

## 4. RESULTS AND DISCUSSION

Results and discussion of this study will be categorized under the following two main topics:

(1) A survey study and (2) Laboratory studies

### 4.1. Survey of the occurrence of As and Cd in the selected waters and soils:

The existence of As in waters and soils was tested in twenty –one water samples and in twelve soil samples. Water and soil samples were collected from different localities distributed mainly in the Greater Cairo area and New Valley. Of 21 water samples arsenic was found in 15 samples in concentrations ranged from 0.17 to 5.54  $\mu\text{g L}^{-1}$ , while it was not detected in the other six samples. The highest concentration of As ( 5.54  $\mu\text{g L}^{-1}$ ) was found in waste water of main drain of cook factory in El-Tabeen, Helwan,while the lowest concentration of As (0.17  $\mu\text{g L}^{-1}$ ) was existed in well water of Gehna in New Valley province (Table 1).

It is worthy to note that the detected range of As did not exceed the water standard level suggested by the Environmental Protection Agency (EPA) of America which was amounted to be 10  $\mu\text{g L}^{-1}$  (Cai,2003).

With regard to As distribution in soils, the collected soil samples revealed two different concentrations of As of 0.053 and 0.125  $\mu\text{g kg}^{-1}$  in the As detected samples. Ten of twelve soil samples did not show a detected As level when measured using Plasma Emission.(Table 1)

The obtained values of As did not exceed to induce a toxicity hazard for both of human being and animals whose their food stuff of originate mainly from such soils as the permissible level of As in soil is  $20 \text{ mg L}^{-1}$

#### **4.1.2.Cadmium:**

Concerning Cd concentrations in waters and soils, data of Table (1) reveal that the concentrations of Cd differ in both of waters and soils. Cadmium concentration in water samples ranged from 0.1 to  $5.8 \text{ } \mu\text{g L}^{-1}$ . Of 21 water samples seven samples did not show Cd. The highest Cd concentration existed in Zenein station of treating sewage waters, while the lowest value was found in water well called Habis located in New Valley area.

Concerning, **AB-DTPA** extractable Cd in the tested soils, data of Table (1) show that Cd concentration considerably differed among soils as their recorded values ranged from 0.140 to  $0.200 \text{ } \mu\text{g kg}^{-1}$ . Only one soil sample did not show a detected concentration of Cd. Neither water nor soil contents of Cd exceeded the permissible levels of them which are  $0.01 \text{ mg L}^{-1}$  for the former and  $20 \text{ mg kg}^{-1}$  for the later.

Worthy to mention that both of As and Cd in waters and soils under investigation are not considered harmful to the human-being except with the highest concentration of water concomitant with intensive consumption of it.

As was less subjected to intensive study by the Egyptian researches, because it needs special sophisticated equipment. For this reason As was carefully studied in this investigation.

Soil sorption studies are commonly performed as described in the following laboratory studies to evaluate the extent of metal retention by a soil or soil constituents (organic matter, clay minerals, zero valent iron and iron oxide namely goethite). Sorption studies can be used to evaluate the effect of pH, ionic strength, addition of cations, inorganic or organic ligands, oxyanions (arsenate and arsenite), as well as metal cadmium retention by soil, goethite and zerovalent iron.



## 4.2. Laboratory studies :

### 4.2.1. Experiment I: Adsorption isotherms of arsenic and cadmium on different adsorbents :

#### 4.2.1.1. Soils

##### Arsenic

Adsorption isotherms of As (V) on two soils differed in their  $\text{CaCO}_3$  content ( loamy soil of 4.83 %  $\text{CaCO}_3$  and clay loam of 27.10 %  $\text{CaCO}_3$ ). were plotted in Figs. (2-3) and data of equilibrium concentration of As(V) as well as the amounts of adsorbed As(V) per the unit of adsorbent ( $\mu\text{g g}^{-1}$ ) were presented in Tables (4-5).

The amount of arsenate (As, V) adsorbed ( $\mu\text{g g}^{-1}$ ) on both loamy and clay loam soils under concentrations of As (V) was increased gradually with increasing its initial concentration from 10 to 100  $\mu\text{g L}^{-1}$ .

