

ADSORPTION ENVELOPES FOR ARSENIC AND CADMIUM VERSUS VARIABLE pH VALUES ON SOIL, GOETHITE AND ZEROVALENT IRON

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ABSTRACT:

Due to arsenic (As) and cadmium (Cd) are considered of human carcinogenic elements, hence a knowledge about their reaction kinetics at the solid-liquid interface under variable pH values is extremely important for understanding the adsorption/desorption processes which controlling As and/or Cd soil-water system. Thus, the objective of this study was to identify adsorption envelopes for As (as arsenate) and Cd versus variable pH values (3-12) on soil (calcareous in nature), synthetic goethite (colloidal system of iron hydroxide) and zerovalent iron (fine powder of iron metal). Therefore, series of well-controlled laboratory experiments were carried out on the adsorption/desorption processes for As and Cd to achieve the previous objective.

The obtained data show that the greatest As adsorption by soil ($59.5 \mu\text{g As g}^{-1}$ soil) was recorded at pH 5, then it was tended to gradually decrease with increasing the pH value more than 5. The lowest value of As adsorbed by soil ($16.5 \mu\text{g As g}^{-1}$ soil ≈ 6.4 % of total added As) was occurred at pH 12. Adsorption of Cd showed an opposite trend to As, where its adsorbed percent tended to increase with increasing the pH values. The greatest Cd adsorption ($98 \mu\text{g Cd g}^{-1}$ soil ≈ 40 % of total added Cd) was noticed at pH 7, with a constant trend for its adsorbed values with increasing pH value more than 7.

On goethite, the adsorption envelopes for As as arsenate at the initial solution concentration equivalent to $10 \mu\text{g As mL}^{-1}$ indicated an adsorption of nearly 100 % of total As added in a range of 3-4 for the pH value. With increasing the pH value > 4 , As adsorbed tended to decline sharply to be 30 % of the total As added at the pH value of 12. In this respect, As adsorption on goethite decreased almost linearly from $3119 \mu\text{g As g}^{-1}$ goethite at pH 4 to $938 \mu\text{g As g}^{-1}$ goethite at pH 11. Lowering the As adsorption at the high pH values is attributable to an increase repulsion between the more negatively arsenate species and negatively charged surface sites. Adsorption of Cd showed an opposite trend to As as its adsorbed values increased with increasing the pH value. However, the greatest value of adsorbed Cd ($3099 \mu\text{g Cd g}^{-1}$ goethite ≈ 49 % of total Cd added) was noticed at pH 7, then a constant trend for Cd values with increasing the pH more than 7.

As for zerovalent iron (ZVI), the adsorption envelopes for As as arsenate at the initial solution concentration equivalent to $10 \mu\text{g As mL}^{-1}$ indicated an adsorbed As value of nearly 100 % of total As added in a range of 3-4 for the pH value. With increasing the pH value more than 4, As adsorption tended to decline sharply to be 16 % of the maximum adsorption of As at pH 12, however, lowering the pH value was associated with a large amount of As retained. The adsorption envelopes exhibited broad adsorption maxima for As at the pH range of 3-4, which was followed by a gradual decline with increasing the pH value more than 4. Such decrease coincided approximately with the second pka (6.9) of H_3AsO_4 . As adsorption

decreased linearly from almost 24960 $\mu\text{g As g}^{-1}\text{ZVI}$ at pH 4 to 4160 $\mu\text{g As g}^{-1}\text{ZVI}$ at pH11. The highest Cd adsorption was noticed at pH 7 with a constant trend for its values with increasing the pH value more than 7. The greatest value of adsorbed Cd was 24973 $\mu\text{g Cd g}^{-1}\text{ZVI}$, which corresponding a percent of 99 % of total Cd added.

Key Words: Arsenic, cadmium, iron metal, goethite, adsorption/desorption processes and calcareous soil.

