DESORPTION OF ARSENIC FROM SOIL, GOETHITE AND ZEROVALENT IRON USING SOME EXTRACTANTS UNDER DIFFERENT pH VALUES

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ABSTRACT:

Arsenic is a toxic element that can occurs in the environment as a result of either natural processes or anthropogenic activities. The accumulation of arsenic in form of arsenate As(V) in soils and sediments threatens the health of plants, wildlife and human. Goethite (α-FeOOH), zerovalent iron (fine powder of iron metal) and clay minerals play an important role in controlling the concentration of soluble arsenic in pure water due to it is formed inner sphere surface complexes. Extraction of arsenic using phosphate, sulphate, molybdate and DTPA had been suggested as a procedure to assess its amounts. Arsenate was equilibrated with soils at 10-100 µg As ml^{-1} surface coverage and extracted by 0.005M DTPA. On the other hand, it was equilibrated with goethite and zerovalent iron at 10 µg As ml^{-1} and pH values of 5 and 9 as well as it was extracted by phosphate, sulphate and molybdate solutions at a ratio of I : 100 ≈ As : each solution and pH values ranging from 3 to 12.

Regarding soils, desorbed As (µg g^{-1}) from both the studied loamy and clay loam soils by DTPA gradually increased with increasing initial As (V) concentration. A slight increase in the desorbed As from the loamy soil was observed with increasing its initial concentration from 30 to 40, 50 to 60 and 60 to 100 µg As ml^{-1}. Whereas, a relatively high increase in the desorbed As(V) from the clay loam soil was noticed with increasing the initial concentration of As(V) from 20 to 30,70 to 80 and 90 to 100 µg As ml^{-1}.

Concerning goethite, the values of As(V) desorbed by using phosphate (at pH 5) depend on the pH values, where the relative increase percentages of As(V) desorbed from goethite reached 31.6, 33.0 and 70.6% at pH values of 3, up to 7 and 12, respectively. The corresponding relative increase percentages of As(V) desorbed in case of phosphate (concentration of 100 times as arsenate and at pH 9) were greatly affected and reached 43.7, 46.0 and 75.5%, respectively. In case of sulphate, the relative increase in As(V) desorbed was negligible either at pH 3 or with increasing its value up to 7, where the relative increase percentage was 0.34% at both pH values, and then greatly increased to 59.8%) at pH 12. As for molybdate (at initial concentration ratio of 100 : 1 of MoO_4 : As), it has a greatest effect on As(V), where the relative increase percentages of As(V) desorbed reached 32.0% at pH 3, and then sharply decreased to 0.10% with increasing pH up to 7. Above pH 7, the relative increase percentages of As(V) desorbed increased again to 58.9% at pH 12.

With respect to zerovalent iron, phosphate (at concentration ratio of 100 solution : 1 As and pH 5) had a moderate effect on As(V) desorbed at pH 3, where the relative increase percentage was 10.1%, and it tended to decrease with increasing pH value up to 7 (7.08%). Above pH 7, the relative increase percentage of As (V) increased again to 48.1% at pH 12. In case of phosphate (at initial adsorption pH of 9), the relative increase percentages were greatly affected, *i.e.*, 23.50, 22.09 and 55.70% at pH values of 3, 7 and 12, respectively. Sulphate (at initial ratio of 100 : 1 As and pH 5) exhibited a very less quantity of As(V) desorbed at pH values of 3 and up to 9 as its relative increases were 0.28 and 0.08%, respectively. Above pH 9.0, the relative increase of As(V) greatly increased to 45.5% at pH 12. While, sulphate at initial pH 9 showed a very less relative increase percentages in As(V) desorbed at pH values of 3 up to 8 reached 0.93 and 1.79%, respectively. Above pH 8, the relative increase of As(V) greatly increased to 65.8% at pH 12. As(V) desorbed as a result of molybdate (at initial adsorption pH 5) addition had no change with increasing pH value up to 7 (0.00), and then a pronounced increase was occurred (39.9%) at pH 12. In case of molybdate (at a ratio 100 MoO_4 : 1 As and pH 9), a greatest relative increase was achieved for As(V) desorbed at pH 3 (51.93%), and then it sharply decreased to 1.30% with increasing pH up to pH 7. Above pH7, As(v) desorbed tended to increase again (55.80%) at pH 12.

Key words: Desorption process, arsenate, goethite, zerovelant iron, phosphate, sulphate, molybdate and variable pH values.

INTRODUCTION

Elevated arsenic concentrations in soil can originate from anthropogenic sources (mining, agriculture, cool combustion) and from natural occurrence of arsenic in the soil parent material. The weathering of arsenic-containing soil minerals and desorption of arsenic from soil media will increase arsenic concentration in soil solution and can contaminate drinking and irrigation water **(Quaghebeur *et al*., 2005)**. High arsenic concentrations in deep well water have been verified to be associated with black foot disease, which was once common on the chianan Taiwan **(Chen-Wuiing *et al*., 2006).** Therefore, understanding arsenic desorption from soil minerals will provide important information about the fate of arsenic in the environment.

The major oxidation states of arsenic in the soil are As(V) arsenate and As(III) (arsenite), with As(V) the most dominant species in aerobic soils. Arsenate is a chemical analogue of phosphate and will therefore adsorb strongly to Fe and Al oxides and hydroxides **(Hingston *et al*., 1971)**. **Xu *et al.* (1988)** observed that adsorption envelopes for As(V) on alumina (α-Al_2O_3)and kaolinite, hence As(V) anions are likely to interact mostly with the aluminol functional group in kaolinite. Recent studies have shown that arsenate predominantly forms inner-sphere complexes via ligand exchange reactions (bidentate and monodentate) with the goethite surface **(Fendorf *et al*., 1997)** and kaolinite mineral **(Arai and Sparks, 2002)**.