Data of As (V) adsorption on both soils were fitted to the linear form of the following adsorption isotherm equations :

Langmuir equation :  $C/q = 1/ab + C/b$

Freundlich equation :  $\text{Log } q = \text{Log } K + n \text{ Log } C$

Where C : equilibrium concentration ( $\mu\text{g mL}^{-1}$ ), q: the amount of As (V) adsorbed ( $\mu\text{g g}^{-1}$ ), b: maximum adsorption of As (V) on the unit weight of soil and a : constant related to the bonding energy. In case of Freundlich, q :the amount of As (V) adsorbed ( $\mu\text{g g}^{-1}$ ), K and n are constants ( $n < 1$ )

In both the loamy and clay loam soils as presented in Table (6) and illustrated in Fig.(3) adsorption of arsenate obeyed the Langmuir adsorption isotherms with coefficient of determination ( $r^2$ ) of 0.796 and 0.610, respectively. Also, adsorption of As (V) on both soils was highly fitted to Freundlich adsorption isotherms with coefficient of determination ( $r^2$ ) of 0.863 and 0.968, respectively.

Values of constant (a) which refer to the bonding energy of As on loamy and clay loam soils were 0.02 and 0.01, respectively. The highest value that revealed by clay loam soil was accompanied with the highest adsorption maximum (b). Such results indicate that As could be strongly adsorbed on clay loam soil comparing with loamy soil.

The higher value of adsorbed As (V) maximum on the clay loam soil could be due to its high content of clay,  $\text{CaCO}_3$  and organic matter which may be carry pH dependent positive charges. These results stand in well agreement with those of Rajan (1979) and Saada et al. (2003) who mentioned that selenite ( $\text{SeO}_3^{2-}$ ) and arsenate ( $\text{AsO}_4^{3-}$ ) are adsorbed to oxides and soils through specific binding mechanisms.

The obtained results for both soils obeyed Freundlich isotherms and revealed higher values of ( $r^2$ ) and binding energy.

Also, clay loam soil showed higher (a) value as compared with loamy soil.









**Table (6) Coefficients of determination ( $r^2$ ) for the fit of arsenate adsorption data on soils to Langmuir and Freundlich adsorption isotherms, and constants of the tested isotherms.**

Adsorption isotherm.	Linear plot	Arsenate	
		Loamy soil	clay loam soil
Coefficients of determination( $r^2$ )			
Langmuir	$C/q=1/ab+C/b$	0.796	0.610
Freundlich	$\text{Log}q=\text{log}k+n\text{log}C$	0.941	0.968
constants of the tested isotherms.			
Langmuir	$a(\text{Lmg}^{-1}\text{As})$	0.02	0.01
	$b(\mu\text{gAsg}^{-1})$	625	1000
Freundlich	$n(\text{mLg}^{-1})$	0.565	0.734
	$k(\mu\text{gAsg}^{-1})$	37.11	17.04

The determination coefficient ( $r^2$ ) obtained from applying Langmuir isotherms to the data of loamy and clay loam soils showed values of 0.796 and 0.610, respectively.

These results are in agreement with those obtained by **Rajan (1979); Neal, et al.(1987b)** in which arsenate is adsorbed to oxides and soils through specific binding mechanisms. Also many adsorption sites in soils are pH dependent, i.e., Fe and Mn oxides, organic matter, carbonates, and the edges of clay minerals. As the pH decreases, the number of negative sites for cation adsorption diminishes, while the number of sites for anion

adsorption increases. Also as the pH becomes more acidic, metal cations face competition for available permanent charged sites by  $\text{Al}^{3+}$  and  $\text{H}^+$ . **Griffin and Shimp. (1978)** in a study of arsenate adsorption by kaolinite and montmorillonite, found that maximum adsorption of As(V) occurred at pH 5. **Essen and El-Bassan (1981)**. reported that the pH of the soil system is very important parameter directly influencing sorption/desorption precipitation, dissolution, complex formation, and oxidation reduction reactions. In general, maximum adsorption of cations occurs at  $\text{pH} > 7$  and maximum retention of anions occurs at  $\text{pH} < 7$ .

### **Cadmium**

Adsorption isotherms of cadmium on soils were plotted in Figs. (4-5) and data of equilibrium concentrations of Cd as well as the amounts of adsorbed Cd per the unit weight of adsorbent were presented in Tables (7-8) The amount of Cd adsorbed ( $\mu\text{g g}^{-1}$ ) on loamy and clay loam soil under different concentrations of Cd was increased with increasing its initial concentration from (10-100)  $\mu\text{g Cd mL}^{-1}$ .

Adsorption values Cd on the clay loam soil were higher than the corresponding ones observed with the loamy soil. Regarding the binding energy of soil, the results of Table (9) show that both soils have almost similar binding energy to Cd.

It seems that, each one of the tested soils adsorbed appreciable quantities of Cd as the adsorption maxima of loamy and clay loam soils were 1428 and 1666  $\mu\text{g Cd g}^{-1}$ . The results of Cd adsorption on soils were highly fitted to Langmuir and Freundlich isotherms.