INTRODUCTION:

Arsenic is known as a human carcinogen, which affecting essentially all human organs Arsenic enters to soils anthropogenically from coal ash deposition, and coal combustion by products, atmospheric fallout and mining related activities, pesticide and herbicide application (Abd El-Haleem, 2001).

In the soil environment arsenic exists as either arsenate (As O_4^{3-}) or as arsenite (As O_2^-), which is the more toxic. Arsenic toxicity, mobility and bioavailability in soil-water systems are highly dependent on its oxidation states and chemical species (Sun and Doner, 1998) as well as the soil properties (*i.e.*, pH), redox potential, clay fraction, organic matter, Fe & Mn oxides and calcium carbonates content (Joan and Bert, 1992). Adsorption of arsenate by kaolinite and montmorillonite as well as aluminum and iron oxides has shown an adsorption maximum at the pH values of 5 and 3-4, respectively, followed by a gradual decrease in adsorption with increasing the pH value (Hingston *et al.*, 1971 and Anderson *et al.*, 1976). A recent study was carried out on synthetic goethite (Abd EL-Haleem, 2001) who found that, at the initial As concentrations of 100, 200 and 400 mmol kg^{-1} goethite, adsorption envelopes crossed at the pH values of 6.0, 4.0 and 3.5, respectively. That means the adsorption envelopes exhibited broad adsorption maxima for arsenate in the pH range of 1-7, which was followed by a gradual decline with increasing the pH value more than 7.

Soil polluted with heavy metals poses serious risks for biota and human health; however, cadmium and other heavy metals reach the soil from the air, phosphatic fertilizers and incorporation of sewage sludge. Adsorption and desorption strongly affect the bioavailability of heavy metals and therefore toxicity in soil (Renella *et al.*, 2004).

However, the measured mobility of Cd also depends on many variables, *i.e.*, the pH value, ionic strength of the extractant (Naidu *et al.*, 1994), contact time between Cd and soils (Gray *et al.*, 1998), competition with other metal ions (Christensen, 1987a,b) and presence of inorganic or organic ligands (Sposito, 1994).

The objective of this study was to investigate the effect of pH variation on adsorption of As as arsenate and Cd on soil, synthetic goethite and zerovalent iron.

MATERIALS AND METHODS:

To achieve the previous target, different laboratory experiments were carried out to evaluate the adsorption of As as arsenate and cadmium under different pH values by a soil calcareous in nature taken from El-Nubariya Governorate, synthetic goethite and zerovalent iron (fine powder of iron metal) with a back ground of 0.1M NaCl.

a. Soil:

Some physical, chemical and mineralogical characteristics of the studied soil were determined according to the standard methods outlined by Black *et al.* (1965) and Page *et al.* (1982), and the obtained data are presented in the Table (1).

Table (1): Some physical, chemical and mineralogical properties of the soil used in the current investigation.

Soil characteristics	Value	Soil characteristics	Value	
<i>Particle size distribution %:</i>		<i>Soluble cations (soil paste, mmolc/L):</i>		
Sand	38.50	Ca ²⁺	15.80	
Silt	27.20	Mg ²⁺	4.12	
Clay	34.30	Na ⁺	22.40	
Textural class	CL*	K ⁺	0.65	
Soil pH**	8.40	<i>Soluble anions (soil paste, mmolc/L):</i>		
CaCO ₃ content %	27.10	CO ₃ ²⁻	0.00	
Organic matter content %	0.35	HCO ₃ ⁻	2.69	
CEC (c mol _c kg ⁻¹ soil)	15.60	Cl ⁻	20.41	
ECe (dS/m, paste extract)	4.27	SO ₄ ²⁻	19.87	
<i>Semi-quantitative of clay %***:</i>		<i>Total and available contents of some heavy metals:</i>		
Smectites	5.14	Metal	Available (mg/kg)	Total %
Kaolinite	62.95	Fe	13.66	1.90
Illite	9.87	Cd	0.01	1.05
Vermiculite	4.63	As	nd****	nd****
Palygorskite	17.41			

*Clay loamy, **1:2.5 soil water suspension, ***Brown (1961) and Venkatarathnam and Ryan (1971) ****not detected

b. Synthesis of goethite:

Goethite was synthesized as follows; 100 mL of 1M Fe (NO₃)₃ freshly prepared, were poured into a 2L-polyethylene 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 h. 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 HCl 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 quantitatively 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).