Some studies indicated that there was a significant change in rhizospher pH when canola (Brassica napus L.) and velvet grass ***(Holcus lanatus L.)*** took up As(V) and P adsorbed on kaolinite **(Quaghebeur and Renglel, 2004)**. Therefore, it was of particular interest to study the effect of pH on As(V) desorption from soil matrix. Changes in pH greatly influence desorption of metals from soils, however, it has been suggested that pH effect on desorption of anionic As species are much less pronounced **(Wenzel *et al*., 2001; Quaghebear *et al*., 2005)**.

The main objective of this study was to evaluate effect of the changes in pH values on As(V) desorbed from soils by using DTPA as well as from goethite and zerovalent iron by using phosphate, sulphate and molybdate.

MATERIALS AND METHODS:

To achieve the aforementioned objective, two laboratory experiments were carried out on two soil types, synthetic goethite and zerovalent iron as adsorbate complexes, the main characteristics of these materials are illustrated in the following brief notes.

a. Soil:

Two surface soil samples (0-30 cm) were chosen from two soil sited having different contents of calcium carbonate and clay fraction, *i.e.*, Tamia-El Fayoum Governorate (soil I, loamy) and El Nubariya-El Behiraa Governorate (soil II, clay loam. Soil samples were air-dried, crushed, sieved through a 2-mm sieve and kept for the different lab analysis. Some physical and chemical characteristics of the studied two soils samples were determined according to **Black *t al.* (1965) and Page *et al*. (1982)** as well as semi-quantitative of clay minerals according to

Brown (1961) and Venkatarathnam and Ryan (1971), the obtained results are presented in Table (1).

Table (1): Some physical, chemical and mineralogical properties of the studied two soil samples.

Soil characteristics	Soil (I)	Soil (II)
Particle size distribution %:		
Sand	33.50	38.50
Silt	48.00	27.20
Clay	18.50	34.30
Textural class	L	CL
♀Soil pH*	8.10	8.40
$CaCO_3$ content %	4.83	27.10
Organic matter content %	0.28	0.35
CEC (c mol_c kg^{-1} soil)	14.75	15.60
ECe (dS/m, paste extract)	52.80	4.27
Semi-quantitative of clay %:		
♀Smectites	50.57	5.15
Kaolinite	22.75	62.95
Illite	14.22	9.72
Vermiculite	8.38	4.63
Palygorskite	--	15.30
Chlorite	4.08	2.25

Soil characteristics	Soil (I)	Soil (II)
Soluble cations (soil paste, mmolc/L):		
Ca^{2+}	37.25	15.80
Mg^{2+}	32.30	4.12
Na^{+}	478.0	22.40
K^{+}	2.72	0.65
Soluble anions (soil paste, mmolc/L):		
CO_3^{2-}	0.00	0.00
HCO_3^{-}	1.62	2.69
Cl^{-}	495.0	20.41
SO_4^{2-}	53.65	19.87

Total and available contents of some heavy metals:

Metal	Available (mg/kg)		Total (mg/kg)	
	Soil (I)	Soil (II)	Soil (I)	Soil (II)
Fe	13.40	13.70	20700	19000
Cd	0.04	0.01	3.10	1.05
As	nd**	nd**	nd**	nd**

Soil (I)=Tamia, soil (II)= Nubariya, L=Loamy, Cl=Clay loam, *1:2.5 soil water suspension, **not detected

b. Synthesis of goethite:

Goethite was synthesized through a lab experiment according to the procedure of **Schwertmann and Cornell (991)** as follows; 100 mL of 1M $Fe(NO_3)_3$ freshly prepared, were poured into a 2L-polyethlene bottle, and 180 mL of 5 M NaOH were added rapidly with stirring to the bottle, the solution was immediately diluted to 2L with deionized water and hold in a closed polyethylene bottle at 65 °C for 70 hrs. During this period, the voluminous red brown suspension of ferrihydrite is converted to a compact, yellow brown precipitate of goethite. The reaction bottle was removed from the oven and its content was washed with deionized water and the pH in the bottle was adjusted to 7.0 with 6 M HCI or 2 M NaOH. The suspension was dialyzed in deionized water with a continuous stirring until the electrical conductivity of dialysis water became 6µS/m. The dialyzed goethite suspension was kept in bottles for experimental use. Iron was determined in goethite suspension by taking one mL of the suspension in a 50 mL–beaker containing 4 mL of 6 M HCl and heated on a hotplate till the goethite was completely dissolved. The clear suspension was transferred quantitively to a 50-mL volumetric flask and brought to volume using deionized water. From that solution one mL was taken and diluted to a 100 mL using deionized water. Iron was measured in the last solution using Atomic Absorption Spectroscopy (Perkin Elmer 3300). The concentration of goethite in the final suspension was 32 gL^{-1}. A small portion of goethite suspension was taken, freeze-dried and the identity of goethite was confirmed by powder X–ray diffraction analysis as presented in Fig. (1).

c. Zerovalent iron:

This material represented by a fine powder of iron metal, however, either the negative or positive charges on particle charged surface sites were synthesized as a result of the changes on the pH values in the reaction media **(Raven *et al.*, 1998)**. Desorption processes of arsenate As(V) from soil, synthetic goethite (α-FeOOH) and zerovalent iron (fine powder of iron metal) under different pH values, with a back ground of 0.1 M NaCl, were carried out throughout two laboratory experiments as follows:

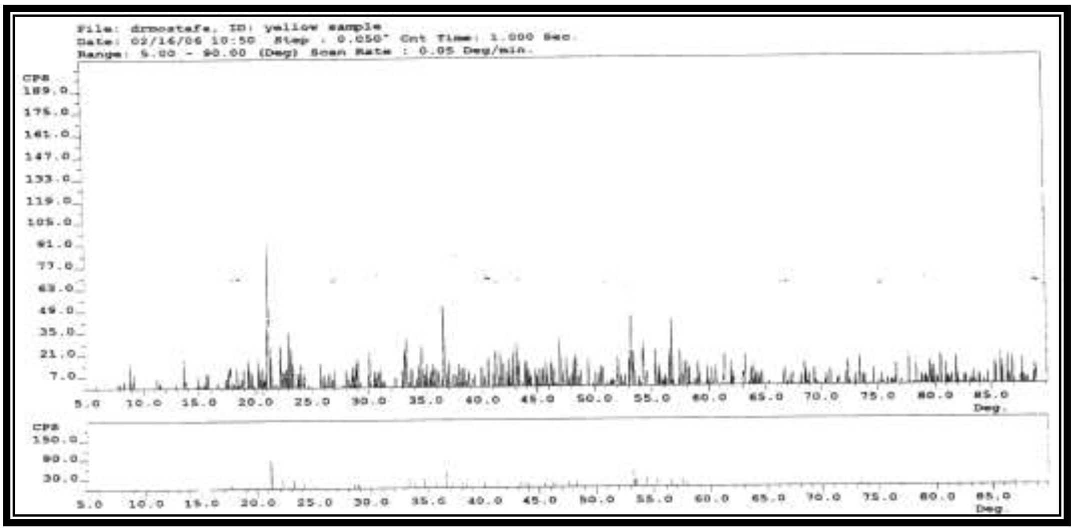

Fig. (1): X–ray diffraction analysis of synthetic goethite

Experiment I:

The first laboratory experiment was executed on the studied two soils, where a portion of one gram of each soil (loamy or clay loam) was equilibrated with 25 ml of (AsO_4^{3-}) [As(V)] solution having 10-100 µg As ml^{-1} in presence of 0.1M NaCl as ionic strength buffer for 24 hrs. Samples were shaken for 16 hrs, centrifuged, filtered and the filtrates were collected. To the settled samples, which remained in the centrifuge tubes, 20 ml of 0.005 M DTPA solution were added. The tubes were shaken for two hrs, centrifuged at 3000 rpm for one min, filtered and As concentration in the filtrate was determined using Inductively Coupled Plasma Spectrometry instrument (Plasma JY Ultima).

Experiment II:

The second laboratory experiment was conduced on both goethite and zerovalent iron, where a portion of 50 mL goethite suspension or 1g zerovalent iron, was equilibrated with 500 mL as a solution had 10 µg As mL^{-1} in presence of 0.1M NaCl as ionic strength buffer for 24 hrs. After adjusting the pH value to be 5 or 9, sub-samples of 10 mL were taken and placed in centrifuge tubes, and then 10 mL of phosphate, sulphate or molybdate solutions were added to obtain a desire ratio of 1 : 100 for As : each one of the studied solutions. To the centrifuge tubes, which did not receive any anion of the abovementioned ones, deionized water was added instead of them. The pH value of these samples was adjusted to be in a range of 3-12, and such samples were shaken for 4 hrs, centrifuged for 30 min at 3000 rpm and filtered through 0.2-µm membrane filters. Arsenic concentration was measured with using the (Plasma JY Ultima).

RESULTS AND DISCUSSION:

Desorption of arsenic from soils, goethite and zerovalent iron:

a. Soil:

Many of scientific studies in environmental soil chemistry have focused on the adsorption or sorption of ions and molecules on soils. Desorption process is also extremely of importance, this is particularly true for soils that are already contaminated. It is often observed that desorption is more difficult process than adsorption and that not all of the adsorbate is desorbate, *i.e.*, the reactions appear to be irreversible. Such apparent irreversible is commonly referred to as hysteresis or non-singularity.

Desorbed values of As(V) [AsO_4^{3-}] from loamy soil by DTPA solution increased gradually with increasing initial As(V) concentration from 10 to 30, and from 60 to 90 µg As mL^{-1} (Table 2). With different rates, As(V) desorption tended to increase with increasing initial As(V) concentration, *i.e.,* a moderate increase in the As(V) desorbed was occurred when initial As(V) concentration increased from 60 to 80 µg As mL^{-1} in the solution. However, a slight increase in the desorbed As(V) was observed with increasing its initial concentrations from 30 to 60 and from 90 to 100 µg As mL^{-1}. Desorbed As(V) % was computed for each initial concentration, and the greatest relative increase percentages of 39.0, 39.4 and 40.5 % were accompanied with the initial concentrations of 90, 30 and 80 µg As mL^{-1}, respectively.

Table (2): Arsenate desorption from loamy soil by DTPA, under experimental condition of 0.1M NaCl as ionic strength and concentrations of 10-100 µg As mL^{-1}.

Initial concentration of As (µg mL^{-1})	Adsorbed As		Desorbed As		
	Concentration (µg mL^{-1})	Quantity (µg g^{-1})	Concentration (µg mL^{-1})	Quantity (µg g^{-1})	%
10.0	5.55	111	1.36	27.2	24.5
20.0	13.4	164	2.52	50.4	30.7
30.0	22.3	193	3.80	76.0	39.4
40.0	26.6	335	4.10	82.0	24.5
50.0	31.5	213	5.65	113	26.5
60.0	38.7	284	6.09	122	38.4
70.0	55.8	355	6.84	137	38.6
80.0	65.2	370	7.48	150	40.5
90.0	71.5	462	9.02	180	39.0
100.0	78.6	535	9.22	184	34.4

Concerning clay loam soil, data in Table (3) showed a greatest relative increase in desorbed As(V) was noticed with increasing the initial As(V) concentration from 20 to 30, 70 to 80 µg As mL^{-1}.