**Table (9) Coefficients of determination ( $r^2$ ) for the fit of Cadmium adsorption data on soils to Langmuir and Freundlich adsorption isotherms, and constants of the tested isotherms.**

Adsorption isotherm.	Linear plot	Cadmium	
		loamy soil	clay loam soil
Coefficients of determination (r <sup>2</sup> )			
Langmuir	C/q=1/ab+C/b	0.973	0.974
Freundlich	Logq=logk+nlogC	0.969	0.929
Constants of the tested isotherms.			
Langmuir	a (Lmg <sup>-1</sup> Cd)	0.15	0.18
	b(μg g <sup>-1</sup> )	1428	1666
Freundlich	n (mLg <sup>-1</sup> )	0.371	0.424
	k (μg g <sup>-1</sup> )	307	350

Adsorption maxima of Cd produced by plotting the equilibrium concentration (C) against the resultants of dividing equilibrium concentrations by the amounts of Cd adsorbed per one gram of soil (C/q)[Langmuir isotherm] were almost similar to those obtained from plotting equilibrium concentrations (C) against the amounts of Cd adsorbed per the unit of soil weight (gram). Such results indicate that data were highly fitted to Langmuir isotherms. Similar trend was noticed with Freundlich isotherms. These results are in agreement with those reported by **Greeitse and Van Driel (1984)** who found that Langmuir isotherm equation was most appropriate for Cd adsorption. Also

**Helal et al. (1996)** found that the Langmuir isotherms were appropriate for Cd adsorption by alluvial, calcareous and desertic sandy soils.

As with cationic metals, the chemistry of Cd in the soil environment is controlled by pH. Under acidic conditions Cd solubility increases and small adsorption of Cd on soil colloids, hydrous oxides, and organic matter takes place ,at pH values greater than 6 cadmium is adsorbed by the soil solid phase or is precipitated.

#### **4.2.1.2. Goethite**

##### **Arsenic**

Adsorption isotherms of arsenite and arsenate on goethite surfaces were plotted at constant pH values of 5 and 9 (Figs. 6 to 8).and tabulated in Tables (10 to 13). The amount of arsenate adsorbed ( $\mu\text{g g}^{-1}$ ) increased with increasing the initial concentration from 3 to 60  $\mu\text{g As mL}^{-1}$  until a condition of surface saturation is reached. Generally, arsenate was adsorbed in large quantities at pH 5 comparing to pH 9. Data of arsenate sorbed by unit weight of goethite ( $q$ ,  $\mu\text{g g}^{-1}$ ) and equilibrium As concentration ( $C$ ,  $\mu\text{g As mL}^{-1}$ ) were fitted to the linear form of adsorption isotherm equations of Langmuir and Freundlich

The adsorption of arsenate on goethite surfaces obeyed the Langmuir adsorption isotherms with coefficients of determination ( $r^2$ ) of 0.992 and 0.989, at pH 5 and 9, respectively. Table (14) shows that arsenate adsorption on goethite surfaces at pH 5 and pH 9 was highly fitted to the Langmuir isotherms. Concerning the goodness of fit of the data of arsenate adsorption on goethite surfaces at pH 5 and 9 to



Freundlich isotherms almost similar results to those obtained with Langmuir were observed at pH 9. These isotherms indicate that the adsorption reactions of As are reversible and the coverage is monolayer. **Wilkie and Hering (1996)** stated that isotherms of anion adsorption onto hydrous ferric oxide (HFO) are generally of Langmuir type, in which adsorption is limited by surface saturation.

Tables (14 and 15) show that the adsorption maxima for arsenate on goethite were 11111 and 5000  $\mu\text{g As (V) g}^{-1}$  goethite at pH 5.0 and 9.0, which approximately corresponded to 13.19 and 5.9 mmol As /mol  $\text{Fe}^{3+}$  at pH 5 and pH 9, respectively.

The adsorption maxima for arsenite on goethite as calculated from the Langmuir isotherms are 10000  $\mu\text{g As (V) g}^{-1}$  goethite at pH 5.0 and 9.0, which approximately corresponded to 1.2 mmol As /mol  $\text{Fe}^{3+}$  at pH 5 and 9, respectively. Langmuir type isotherm was appropriate for describing the adsorption of both As (III) and As(V) on HFO with arsenic concentration of  $5 \times 10^{-5}\text{M}$  (**Pierce and Moor, 1982**).