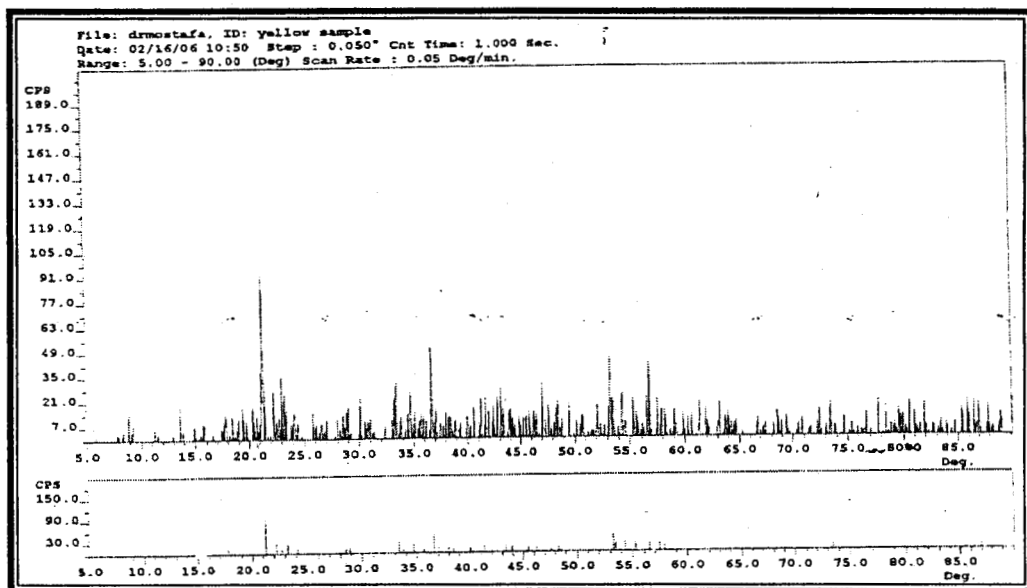


Fig. (1): X-ray diffraction analysis of synthetic goethite

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).

Adsorption envelopes for As as arsenate and Cd versus variable pH values on the following materials was carried out throughout different lab experiments as follows:

a. Soil:

The technique used was executed as 2.5 g of the soil sample placed in a 50-mL reaction vessel, 250 μg As as $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ or Cd solution was added to be 10 $\mu\text{g mL}^{-1}$ in the total volume (25 mL). The total volume of containing an electrolyte background of 0.1M NaCl was brought to volume using distilled water. After the pH values of the soil and AsO_4^{3-} or Cd suspension were adjusted to be in the range of 3-12, the reaction vessels were shaken for 4 h in the dark, and then centrifuged for 30 min at 3000 rpm. The supernatants were filtered and collected in polyethylene bottles. AsO_4^{3-} or Cd content in the filtrate was determined using Inductively Coupled Plasma Spectrometry (Plasma JY Ultima). The amounts of adsorbed AsO_4^{3-} or Cd on the soil were calculated as the difference between the initial and equilibrium amounts of either As or Cd in the final solution.

b. Goethite and zerovalent iron:

To study the effect of pH on arsenate or cadmium adsorption on goethite and zerovalent iron, an experiment was conducted as 2.5 mL goethite suspension or 0.01 g zerovalent iron, 2.5 mL of electrolyte back ground (1.0 M NaCl) and 250 μL of arsenate in the form of As or Cd (stock solution 1000 $\mu\text{g mL}^{-1}$) were added in a 50-mL reaction vessel, and then the volume was completed to be 25 mL with deionized water. Hence, the concentration of As or Cd in the reaction vessels was 10 $\mu\text{g mL}^{-1}$. After that, the pH value in the

reaction vessels was adjusted to be between 3 and 12. The reaction vessels were shaken for 4 h, and then centrifuged at 3000 rpm for 30 min, filtrated and the pH in the filtrates was measured. The filtrates were sealed in vials and kept for As or Cd determination. The adsorbed As or Cd on either goethite and zerovalent iron was calculated as the difference between the initial and equilibrium As or Cd amounts in the solution, and plotted against the pH values.