Table (3): Arsenate desorption from clay loam soil by DTPA, under experimental condition of 0.1M NaCl as ionic strength and concentrations of 10-100 µg As mL^{-1}.

Initial concentration of As (µg mL^{-1})	Adsorbed As		Desorbed As		
	Concentration (µg mL^{-1})	Quantity (µg g^{-1})	Concentration (µg mL^{-1})	Quantity (µg g^{-1})	%
10.0	6.84	79	1.08	21.6	27.3
20.0	15.6	109	2.01	40.2	36.9
30.0	23.1	173	3.22	64.4	37.2
40.0	31.3	216	3.94	78.8	36.5
50.0	40.4	241	4.59	91.8	38.1
60.0	48.1	297	5.54	111	37.4
70.0	57.5	312	6.12	122	39.1
80.0	66.6	336	7.34	147	43.8
90.0	73.6	411	8.07	161	39.2
100.0	79.6	511	8.60	172	34.7

However, a moderate increase was observed with increasing the initial As (V) concentration from 10 to 90 µg As mL^{-1}. The greatest As(V) desorbed percentages were observed with the low coverage of As(V), which were accompanied with the low initial As(V) concentration, *i.e.*, almost 43.7 and 39.3 % of adsorbed As (V) were desorbed using DTPA solution when the initial As(V) concentrations were 70 and 80 µg As mL^{-1}, respectively.

b. Goethite:

Desorption of arsenic by phosphate:

Arsenic as arsenate was added to the goethite suspension at a low- coverage rate of 10 µg As mL^{-1} to ensure a completely adsorption on goethite surfaces at pH values of 5 and 9 (Tables 4 and 5).

Table (4): Arsenate desorption from goethite, at the initial pH 5, by PO_4, SO_4 and MoO_4 under a wide range of pH, concentration of 10 µg As mL^{-1} and 0.1M NaCl as ionic strength.

Initial concentration of As (µg mL^{-1})	Adsorbed As			Desorbed As			Final pH	Desorbed As
	Initial pH	Concentration (µg mL^{-1})	Quantity (µg g^{-1})	Initial pH	Concentration (µg mL^{-1})	Quantity (µg g^{-1})		
PO_4								
10	5.00	0.026	3117	3.00	1.56	978	3.30	31.4
10	5.00	0.026	3117	4.00	1.57	983	4.15	31.5
10	5.00	0.026	3117	5.00	1.55	966	4.91	31.0
10	5.00	0.026	3117	6.00	1.58	986	5.57	31.6
10	5.00	0.026	3117	7.00	1.66	1034	6.46	33.2
10	5.00	0.026	3117	8.00	1.84	1148	7.34	36.8
10	5.00	0.026	3117	9.00	2.14	1335	7.60	42.8
10	5.00	0.026	3117	10.00	2.39	1494	7.76	47.9
10	5.00	0.026	3117	11.00	2.85	1783	10.15	57.2
10	5.00	0.026	3117	12.00	3.52	2201	11.36	70.6
SO_4								
10	5.00	0.026	3117	3.00	0.017	10.6	3.28	0.34
10	5.00	0.026	3117	4.00	0.020	12.5	4.09	0.40
10	5.00	0.026	3117	5.00	0.022	13.8	4.44	0.44
10	5.00	0.026	3117	6.00	0.020	12.5	4.74	0.40
10	5.00	0.026	3117	7.00	0.017	10.6	5.55	0.34
10	5.00	0.026	3117	8.00	0.201	126.0	6.26	4.03
10	5.00	0.026	3117	9.00	0.540	338.0	6.52	10.80
10	5.00	0.026	3117	10.00	0.778	486.0	6.81	15.60
10	5.00	0.026	3117	11.00	1.330	833.0	8.43	26.70
10	5.00	0.026	3117	12.00	2.990	1866.0	11.72	59.90
MoO_4								
10	5.00	0.026	3117	3.00	1.600	997.0	3.24	32.00
10	5.00	0.026	3117	4.00	1.090	681.0	5.02	21.90
10	5.00	0.026	3117	5.00	0.837	523.0	5.36	16.80
10	5.00	0.026	3117	6.00	0.335	209.0	5.64	6.72
10	5.00	0.026	3117	7.00	0.005	3.1	6.21	0.10
10	5.00	0.026	3117	8.00	0.021	13.1	6.38	0.42
10	5.00	0.026	3117	9.00	0.469	293.0	6.66	9.40
10	5.00	0.026	3117	10.00	0.781	488.0	6.76	15.70
10	5.00	0.026	3117	11.00	1.970	1233.0	10.30	39.60
10	5.00	0.026	3117	12.00	2.940	1838.0	11.76	59.00

Table (5): Arsenate desorption from goethite, at the initial pH 9, by PO_4, SO_4 and MoO_4 under a wide range of pH, concentration of 10 μg As mL^{-1} and 0.1M NaCl as ionic strength.