Similar results on Ferrihydrite were reported by **Raven et al. (1998)** with equilibrium arsenite concentrations adsorption at pH 8 being greatly higher than at pH 5. Also, these results are in agreement with those of **Griffin and shimp (1978)** in which arsenate adsorption was done on kaolinite and montmorillonite and the highest maximum adsorption was found at pH 5. Adsorption of arsenate by aluminum and iron oxides has shown an adsorption maximum at pH 3 to 4 followed by a gradual decrease in adsorption with increasing pH (**Hingston et al., 1971; Anderson et al., 1976**). The mechanism of adsorption has been ascribed to the innersphere complexation (Specific

adsorption), which is the same mechanism controlling the adsorption of phosphate by oxide surface. (**Hingston et al., 1971; Anderson et al., 1976; Anderson and Malotky, 1979**).















## Cadmium

All soils naturally contain levels of trace metals and the presence of metals in soils, therefore, not indicative of contamination. The concentration of metals in uncontaminated soil is primarily related to the geology of the parent material from which soil was formed.

Adsorption of Cd on goethite was studied through a laboratory experiment and the relationships between equilibrium concentrations and amounts of adsorbed Cd were illustrated in Figs.(9-10).and tabulated in Tables (16-17).

Regarding the adsorption of Cd on goethite at pH 5.0, adsorbed Cd was increased gradually with increasing equilibrium concentration of Cd and the highest increase of  $435\mu\text{g Cd g}^{-1}$  goethite was recorded with the highest initial Cd concentration of  $60\mu\text{g mL}^{-1}$ . It seems that surface saturation with Cd was not complete and maximum adsorption was not achieved.

At pH 9.0 the adsorbed Cd increased with increasing Cd concentration with the highest adsorption of  $173\mu\text{g Cd g}^{-1}$  goethite in case of using the highest initial Cd concentration of  $60\mu\text{g Cd mL}^{-1}$ , while at pH 5.0 similar trend was achieved with more increases of Cd adsorption at the tested initial Cd concentrations (  $3\text{-}60\mu\text{g Cd mL}^{-1}$  )

The obtained results reveal that at pH 5.0 there was higher adsorption of Cd on goethite than, at pH 9.0. The decrease of Cd adsorption may be due to all trace metal precipitate as hydroxide, oxide, carbonate and phosphate, form under alkaline conditions (**Lindsay,1979**) and the dissolution of these metal precipitates is







strongly dependent on pH of the system which increases with lowering pH and vis versa.

**Jenne (1968)** stated that hydrous oxides of Fe and Mn play a principal role in the retention of metals in soils. Solubility of Fe and Mn oxides is also pH related. Below pH 6.0, the oxides of Fe and Mn dissolved, and releasing adsorbed metal ions to solution (**Essen and El Bassam, 1981**).

Data of Cd adsorbed on goethite were fitted to the linear form of the Langmuir and Freundlich adsorption isotherms. Investigating Cd adsorption on goethite using Langmuir adsorption isotherms reveals that adsorption data of Cd on goethite at pH 5.0 and 9.0 obeyed Langmuir and Freundlich isotherms with ( $r^2$ ) values of 0.970, 0.991, 0.864 and 0.936. Data in Table (18) show that the adsorption maxima for Cd on goethite are 435 and 188.7  $\mu\text{g Cd g}^{-1}\text{goethite}$ , which approximately corresponded to 0.35 and 0.15  $\mu\text{g Cd mol Fe}$  at pH 5.0 and pH 9.0, respectively.

**Table ( 18 ) Coefficients of determination ( $r^2$ ) for the fit of cadmium adsorption data on goethite at pH 5 and pH 9 to Langmuir and Freundlich adsorption isotherms, and constants of the tested isotherms.**

Adsorption isotherm.	Linear plot	Cadmium pH 5	Cadmium pH 9
Coefficients of determination ( $r^2$ )			
Langmuir	$C/q=1/ab+C/b$	0.970	0.991
Freundlich	$\text{Log}q=\text{log}k+n\text{log}C$	0.864	0.936
Constants of the tested isotherms.			
Langmuir	$a (\text{Lmg}^{-1})$	0.5	0.2
	$b(\mu\text{g g}^{-1})$	434.8	188.7
Freundlich	$n (\text{mLg}^{-1})$	0.439	0.395
	$k (\mu\text{g g}^{-1})$	130.80	43.82

#### 4.2.1.3. Zerovalent iron

##### Arsenic

Although the principles affecting sorption and precipitation are similar for cationic and anionic metals, arsenate and arsenite are preferentially adsorbed over major anions ( $\text{SO}_4^-$ ,  $\text{NO}_3^-$ , soluble ionized organic acids). However, when the specific adsorption sites become saturated, exchange reactions dominate and competition for these sites with soil major ions become important. Then surface adsorption and chemical properties of soil can regulate the solubility of heavy metals in the soil

solution and influence their uptake by plant (**Kuo and Baker, 1980**).