RESULTS AND DISCUSSION

Lab experiments were conducted to identify the actual behaviour techniques of adsorption envelopes for As and Cd versus variable pH values on the following materials:

I. Soil:

a. Arsenic (As) as arsenate:

The obtained data in Table (2) showed that the maximum As adsorbed (as arsenate, AsO_4^{3-}) versus variable pH values ranged between 3 and 12 on one gram of a calcareous clay loam soil, throughout an initial concentration of $10 \mu\text{g As mL}^{-1}$, should be reached $250 \mu\text{g As g}^{-1}$ soil if all AsO_4^{3-} added was adsorbed by soil. Under the condition of this experiment, the greatest AsO_4^{3-} adsorbed value by soil was not exceeding $59.5 \mu\text{g As g}^{-1}$ soil at pH 5. Then, adsorbed As was gradually decreased with increasing the pH value more than 5. While, the lowest adsorbed As value (6.4 % of total As added) on the studied soil occurred at pH 12. These results are in agreement with that of arsenate adsorption onto kaolinite, which reached its maximum at pH 5, followed by an abrupt decrease above pH 6 (Griffin *et al.*, 1977; Goldberg and Glaubing, 1988 and Xu *et al.*, 1988)

b. Cadmium (Cd):

In case of Cd adsorption on the same selected soil, results of Table (3) indicated that adsorption of Cd showed an opposite trend to As (as arsenate) adsorption, as its adsorbed values tended to increase with increasing the pH values.

Table (2): As adsorption (as arsenate on a calcareous clay loam soil) as a function of variable pH values in a solution of $10\mu\text{g As mL}^{-1}$ and ionic strength of 0.1M NaCl.

Initial concentration of As ($\mu\text{g mL}^{-1}$)	Initial pH value	As concentration at equilibrium ($\mu\text{g mL}^{-1}$)	Adsorbed As ($\mu\text{g g}^{-1}$)	Final pH value
10.00	3.00	4.54	54.6	3.00
10.00	4.00	4.12	58.8	4.00
10.00	5.00	4.05	59.5	5.11
10.00	6.00	4.10	59.0	5.48
10.00	7.00	4.81	51.9	5.50
10.00	8.00	4.64	53.6	5.50
10.00	9.00	5.92	40.9	8.50
10.00	10.00	6.44	35.6	9.29
10.00	11.00	6.85	31.5	11.0
10.00	12.00	8.35	16.5	11.8

Table (3): Cd adsorption on a calcareous clay loam soil as a function of variable pH values in a solution of $10\mu\text{g Cd mL}^{-1}$ and ionic strength of 0.1M NaCl .

Initial concentration of Cd ($\mu\text{g mL}^{-1}$)	Initial pH value	Cd concentration at equilibrium ; ($\mu\text{g mL}^{-1}$)	Adsorbed Cd ($\mu\text{g g}^{-1}$)	Final pH value
10.00	3.00	5.23	48.0	3.70
10.00	4.00	4.63	54.0	3.80
10.00	5.00	2.20	78.0	3.50
10.00	6.00	1.47	85.0	3.80
10.00	7.00	0.16	98.0	4.00
10.00	8.00	0.12	99.0	3.20
10.00	9.00	0.09	99.0	4.20
10.00	10.00	0.01	100.0	8.70
10.00	11.00	0.00	100.0	9.12
10.00	12.00	0.00	100.0	11.0