Initial concentration of As (μg mL^{-1})	Adsorbed As			Desorbed As			Final pH	Desorbed As
	Initial pH	Concentration (μg mL^{-1})	Quantity (μg g^{-1})	Initial pH	Concentration (μg mL^{-1})	Quantity (μg g^{-1})		
PO_4								
10	9.00	0.266	3042	3.00	2.130	1329.0	2.92	43.70
10	9.00	0.266	3042	4.00	1.960	1225.0	4.04	40.30
10	9.00	0.266	3042	5.00	2.000	1249.0	4.66	41.10
10	9.00	0.266	3042	6.00	2.260	1414.0	6.32	46.50
10	9.00	0.266	3042	7.00	2.250	1406.0	6.60	46.20
10	9.00	0.266	3042	8.00	2.330	1456.0	7.01	47.90
10	9.00	0.266	3042	9.00	2.440	1526.0	7.36	50.20
10	9.00	0.266	3042	10.00	2.630	1644.0	8.19	54.10
10	9.00	0.266	3042	11.00	3.080	1923.0	10.60	63.20
10	9.00	0.266	3042	12.00	3.680	2297.0	11.43	75.50
SO_4								
10	9.00	0.266	3042	3.00	0.022	13.8	2.88	0.45
10	9.00	0.266	3042	4.00	0.015	9.4	4.01	0.31
10	9.00	0.266	3042	5.00	0.019	11.9	4.26	0.39
10	9.00	0.266	3042	6.00	0.033	20.6	5.22	0.68
10	9.00	0.266	3042	7.00	0.043	26.9	5.66	0.88
10	9.00	0.266	3042	8.00	0.166	104.0	6.12	3.41
10	9.00	0.266	3042	9.00	0.202	126.0	6.31	4.15
10	9.00	0.266	3042	10.00	1.500	934.0	6.96	30.70
10	9.00	0.266	3042	11.00	2.810	1756.0	11.23	57.70
10	9.00	0.266	3042	12.00	3.210	2008.0	11.63	66.00
MoO_4								
10	9.00	0.266	3042	3.00	2.100	1314	3.12	43.20
10	9.00	0.266	3042	4.00	1.720	1073	4.60	35.30
10	9.00	0.266	3042	5.00	1.490	931	4.77	30.60
10	9.00	0.266	3042	6.00	0.307	192	5.43	6.31
10	9.00	0.266	3042	7.00	0.327	204	5.56	6.72
10	9.00	0.266	3042	8.00	0.303	189	6.10	6.23
10	9.00	0.266	3042	9.00	0.458	286	6.33	9.41
10	9.00	0.266	3042	10.00	1.320	826	7.12	27.10
10	9.00	0.266	3042	11.00	2.180	1360	10.38	44.70
10	9.00	0.266	3042	12.00	3.140	1960	10.57	64.40

Arsenate was adsorbed completely at pH < 9 in the absence of phosphate. Phosphate (at pH 5) had the greatest effect on As(V) desorbed from goethite at pH 3 (31.6 %), and then its value tended to slightly increase with increasing pH up to 7 (33 %). Above pH 7, As(V) greatly increased to 70.6 % at pH value of 12. On the other hand, phosphate (at a concentration of 100 times as arsenate and pH 9) exhibited a more effect on As(V) desorbed, where its relative increase percentage reached 43.7 % at pH 3, and increased slightly to 46.0 % with increasing pH up to 7. Above pH 7, the relative increase percentage of As(V) exhibited a greatest value of 75.5 % at pH 12. These results indicated that desorption of As(V) is very sensitive to the changes in pH values. Similar results obtained by **Masscheleyn *et al.* (1991)**. The greatest As(V) desorbed as a (76.0 %) was achieved by using phosphate at pH 5, yet the desorption of arsenate by phosphate was not complete. Such incomplete desorption of As(V) may be attributed to the formation of bionulear adsorbate complexes of As(V) on goethite surfaces which restrict the rate of desorption process **(Sun and Doner, 1996; Fendorf *et al.*, 1997 and Abd El-Haleem *et al.*, 2002)**.

The sorption of AsO_4^{3-} or PO_4^{3-} on goethite and gibbsite decreased with increasing the initial molar ratio of PO_4^{3-}/AsO_4^{3-} up to 2.0. However, PO_4^{3-} inhibited AsO_4^{3-} sorption more on gibbsite than on goethite. Whereas, AsO_4^{3-} prevent a more adsorbed of PO_4^{3-} on goethite than gibbsite **(Violante and pigna, 2002)**. Arsenate adsorption on amorphous Fe oxide **(Jain and Loeppert, 2000)**, goethite, gibbsite **(Hingston *et al.*, 1971 and Manning and Goldberg, 1996a)**, kaolinite, montmorillonite, and illite **(Manning and Goldberg, 1996b)** was significantly reduced by the presence of competing phosphate concentrations.

Desorption of arsenic by sulphate:

Data illustrated in Tables (4 and 5) showed that sulphate (at pH 5) had no appreciable effect on As(V) desorbed at pH 3 (0.34 %) as well as it was negligible (0.34 %) with increasing the pH up to 7. Above pH 7, As(V) greatly increased to 59.8 % at pH 12.0. While, desorbtion of As(V) by sulphate (at pH 9) showed an almost similar results to those at pH 3 and 7. Similar results were obtained by **(Wilkie and Hering, 1996 and Jain and Loeppert, 2000)**. Arsenate adsorbed on alumina **(Xu *et al.*, 1988)** and arsenite adsorption on amorphous Fe oxide were reduced by competing sulphate concentrations, although to a lesser degree than by competing phosphate concentrations**. (Wilkie and Hering, 1996 and Jain and Loeppert, 2000)**.

