} by EDTA

Amount of Zn^{2+} adsorbed		Amount of Zn^{2+} desorbed	
ppm	meq/g	ppm	meq/g
140	2.141	94.53	1.446
229	3.502	125.51	1.920
303	4.634	151.00	2.310
376	5.751	177.15	2.710

Figure (3 & 4) presents a linear relationship between the amounts of metal cations adsorbed onto bentonite and the amounts desorbed by EDTA. It reveals that Cu^{2+} amount comparatively exerted a higher affinity to be adsorbed onto bentonite than Zn^{2+} and as well is more readily released from the surface.

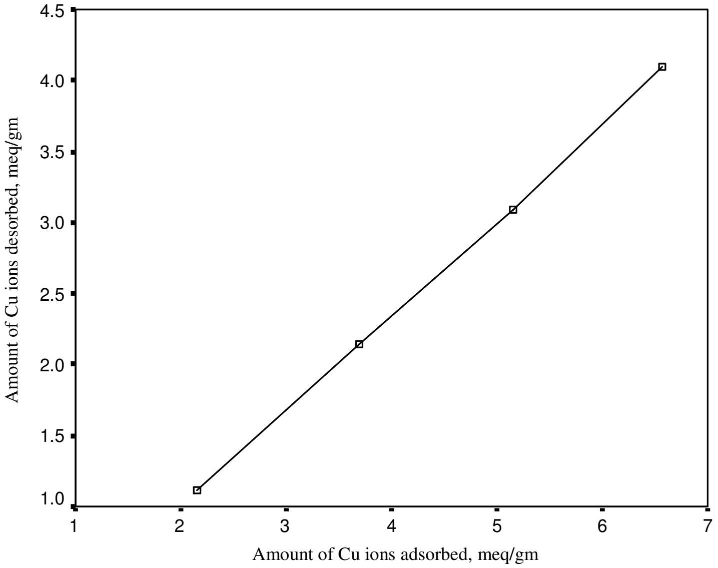

Figure 3. Relationship between the amount of Cu^{+2} adsorbed and desorbed by EDTA / OAc

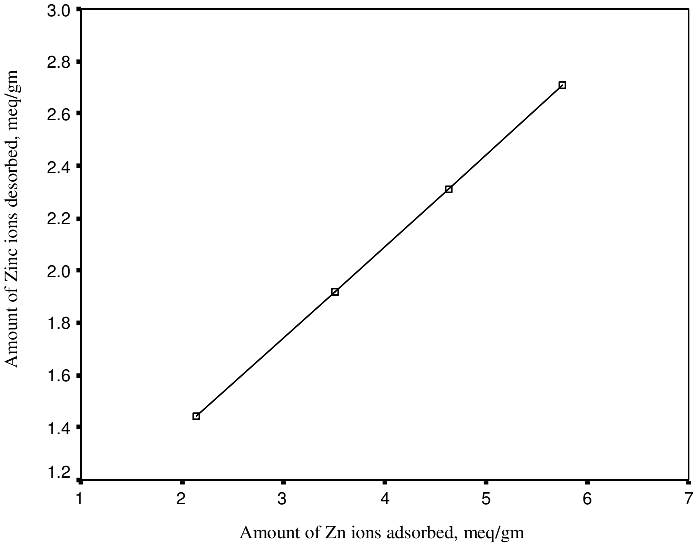

Figure 4. Relationship between the amount of Zn^{+2} adsorbed and desorbed by EDTA / OAc

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