The greatest adsorbed Cd value ($98 \mu\text{g Cd g}^{-1}$ soil $\approx 40\%$ of the total Cd added) was noticed at pH 7, and then a constant trend for its values with increasing the pH more than 7. It could be explained this behavior on the basis of the adsorption process may be responsible for decreasing Cd concentration in equilibrium solution until pH value at < 7.0 , however, both adsorption and precipitation may be hold the responsibility for decreasing Cd concentration in equilibrium solution and account for the retention of Cd by soil. These results confirmed by those of Makler *et al.* (1980) and Alloway (1990) who reported that soil pH is one of major factors that affecting the availability of heavy metals in soil. In this respect, Abdel Aziz *et al.* (1993) found that the higher pH value of calcareous soil resulted in less content of soluble Cd, may be due to precipitating Cd in the form of Cd hydroxide.

II. Goethite:

a. Arsenic (As) as arsenate:

Adsorption of As as arsenate on goethite was studied throughout pH range of 3-12. Goethite, an iron hydroxide commonly found in soil, surface consists of a layer of Fe^{3+} ions octahedrally coordinated with OH^- ions and H_2O molecules. Specific adsorption of oxyanions varied with pH. Breaks in slopes of the curves represent anion adsorption over wide range of pH corresponded with pk values for the acid forms of each anion. The obtained data of the adsorption envelopes for arsenate at an initial solution attained a concentration equivalent to $10 \mu\text{g As mL}^{-1}$, indicated that the adsorbed As value could be reached about 100% of total As added at a range of 3-4 for the pH value (Table, 4). With increasing the pH value more than 4, the adsorbed values of As as arsenate tended to decline sharply to be 30% of the total As added at pH 12. However, arsenate was retained in larger amounts at the relatively low pH values (Sun and Doner, 1998).

Table (4): As adsorption (as arsenate on a calcareous clay loam soil) as a function of variable pH values in a solution of 10µg As mL⁻¹ and ionic strength of 0.1M NaCl.

Initial concentration of As (µg mL ⁻¹)	Initial pH value	As concentration at equilibrium (µg mL ⁻¹)	Adsorbed As (µg g ⁻¹)	Final pH value
10.00	3.00	0.018	3119	3.50
10.00	4.00	0.022	3118	3.90
10.00	5.00	0.033	3115	3.90
10.00	6.00	0.038	3113	4.00
10.00	7.00	0.048	3110	3.70
10.00	8.00	0.600	2938	8.70
10.00	9.00	0.747	2875	9.30
10.00	10.0	2.58	2313	9.60
10.00	11.0	4.68	1656	11.0
10.00	12.0	6.98	938	11.5

Similar results observed by **Abd El- Haleem (2001)** who found that the adsorbed AsO₄³⁻ reached its maximum value at the relatively low pH value of < 4. That was true, since the adsorption envelopes exhibited broad adsorption maxima for arsenate in the pH range of 3-4, and then it tended to a gradual decline with increasing the pH value more than 4. Such decrease coincided approximately with the second pKa (6.9) of H₃AsO₄. Inflections or maxima in the adsorption envelopes of anions at pH values close to their pKa, which are documented phenomenon (**Stumm, 1992 and Abd El- Haleem, 2001**).

Arsenate adsorption decreased linearly from almost 3119 µg As g⁻¹ goethite at pH 4 to 938 µg As g⁻¹ goethite at pH 11. Lower the adsorbed As as arsenate at high pH values is attributable to an increased repulsion between the more negatively arsenate species and negatively charged surface sites (**Raven et al., 1998**). Such species introduce the least negative charge in the outer plane will be preferred, *i.e.*, the bidentate species like arsenite. Loading also affects the formation of protonated bidentate species. At the low pH value, the positive particle charge decreases upon adsorption of negatively charged ions like arsenate.