Desorption of arsenic by molybdate:

Results of Tables (4 and 5) indicated that molybdate (at an initial concentration of ratio 100 MoO_4 :1 As and pH values of 5 and 9) had a greatest effect on As(V) desorbed at pH 3, where its relative increase percentages reached 32.0 and 43.2%, respectively. With increasing pH up to 7, the relative increase of As(V) desorbed sharply decreased to 0.10%, and then greatly increased again to 58.9% at pH 12. Also, molybdate showed a slightly increased (6.23 %) for As(V) desorbed with increasing pH up to 8, and then As(V) desorbed increased markedly to 64.4 % at pH 12. A similar result obtained by **Manning and Goldberg (1996 a & b)** who pointed that there was a competitive effect of molybdate on arsenate adsorption on goethite, gibbsite, kaolinite, montmorillonite and illite.

c. Zerovalent iron:

Desorption of arsenic by phosphate:

Arsenate was initially adsorbed at both pH values of 5 and 9 in the absence of phosphate, Tables (6 and 7), however, the obtained data showed a slightly effect of phosphate on As(V) desorbed at pH of 3 and when its value increased up to 7, where the corresponding relative increase percentages reached 10.10 and 7.08 %, respectively. As(V) desorbed increased markedly to 48.1 % at pH 12 in case of phosphate (at pH 5). While, phosphate at initial pH 9 had a moderate effect on As (V) desorbed, where the relative increases reached 23.50 and 22.09 at pH 3 and when its value increased up to 7, respectively. Above pH 7, As(V) greatly increased to 55.7 % at pH 12 at a concentration ratio of (100:1).

Desorption of arsenic by sulphate:

Arsenate was initially adsorbed at pH values of 5 and 9 in the absence of sulphate as shown in Tables (6 and 7), and lowest relative increase percentages of 0.28 and 0.08 % of As(V) desorbed in presence of sulphate were recorded at pH 3 and with increasing its values up to 9, respectively. Above pH 9 in presence of sulphate and at initial pH 5, As(V) desorbed greatly increased to 45.5 % at pH 12.0. On the other hand, in presence of sulphate and at initial pH 9, As(V) desorbed showed also lowest relative increases of 0.93 and 1.79 % at pH 3 and with increasing its values up to pH 8, respectively. Above pH 8, As(V) increased markedly to 65.8 % at pH 12 and at a concentration ratio of 100 sulphate : 1 arsenate.

Table (6): Arsenate desorption from zerovalent, at the initial pH 5, by PO_4, SO_4 and MoO_4 under a wide range of pH, concentration of 10 µg As mL^{-1} and 0.1M NaCl as ionic strength.

Initial concentration of As (µg mL^{-1})	Adsorbed As			Desorbed As			Final pH	Desorbed As
	Initial pH	Concentration (µg mL^{-1})	Quantity (µg g^{-1})	Initial pH	Concentration (µg mL^{-1})	Quantity (µg g^{-1})		
PO_4								
10	5.00	0.000	25000	3.00	0.504	2520	3.50	10.10
10	5.00	0.000	25000	4.00	0.366	1830	3.50	7.32
10	5.00	0.000	25000	5.00	0.356	1780	3.80	7.12
10	5.00	0.000	25000	6.00	0.359	1795	4.45	7.18
10	5.00	0.000	25000	7.00	0.354	1770	6.48	7.08
10	5.00	0.000	25000	8.00	0.382	1910	7.42	7.64
10	5.00	0.000	25000	9.00	0.421	2105	8.00	8.42
10	5.00	0.000	25000	10.00	1.890	9450	8.00	37.80
10	5.00	0.000	25000	11.00	2.270	11325	8.00	45.30
10	5.00	0.000	25000	12.00	2.410	12025	10.00	48.10
SO_4								
10	5.00	0.000	25000	3.00	0.014	70	2.55	0.28
10	5.00	0.000	25000	4.00	0.024	120	3.55	0.48
10	5.00	0.000	25000	5.00	0.011	55	3.60	0.22
10	5.00	0.000	25000	6.00	0.016	80	4.50	0.32
10	5.00	0.000	25000	7.00	0.004	20	4.50	0.08
10	5.00	0.000	25000	8.00	0.000	0.00	5.00	0.00
10	5.00	0.000	25000	9.00	0.000	0.00	6.00	0.00
10	5.00	0.000	25000	10.00	0.322	1610	8.00	6.44
10	5.00	0.000	25000	11.00	1.940	9715	11.00	38.90
10	5.00	0.000	25000	12.00	2.280	11375	12.00	45.50
MoO_4								
10	5.00	0.000	25000	3.00	1.660	8310	3.00	33.20
10	5.00	0.000	25000	4.00	0.060	300	4.80	1.20
10	5.00	0.000	25000	5.00	0.000	0.00	4.80	0.00
10	5.00	0.000	25000	6.00	0.000	0.00	5.11	0.00
10	5.00	0.000	25000	7.00	0.000	0.00	5.20	0.00
10	5.00	0.000	25000	8.00	0.015	75	6.00	0.30
10	5.00	0.000	25000	9.00	0.035	175	6.00	0.70
10	5.00	0.000	25000	10.00	1.230	6125	7.00	24.50
10	5.00	0.000	25000	11.00	1.710	8570	8.00	34.30
10	5.00	0.000	25000	12.00	1.990	9965	9.00	39.90

Desorption of arsenic by molybdate:

Arsenate was desorbed or extracted by molybdate at initial pH 5, and the obtained data in Tables (6 and 7) declared a greatest value of As(V) desorbed (33.2 %) at pH 3, and it tended to decreased sharply (0.00) with increasing pH up to 7, while it greatly increased again to 39.9 % at pH 12. Also, As(V) was initially desorbed at pH 9 by molybdate, where a greatest value of As(V) desorbed (51.93 %) was achieved at pH 3, then it tended to a sharply decrease (1.30 %) with increasing pH up to 7. Above pH 7, As(V) greatly increased again to 55.8 % at pH 12 at a concentration ratio of 100 MoO_4 : 1 As. Desorption of As(V) from goethite by phosphate, sulphate and molybdate was highly dependent on pH values, the greatest As(V) desorbed values were recorded at the relatively low and high pH values, which in no case achieved greater than (70-75%), (59.9-66%) and (59-64%) in cases of using phosphate, sulphate and molybdate on goethite at pH (5-9), respectively.