Adsorption of As (V) on zerovalent iron (ZVI) was studied through laboratory experiments and the relationships between equilibrium concentrations and amounts of adsorbed As per gram of adsorbent were illustrated in Figs. (11 to 13) and tabulated in Tables (19 to 22 )

Regarding the adsorption of As on zerovalent iron (ZVI) at pH 5, adsorbed As (V) was increased gradually with increasing equilibrium concentration of As and the highest adsorption of 114.678 mg As g<sup>-1</sup> zerovalent iron (ZVI) was recorded with the highest initial As concentration of 60 µg mL<sup>-1</sup>.

It seems that surface saturation with As (V) was not complete and maximum adsorption was not achieved. At pH 9 As (V) was adsorbed in small quantities as compared to pH 5 and the amount of adsorbed As (V) per gram of (ZVI) decreased by a proportion higher than that at pH 5, the highest amount of adsorbed As was 69.315 mg g<sup>-1</sup> under the condition of the experiment.

Data of As (V) adsorbed on zerovalent iron (ZVI) were fitted to the linear form of the Langmuir and Freundlich adsorption isotherms. Investigating As (V) adsorption on zerovalent iron (ZVI) using Langmuir adsorption isotherms reveals that adsorption data of As on zerovalent iron (ZVI) at pH 5 and 9 obeyed Langmuir isotherms with ( $r^2$ ) values of 0.989 and 0.953. Also the obtained data obeyed Freundlich isotherms with ( $r^2$ ) values of 0.768 and 0.873 at pH 5 and 9 respectively.

However, at pH 5 the adsorption data were highly fitted Langmuir isotherms as compared with Freundlich isotherms.

These results agree well with those of **Kalbasi et al. (1978)**. Hydrous oxides have high specific surface area and possess OH<sup>-</sup> functional groups capable of reacting with metals, phosphate and other specifically sorbed ions, hydrous oxides are considered important in controlling the concentration of heavy metals in soil solution and natural water. **Griffin and Shimp (1978)** in a study on arsenate adsorption by kaolinite and montmorillonite, found that maximum adsorption of As (V) occurred at pH 5. Adsorption of arsenate by aluminum and iron oxides has shown an adsorption maximum at pH 3 to 4 followed by a gradual decrease in adsorption with increasing pH (**Hingston et al., 1971; Anderson et al., 1976**).

The relationships between equilibrium concentration and amounts of adsorbed As (III) were illustrated in Figs.(12-13).Regarding the adsorption of As (III) on zerovalent iron (ZVI) at pH 9, the adsorbed As (III) on zerovalent iron (ZVI) increased gradually with increasing equilibrium concentration of As (III) and the highest value was obtained with increasing pH from 5 to 9.

Zerovalent iron (ZVI) showed a good ability to adsorb either As (V) or As(III) at the selected pH values (5 and 9). The obtained results reveal that the determination coefficient of As (V) at pH 5 and 9 were 0.989 and 0.953, the corresponding values in case of As (III) were 0.999 and 0.922 .The adsorbed As in both forms exceeded that occurred on goethite. This result should be taken in to consideration when the purification of water from As is needed. Zerovalent iron (ZVI) is easy to be



obtained and to be used in manufacturing the columns of water purifiers. Beside the advantages of zerovalent iron (ZVI), there is a disadvantage of it which is it could not last for long time and it could be decomposed.

Tables (23 and 24) show that the adsorption maxima for As (V) and As(III) on zerovalent iron were 125000 and 50000  $\mu\text{g As (V) g}^{-1}$  zerovalent iron at pH 5 and 9, respectively, while the corresponding values of adsorption maxima of As(III) were 8336 and 16165.













## Cadmium

Cadmium may be adsorbed by clay minerals, carbonates or hydrous oxides of iron and manganese or may be precipitated as cadmium carbonate, hydroxide and phosphate.

Adsorption of Cd on zerovalent iron (ZVI) under pH values of 5 and 9 is graphically illustrated in Figs.(14-15) and tabulated in Tables ( 25-26).

At pH 5 there was a gradual increase in Cd adsorption with increasing Cd concentration.. Cadmium adsorption on zerovalent iron (ZVI) showed goodness of fit to Freundlich equation with (  $r^2$  ) values of 0.858 and 0.735 at pH 5 and 9, respectively.