At the highest initial concentration of arsenate solution, a distinct adsorption maximum was observed at approximately pH 4. This adsorption maximum of the adsorption envelopes was close to the second pka (6.9) of H₃AsO₄. The adsorption envelope for arsenate obtained in this study were almost similar to those observed by other workers, *i.e.*, **Manning et al. (1998)**; **Raven et al. (1998)**; **Sun and Doner (1998)** and **Abd El-Haleem (2001)**.

b. Cadmium (Cd):

In case of Cd adsorption on goethite, results of Table (5) indicated that adsorption of Cd showed an opposite trend to arsenate as its adsorbed quantities increased with increasing the pH values.

Table (5): Cd adsorption on a calcareous clay loam soil as a function of variable pH values in a solution of $10\mu\text{g Cd mL}^{-1}$ and ionic strength of 0.1M NaCl.

Initial concentration of Cd ($\mu\text{g mL}^{-1}$)	Initial pH value	Cd concentration at equilibrium ($\mu\text{g mL}^{-1}$)	Adsorbed Cd ($\mu\text{g g}^{-1}$)	Final pH value
10.00	3.00	7.01	938	3.50
10.00	4.00	7.17	875	3.90
10.00	5.00	5.17	1500	3.90
10.00	6.00	1.80	2563	4.00
10.00	7.00	0.304	3031	3.70
10.00	8.00	0.531	2959	8.70
10.00	9.00	0.082	3099	9.30
10.00	10.00	0.027	3116	9.60
10.00	11.00	0.001	3125	11.00
10.00	12.00	0.002	31240	11.50

The greatest Cd adsorbed was 3099 $\mu\text{g Cd g}^{-1}$ goethite, which corresponding 49 % of total Cd added, and it was noticed at pH 7, then a constant trend for its values with increasing the pH value more than 7. The adsorption process may be responsible for decreasing Cd concentration in the equilibrium solution, particularly at $\text{pH} < 7.0$. However, at $\text{pH} > 7$ both adsorption and precipitation may be hold the responsibility for decreasing Cd concentration in equilibrium solution and account for the retention of Cd by goethite. These results confirmed the results of **Al-Sewailem et al. (2000)** who reported that the effect of increasing pH on cadmium adsorption could be explained by two complimentary trends, *i.e.*, an increasing proportion of CdOH^+ ions and a decreasing electrostatic potential of the goethite surface.

III. Zerovalent iron (ZVI):

a. Arsenic (As) as arsenate:

The adsorption envelopes for As as arsenate at the initial solution concentration equivalent to $10\mu\text{g As mL}^{-1}$, indicated adsorbed As value reached about 100 % of the total As added at the pH of 3-4 (Table, 6). With increasing the pH value more than 4, As adsorption declined sharply to be 16 % at pH 12. That means at the lower pH values, adsorbed values of arsenate were retained in higher percentages (**Sun and Doner, 1998**). Similar results were reported by **Abd El-Haleem (2001)** who found that adsorption envelopes for AsO_4^{3-} in higher percentages at the relatively low pH values of 4.

The adsorption envelopes exhibited broad adsorption maxima for arsenate in the pH range of 3-4, which was followed by a gradual decline with increasing $\text{pH} > 4$. Such decrease coincided approximately with the second pKa (6.9) of H_3AsO_4 . Inflections or maxima in the adsorption envelopes of anions at pH values close to their pKa, which are documented phenomenon (**Stumm, 1992 and Abd El-Haleem 2001**).

Arsenate adsorption decreased linearly from almost $24960\mu\text{g As g}^{-1}$ ZVI at pH 4 to $4160\mu\text{g As g}^{-1}$ ZVI at pH 11. The lower adsorption of arsenate at high pH values is attributable to an increased repulsion between the more negatively arsenate species and negatively charged surface sites (**Raven et al., 1998**). These results confirmed the results of **Griffin and Shimp (1978)** in

which maximum adsorption of arsenate by kaolinite and montmorillonite, occurred at pH 5. Adsorption of arsenate by aluminum and iron oxides has shown an adsorption maximum at pH 3-4, followed by a gradual decrease in adsorption with increasing the pH value (Hingston *et al.*, 1971 and Anderson *et al.*, 1976)

Table (6): As adsorption (as arsenate on a calcareous clay loam soil) as a function of variable pH values in a solution of 10µg As mL⁻¹ and ionic strength of 0.1M NaCl.