Table (7): Arsenate desorption from zerovalent, at the initial pH 9, by PO_4, SO_4 and MoO_4 under a wide range of pH, concentration of 10 µg As mL^{-1} and 0.1M NaCl as ionic strength.

Initial concentration of As (µg mL^{-1})	Adsorbed As			Desorbed As			Final pH	Desorbed As
	Initial pH	Concentration (µg mL^{-1})	Quantity (µg g^{-1})	Initial pH	Concentration (µg mL^{-1})	Quantity (µg g^{-1})		
PO_4								
10	9.00	0.303	24243	3.00	1.14	5700	2.70	23.50
10	9.00	0.303	24243	4.00	1.04	5175	4.00	21.40
10	9.00	0.303	24243	5.00	1.07	5370	4.11	22.20
10	9.00	0.303	24243	6.00	1.10	5505	5.29	22.70
10	9.00	0.303	24243	7.00	1.07	5355	7.00	22.10
10	9.00	0.303	24243	8.00	1.16	5820	7.30	24.00
10	9.00	0.303	24243	9.00	1.33	6630	7.46	27.40
10	9.00	0.303	24243	10.00	1.67	8365	7.63	34.50
10	9.00	0.303	24243	11.00	2.41	12050	11.00	49.70
10	9.00	0.303	24243	12.00	2.70	13520	11.50	55.80
SO_4								
10	9.00	0.303	24243	3.00	0.045	225	3.00	0.93
10	9.00	0.303	24243	4.00	0.061	305	3.36	1.26
10	9.00	0.303	24243	5.00	0.201	1005	4.50	4.15
10	9.00	0.303	24243	6.00	0.000	0.00	5.00	0.000
10	9.00	0.303	24243	7.00	0.105	525	6.00	2.17
10	9.00	0.303	24243	8.00	0.087	435	6.00	1.79
10	9.00	0.303	24243	9.00	0.283	1415	6.40	5.84
10	9.00	0.303	24243	10.00	0.628	3140	6.50	13.00
10	9.00	0.303	24243	11.00	2.09	10440	8.00	43.10
10	9.00	0.303	24243	12.00	3.19	15950	12.00	65.80
MoO_4								
10	9.00	0.303	24243	3.00	2.52	12590	2.00	51.90
10	9.00	0.303	24243	4.00	1.32	6605	4.75	27.30
10	9.00	0.303	24243	5.00	0.115	575	4.75	2.37
10	9.00	0.303	24243	6.00	0.102	510	5.00	2.10
10	9.00	0.303	24243	7.00	0.063	315	5.20	1.30
10	9.00	0.303	24243	8.00	0.187	935	6.00	3.86
10	9.00	0.303	24243	9.00	0.191	955	6.00	3.94
10	9.00	0.303	24243	10.00	0.862	4310	7.00	17.80
10	9.00	0.303	24243	11.00	1.48	7400	7.30	30.50
10	9.00	0.303	24243	12.00	2.70	13520	12.00	55.80

Also, The greatest As desorbed from ferrihydrite was at low and high pH values, but in no case achieved greater than (73-68.8%), (70-64%) and (69.9-53.9%) in case of using phosphate, sulphate and molybdate at pH (5-9), respectively **(Jain and Loeppert, 2000)**. The corresponding values for zerovalent iron were (48.1-55.7%), (45.4-65.8%) and (39.9-55.8%) in cases of presence phosphate, sulphate and molybdate at pH (5-9), respectively. These results are in agreement with those reported by **Hiemstra and Riemsdijk (1999)** who showed that application of phosphate fertilizer has been affected the mobility of arsenic in soils. Also, excess of phosphate has been used to displacement As(V) from sediments, fly ash, and soils, but the displacement is slow and often incomplete **(Peryea, 1991)**.

It could be concluded that $SO_4^{=}$ ions, under the initial pH values of 5 and 9, failed to extract or replace arsenate adsorbed on goethite and zerovalent iron at pH range of 3 to 8. At pH < 6 and > 9, both of phosphate and molybedate were able to extract appreciable quantities of As(V) initially adsorbed on goethite and zerovalent iron at pH values of 5 and 9. Also, phosphate and molybedate can be extracted As (V) adsorbed, except in the case of As(V) adsorbed on zerovalent iron at pH 5 where phosphate did not succeed to extract appreciable quantities of the adsorbed As(V) at pH ranged from 3 to 9.