Cadmium adsorption on (ZVI) obeyed Langmuir isotherms either at pH 5 or 9 with values of determination ( $r^2$ ) of 0.965 and 0.962 at pH 5 and 9, respectively. Data illustrated in Figs. (14-15) and tabulated in Tables ( 25 and 26) reveal that both of equilibrium concentrations and the quantities of Cd adsorbed  $\text{g}^{-1}$  (ZVI) were gradually increased with increasing initial Cd concentration. The increases reached  $50 \mu\text{g Cd mL}^{-1}$  and  $50 \text{ mg Cd g}^{-1}$  (ZVI) at pH 5. However, at pH 9 there was a gradually increase in both above-mentioned parameters reaching  $3.5 \mu\text{g Cd mL}^{-1}$  for equilibrium concentration and  $120 \text{ mg Cd g}^{-1}$  (ZVI).

The higher adsorbed quantities of Cd at pH 9 may be due to the adsorption and precipitation processes which played an important role in Cd chemistry in solutions. The higher adsorption and Cd on (ZVI) at pH 9 may be ascribed to



increasing the negative charge (negative sites) which responsible for attraction of Cd from the equilibrium solution.

Values of adsorption Cd maxima at pH 5.0 and 9.0 were calculated as  $1/\text{slope}$  (equals  $b$ ) according to Langmuir adsorption isotherms and compared with the adsorption maxima noticed or showed by plotting  $(q)$  against  $(C)$ . At pH 5 the two integrated values were almost similar which indicate the goodness of fit of Langmuir equation to the practical data. On the other hand, there is a discrepancy between values of  $(b)$  adsorption maxima derived from applying the Langmuir equation to the practical data or from using practical data themselves at pH 9.

Cadmium adsorption maxima calculated from Langmuir equation recorded  $0.136 \text{ mg Cd g}^{-1}$  (ZVI), while that derived from plotting  $(q)$  against  $(c)$  recorded  $120 \text{ mg Cd g}^{-1}$  (ZVI). This result indicates that Cd may be precipitated at high pH more than adsorbed. In case of Freundlich isotherms, the obtained data showed highly significant ( $r^2$ ) values at pH 5 and 9. Also, the obtained data showed the highest Cd adsorption maxima of  $8.199$  and  $89.104 \text{ mg Cd g}^{-1}$  (ZVI) at pH 5 and 9, respectively.

The obtained results indicate the hypothesis of ZVI could be efficient to adsorb and retain Cd in solutions of the high Cd concentrations. It could be effectively used in the columns of water purifiers.







Such results corroborate the results of **McBride (1980)** and **Papadopoulos and Rowell (1988)** who declared that calcite has a high affinity for Cd at low Cd concentrations but at the higher concentration  $\text{CdCO}_3$  precipitation dominates. Moreover, the high pH of the calcareous soil may enhance precipitation of Cd in from of hydroxides.

**Table (27) Coefficients of determination ( $r^2$ ) for the fit of cadmium adsorption data on zerovalent iron at pH 5 and pH 9 to Langmuir and Freundlich adsorption isotherms, and constants of the tested isotherms.**

Adsorption isotherm.	Linear plot	Cadmium pH 5	Cadmium pH 9
Coefficients of determination ( $r^2$ )			
Langmuir	$C/q=1/ab+C/b$	0.965	0.962
Freundlich	$\text{Log}q=\text{log}k+n\text{log}C$	0.858	0.735
Constants of the tested isotherms.			
Langmuir	$a (\text{Lmg}^{-1})$	0.1	3.17
	$b(\mu\text{g g}^{-1})$	50000	136
Freundlich	$n (\text{mLg}^{-1})$	0.489	0.453
	$k (\mu\text{g g}^{-1})$	8199	89104

#### 4.2.2.Experiment II :Adsorption envelopes (adsorption versus pH)

##### 4.2.2.1.Soil

##### **Arsenic**

The clay loam soil was chosen to be used in the pH envelopes experiment (Table 28 and Fig 17) Arsenate adsorption on clay loam soil versus pH values ranged from 3 to 12 was tested. The initial concentration of As (V) was  $10 \mu\text{g mL}^{-1}$  and soil weight was one gram. The maximum adsorption of As if all As added was adsorbed by soil should be  $250 \mu\text{g As g}^{-1}$  soil. Under the condition of this experiment the highest As adsorption by soil was  $59.5 \mu\text{g As g}^{-1}$  soil at pH 5.0. Adsorbed As was gradually decreased with increasing pH > 5.0 and the lowest value occurred at pH 12, when 6.4% of total As was adsorbed by soil. The obtained results agree well with that of arsenate adsorption onto kaolinite which reached its maximum at pH 5.0, followed by an abrupt decrease above pH 6.0 (Griffin et al. 1977, Goldberg and Glaubing 1988, Xu et al. 1988; Goldberg and Glaubing, 1988)