Initial concentration of As (µg mL ⁻¹)	Initial pH value	As concentration at equilibrium (µg mL ⁻¹)	Adsorbed As (µg g ⁻¹)	Final pH value
10.00	3.00	0.016	24960	3.50
10.00	4.00	0.058	24855	3.90
10.00	5.00	0.073	24818	3.90
10.00	6.00	0.103	24743	4.00
10.00	7.00	0.197	24508	3.70
10.00	8.00	0.586	22860	8.70
10.00	9.00	1.83	20415	9.30
10.00	10.00	6.38	9058	9.60
10.00	11.00	8.34	4160	11.00
10.00	12.00	9.65	875	11.50

b. Cadmium (Cd):

Data in Table (7) indicated that adsorption of Cd showed an opposite trend to arsenate, as its quantities increased with increasing the pH values. The greatest value of Cd adsorbed on ZVI (24973 µg Cd g⁻¹ ZVI ≈ 99 % of the total Cd added) was noticed at pH 7, and then a constant trend for its values with increasing the pH more than 7. The adsorption process may be responsible for decreasing Cd concentration in equilibrium solution, particularly at pH < 7, however, both adsorption and precipitation may be the responsible for decreasing Cd concentration in equilibrium solution and account for the retention of Cd by ZVI.

Table (7): Cd adsorption on a calcareous clay loam soil as a function of variable pH values in a solution of 10µg Cd mL⁻¹ and ionic strength of 0.1M NaCl.

Initial concentration of Cd (µg mL ⁻¹)	Initial pH value	Cd concentration at equilibrium (µg mL ⁻¹)	Adsorbed Cd (µg g ⁻¹)	Final pH value
10.00	3.00	9.90	253	3.70
10.00	4.00	9.72	705	3.80
10.00	5.00	8.57	3575	3.50
10.00	6.00	7.01	7473	3.80
10.00	7.00	4.66	13345	4.00
10.00	8.00	1.90	20240	3.20
10.00	9.00	0.243	24393	4.20
10.00	10.00	0.011	24973	8.70
10.00	11.00	0.001	24998	9.12
10.00	12.00	0.001	24998	11.0

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مطارييف الإدمصاص للزرنىخ و الكادميوم مقابل قيم متغيرة من الرقم الهيدروجينى على التربة والحيويات والزيروفالنت أيرن

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الزرنىخ والكادميوم من أهم العناصر المسببة للسرطان فى الإنسان، لذا فان معرفة حركات التفاعل لهما عند تداخل المحاليل مع المواد الصلبة مقابل قيم متغيرة من الـ pH يعتبر فى غاية الأهمية لتفهم عمليات الإدمصاص والإنطلاق على أسطح التبادل التى تتحكم فى ذوبانية العنصرين وتركيزاتها فى نظام تربة- ماء. ومن ثم فان الهدف من هذه الدراسة هو إستبيان مدى تأثير التغير فى قيم الـ pH ما بين 3- 12 على إدمصاص الزرنىخ والكادميوم على أسطح كل من التربة والحيويات والزيروفالنت أيرن، وذلك من خلال إجراء عدة تجارب معملية محكمة الأداء.