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إنطلاق الزرنيخ المدمص من التربة والجيوثايت والزيروفالنت أيرن باستخدام بعض المستخلصات تحت قيم متغيرة من الرقم الهيدروجينى

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الزرنيخ عنصر سام قد يتواجد فى البيئة نتيجة للعمليات الطبيعية أو للنشاط الإنسانى، لذا فان تراكمه فى صورة زرنيخات فى الأراضى أو الرواسب يهدد صحة النبات والإنسان والحياه البرية. والجيوثايت (أكسيد حديديك متأدرت α- FeOOH والزيروفالنت أيرن (ناعم الحديد المعدنى) ومعادن الطين تلعب دورا هاما فى التحكم فى تركيز وذوبان الزرنيخ فى الماء وذلك لتكوين معقد ذات أسطح داخلية. وإستخلاص الزرنيخ بواسطة محاليل الفوسفات، الكبريتات، المولبيدات، DTPA قد اقترح كإجراء لتحديد الكميات المستخلصة منه. وقد تم إجراء الإتزان بين الزرنيخات وعينات التربة عند تركيزات تتراوح بين ١٠-١٠٠ ميكروجرام زرنيخ/مل بواسطة محلول DTPA بتركيز ٠.٠٠٥ مولر، بينما فى حالتى الجيوثايت والزيروفالنت أيرن تم الإتزان عند تركيز ١٠ ميكروجرام زرنيخ/مل تحت رقمى pH ٥، ٩، وأيضا تم الإستخلاص بواسطة محاليل الفوسفات، الكبريتات والموليبدات عند نسبة ١ زرنيخ : ١٠٠ من هذه المحاليل، وعند قيم pH تراوحت من ٣- ١٢.

وفيما يتعلق بالنتائج الخاصة بانطلاق الزرنيخ من التربة، وجد ان كمية الزرنيخ المنطلقة بواسطة محلول DTPA من كل من نوعى التربة تحت الدراسة (الطميية، الطميية الطينية) تزداد بصورة تدريجية بزيادة التركيز الأولى للزرنيخات، مع وجود زيادة نسبية لكمية الزرنيخ المنطلق من التربة الطميية. بزيادة التركيز الأولى من ٢٠ إلى ٣٠، من ٧٠ إلى ٨٠، من ٩٠ إلى ١٠٠ ميكروجرام زرنيخ/مل. وبالنسبة للجيوثايت، فقد كانت الكميات المنطلقة من الزرنيخات بواسطة الفوسفات (فى حالة pH ٥ عند الإدمصاص) تعتمد على قيم الـpH ، حيث وصلت الكمية المنطلقة من الزرنيخات إلى ٣١.٦، ٣٣.٠، ٧٠.٦٪ عند قيمpH ٣، ٧، ١٢ على التوالى، وكانت القيم المنطلقة المقابلة من الزرنيخات بواسطة الفوسفات (فى حالة pH٩ عند الإدمصاص) هى ٤٣.٧، ٤٦.٠، ٧٥.٥٪ على التوالى. اما الإستخلاص بواسطة الكبريتات فلم يكن له تاثير ملحوظ على كمية الزرنيخات المنطلقة بزيادة قيم الـpH ، حيث كانت الكمية المنطلقة من الزرنيخات هى ٠.٣٤٪ عند قيمتى pH ٣، ٧ ثم حدثت زيادة كبيرة وصلت إلى ٥٩.٨٪ عند pH 12 . وهناك تأثير أكبر للمولبيدات (pH 9) على كمية الزرنيخات المنطلقة حيث وصلت إلى ٣٢.٠٪ عند pH 3 ، ثم تناقصت إلى ٠.١٠٪ عند pH 7، ثم زادت مرة أخرى إلى٥٨.٩٪ عند pH 12 .

وفيما يختص بالزيروفالنت أيرن، فان النتائج تشير إلى أن الكميات المنطلقة من الزرنيخات بواسطة الفوسفات (فى حالة pH ٥ عند الإدمصاص) تزيد بنسب بسيطة وصلت إلى ١٠.١، ٧.٠٨٪ عند قيم pH ٣، ٧ على الترتيب وبزيادة قيم الـpH عن ٧ وصلت الكمية المنطلقة من الزرنيخات إلى ٤٨.١٪ عند pH 12 ، أما فى حالة القيم المنطلقة من الزرنيخات بواسطة الفوسفات (فى حالة pH ٩ عند الإدمصاص) فقد كانت أكثر تأثيرا حيث وصلت الزيادات كنسبة مئوية إلى ٢٣.٥، ٢٢.٠٩٪ عند قيم الـpH ٣، ٧. ثم حدثت زيادة كبيرة وصلت إلى ٥٥.٧٪ عند pH 12 . اما بالنسبة للإستخلاص بواسطة الكبريتات (pH 5) فلم يكن هناك تاثير ملحوظ على الكمية المنطلقة من الزرنيخات بزيادة قيم الـpH ، حيث كانت الكمية المنطلقة من الزرنيخات منخفضة جدا وصلت إلى ٠.٢٨، ٠.٠٨٪ عند قيمتى pH ٣، ٩ على الترتيب ثم حدثت زيادة كبيرة وصلت إلى ٤٥.٥ ٪ عند pH 12 . وفى حالة الإستخلاص بواسطة الكبريتات (فى حالة pH ٩ عند الإدمصاص) فان الزيادة فى الكمية المنطلقة من الزرنيخات كانت بسيطة جدا وصلت إلى ٠.٩٣، ١.٧٩٪ عند قيمتى pH ٣، ٨ ثم زادت كثيرا إلى ٦٨.٨٪ عند pH 12. كما لم يحدث أى تغير فى الكمية المنطلقة من الزرنيخات بواسطة المولبيدات (فى حالة pH ٥ عند الإدمصاص) بزيادة قيم الـpH حتى ٧، ثم حدثت زيادة كبيرة (١.٧٩٪) عند pH 12. وفى حالة المولبيدات (pH 9) كانت الزيادة كبيرة من الزرنيخات المنطلقة وصلت إلى ٥١.٩٣٪ عند pH 3 ، ثم تناقصت بشدة إلى ١.٣ ٪ عند pH 7، ثم زادت مرة أخرى إلى٥٥.٨٪ عند pH 12.