##### **Cadmium**

In case of Cd adsorption on the same selected soil, results of (Table 29 and Fig 16) indicate that adsorption of Cd showed an opposite behavior to arsenate as its quantities increased with increasing pH. The highest Cd adsorption was noticed at pH 7.0 with a relatively constant adsorption values with pH >7.0. The highest Cd adsorption was  $98 \mu\text{g Cd g}^{-1}$  soil which corresponded to 40% of total added Cd. The adsorption process may be responsible for decreasing Cd concentration in equilibrium

solution, particularly at  $\text{pH} < 7.0$ . However, at  $\text{pH}$  values  $> 7.0$  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 the results of **Makler et al.(1980)**, **Alloway (1990)** who stated that soil pH is one of major factors that affect the availability of heavy metals in soil. **Abdel Aziz et al (1993)** found that the higher pH of calcareous soil as compared with alluvial and sandy ones results in less content of soluble Cd. Moreover, high pH may precipitate Cd as Cd hydroxide.

#### **4.2.2.2.Goethite**

##### **Arsenic**

Adsorption of arsenite and arsenate on goethite was studied throughout pH range of 3-12. Goethite, an iron oxide commonly found in soil, its surface consists of a layer of  $\text{Fe}^{3+}$  ions octahedrally coordinated with  $\text{OH}^-$  ions and  $\text{H}_2\text{O}$  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 adsorption envelopes for arsenate at the initial solution concentration equivalent to  $10 \mu\text{g As mL}^{-1}$  indicated adsorption of nearly 100% of total arsenate added throughout the pH of 3-4 (Fig. 16 and Table 30). With increasing  $\text{pH} > 4$ , arsenate adsorption declined sharply to be 30% of the total As added at pH 12.

At lower pH values, arsenate was retained in larger amounts (**Sun and Doner, 1998**). Similar results were reported

by **Abd El- Haleem (2001)** in which adsorption envelopes of As (V) revealed that the highest As (V) adsorption occurred at low pH (<4.0)

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 pH > 4. Such decrease coincided approximately with the second pKa (6.9) of H<sub>3</sub>AsO<sub>4</sub>. Inflections or maxima in the adsorption envelopes of anions at pH values close to their pKa are well documented phenomenon (**Stumm,1992 and Abd El- Haleem 2001**).

Arsenate adsorption decreased almost linearly from almost 3119 µg As g<sup>-1</sup> goethite, at pH 4 to 938 µg As g<sup>-1</sup> goethite 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**). Since arsenite species have less negative charge character as compared to arsenate species at the same pH value, they do not exhibit as much repulsion, and as a result, the adsorption decreases less with increasing pH and with increasing anion loading more negative charge becomes present in the outer plane, increasing its negative (repulsive) potential. In this plane the outer ligands were take place (**Hiemstra and Riemsdijk, 1999**).

The species which introduces 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 low pH 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 envelope was close to the second pka (6.9) of  $H_3AsO_4$ . The adsorption envelopes for arsenate obtained in this study were almost similar to those observed by other workers (**Manning et al., 1998, Raven et al., 1998, and Sun and Doner, 1998 and Abd El-Haleem 2001**).

### **Cadmium**

In case of Cd adsorption on goethite, results of (Fig 16 and 31) indicate that adsorption of Cd showed an opposite behavior to arsenate as its adsorbed quantities increased with increasing pH. The highest Cd adsorption was noticed at pH 7.0 with a constant adsorption values with pH >7.0. The highest Cd adsorption was  $3099 \mu\text{g Cd g}^{-1}$  goethite which corresponded to 49% of total added Cd. The adsorption process may be responsible for decreasing Cd concentration in the equilibrium solution, particularly at pH < 7.0. However, at pH values > 7.0 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)** in which the effect of increasing pH on cadmium adsorption could be explained by two complimentary trends an increasing proportion of  $\text{CdOH}^+$  ions and a decreasing electrostatic potential of the goethite surface

#### 4.2.2.3. Zerovalent iron (ZVI) :

##### Arsenic

The adsorption envelopes for arsenate at the initial solution concentration equivalent to  $10 \mu\text{g As mL}^{-1}$  indicated adsorption of nearly 100% of total arsenate added throughout the pH of 3-4. (Fig, 16 and Table, 32). With increasing pH > 4, arsenate adsorption declined sharply to be 16% of the maximum adsorption of As at pH 12. At lower pH values, arsenate was retained in larger amounts (**Sun and Doner, 1998**). Similar results were reported by **Abd El- Haleem (2001)** in which adsorption envelopes of As (V) reveal that the highest As(V) adsorption occurred at low pH (<4.0)

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 pH > 4. Such decrease coincided approximately with the second pKa (6.9) of  $\text{H}_3\text{AsO}_4$ . Inflections or maxima in the adsorption envelopes of anions at pH values close to their pKa are well documented phenomenon (**Stumm, 1992 and Abd El- Haleem 2001**).