وتشير النتائج المتحصل عليها إلى أن أعلى قيمة للزرنىخ المدمص كزرنىخات (0.09، 0.05 ميكروجرام زرنىخ/جم تربة) على حبيبات التربة كانت عند 5 pH، ثم تميل إلى التناقص التدريجى مع الزيادة فى قيم الـ H عن 5، بينما سجلت أقل قيمة للزرنىخ المدمص (0.6، 0.4٪ من الزرنىخ الكلى) على التربة عند 12 pH. وبالنسبة لإدمصاص الكادميوم على أسطح حبيبات التربة، فقد سلك إتجاه عكسى للزرنىخ، حيث زادت قيمه المدمصه مع زيادة قيم الـ pH، حيث سجل أقصى إدمصاص للكادميوم (98 ميكروجرام/ جم تربة ≈ 0.4 ٪ من الكمية الكلية للكادميوم المضاف) عند 7 pH.

اما بالنسبة للإدمصاص على الجيوثايت، فان مظاريف الإدمصاص بالنسبة للزرنبيخات عند التركيز الأساسي (١٠ ميكروجرام زرنبيخ لكل مليلتر) تشير الى اقتراب نسبة الإدمصاص من ١٠٠٪ من الكمية المضافة من الزرنبيخ عند مدى من قيم الـpH تتراوح ما بين ٣-٤، ومع زيادة قيم الـpH عن ٤ فان إدمصاص الزرنبيخ يقل بشدة حتى وصل الى ٣٠٪ من الكمية المضافة عند pH 12، وفي هذا الخصوص فان إدمصاص الزرنبيخات يقل خطيا من ٣١١٩ ميكروجرام/جم جيوثايت عند pH 4 إلى ٩٣٨ ميكروجرام/جم عند pH 12، ويعزى إنخفاض الزرنبيخات المدمصة عند قيم الـpH المرتفعة إلى زيادة مضادة ما بين الشحنة السالبة الكبيرة للزرنبيخات وتلك المتواجدة على أسطح الجيوثايت. وبالنسبة لإدمصاص الكاديوم، فان قيمه المدمصة أظهرت إتجاها معاكسا لسلوك الزرنبيخات، حيث تزايدت الكمية المدمصة من الكاديوم بزيادة قيم الـpH، قد سجلت أعلى قيمة للكاديوم المدمص (٣٠٩٩ ميكروجرام/جم جيوثايت \approx ٤٩٪ من الكمية الكلية من الكاديوم المضاف) عند pH 7، مع ثبات تقريبي للقيم المدمصة من الكاديوم ما بعد pH 7.

أما بالنسبة لعملية الإدمصاص على المسحوق الناعم لبرادة الحديد، فان مظاريف الإدمصاص للزرنبيخات عند التركيز الأساسي (١٠ ميكروجرام زرنبيخ/جم برادة حديد) تشير الى أن القيمة المدمصة من الزرنبيخات تقترب من ١٠٠٪ من الكمية الكلية للزرنبيخ المضاف) عند مدى من قيم الـpH تتراوح ما بين ٣-٤. وبزيادة قيم الـpH عن ٤ تميل الكمية المدمصة من الزرنبيخات إلى التناقص بشدة حيث وصلت إلى ١٦٪ من أقصى إدمصاص عند pH 12، مصحوبا باحتجاز كمية كبيرة من الزرنبيخات عند أقل قيم من الـpH.

توضح مظاريف الإدمصاص أن أقصى إدمصاص للزرنبيخات قد تم عند مدى من قيم الـpH تتراوح ما بين ٣-٤، يتبعه إنخفاض تدريجي بزيادة قيم الـpH عن ٤، ومثل هذا الإنخفاض يتفق تقريبا مع ثابت التحلل الثاني (pka, 6.5) للزرنبيخات. وقد لوحظ تناقص في إدمصاص الزرنبيخات في صورة خطية من ٢٤٩٦٠ ميكروجرام/جم برادة حديد عند pH 4 لتصل الى ٤١٦٠ ميكروجرام/جم عند pH 11، وقد سجلت أعلى قيمة لإدمصاص الكاديوم (٢٤٩٧٣ ميكروجرام/جم برادة حديد \approx ٩٩٪ من الكمية الكلية من الكاديوم المضاف) عند pH 7، مع إتجاه ثابت تقريبا لقيمتها عند زيادة قيم الـpH عن ذلك.