Arsenate adsorption decreased almost 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 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**). The species which introduces 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 low pH the

positive particle charge decreases upon adsorption of negatively charged ions like arsenate.

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 pH (**Hingston et al., 1971; Anderson et al., 1976**)

### **Cadmium**

In case of Cd adsorption by ZVI, results of Fig. (16) and Table. (33) indicate that adsorption of Cd showed an opposite trend to arsenate as its quantities increased with increasing pH. The highest Cd adsorption was noticed at pH 7.0 with a constant adsorption values with pH >7.0. The highest Cd adsorption was 24973  $\mu\text{g Cd g}^{-1}$  ZVI which corresponded to 99 % of total added Cd. The adsorption process may be responsible for decreasing Cd concentration in equilibrium solution, particularly at pH < 7.0. However, at pH values > 7.0 both adsorption and precipitation may be the responsible for decreasing Cd concentration in equilibrium solution and account for the retention of Cd by ZVI.









### **4.2.3.Experiment III :Competitive adsorption of arsenate with phosphate, molybdate, selenate, and sulfate on goethite and zerovalent iron (ZVI).**

#### **4.2.3.1.Goethite.**

##### **Arsenate and phosphate.**

The mobility of arsenic in soils depends on several factors including redox potential, soil mineralogy, pH, and the presence of other oxyanions that compete with As for soil retention sites. The effects of pH and competing anions on the adsorption of arsenate (As,V) on goethite were investigated.

The competitive adsorption of (As,V) and P on goethite versus pH was studied using As : P ratios of 1:0,1:1 and 1:2 as presented in Fig. (17 ) and Table (34)

In the absence of  $\text{PO}_4$ , adsorption of As on goethite was slightly decreased with increasing pH. At pH 7.0 a quantity of  $2891 \mu\text{g As (V)g}^{-1}$  goethite was adsorbed from the added As (V) per gram goethite, while at pH 8.0 the adsorbed As (V) was decreased to be  $2881 \mu\text{g As g}^{-1}$  goethite followed by a sharp reduction with increasing the pH above pH 9.0 and recorded 1662 and  $945 \mu\text{g As g}^{-1}$  goethite at pH 11.0 and 11.8, respectively.

The preference of the adsorbent (goethite) to As over  $\text{PO}_4$  was indicated when they added together (at a ratio of 1:1), as the amount of As (V) adsorbed was decreased gradually with increasing pH with slight differences as compared with no P addition at  $\text{pH} > 5.84$ . However, arsenate was more affected by phosphate and the amount of adsorbed arsenate being  $2678 \mu\text{g}$



As  $\text{g}^{-1}$  goethite at pH 6.0, decreased to 2190  $\mu\text{g As g}^{-1}$  goethite at pH 7.0 and decreased sharply with increasing pH to achieve 975  $\mu\text{g As g}^{-1}$  goethite at pH 11.2.

Data of the competitive adsorption between As (V) and  $\text{PO}_4$  on goethite which are shown in Fig (17 ) and Table (34) indicate that adsorption of As (V) was decreased with increasing pH when As (V) was added alone or with  $\text{PO}_4$  at As : P ratios of 1 : 0, 1:1 and 1 : 2 However, more pronounced increases in As (V) adsorption was noticed when As (V) was added at 2: 1 As: P ratio with all tested pH values.

The affinity of goethite to As (V) was affected largely by pH and by As (V) concentration in equilibrium solution. The lowest As(V) adsorption was noticed with As (V) : P ratio of 1 : 2 particularly at the high pH values.

At the initial concentration of 10  $\mu\text{g L}^{-1}$ , As (V) surface coverage reached its maximum of 3119  $\mu\text{g As g}^{-1}$  goethite at pH 3.0 as shown in Fig. ( 17 ), at that initial As (V) concentration, As (V) was almost completely adsorbed on goethite below pH 4.0 in the absence of  $\text{PO}_4$ . Both As (V) and  $\text{PO}_4$  when added as single anions displayed broad adsorption envelopes with 100% adsorption of As (V) below pH 4.0 and 98% at ratio of 1:1 As: P.

The results obtained revealed that at pH 4.0 As was almost completely adsorbed when its ratios with  $\text{PO}_4$  were 1:0 (100%), 1:1 (98%) and 2:1 (99%), while only 73% of As was adsorbed with As: $\text{PO}_4$  ratio of (1:2). It could be mentioned that  $\text{PO}_4$  could not compete well with arsenate on the specific sites of As if its ratio to As was less than 2:1.

With such ratio of As:PO<sub>4</sub> (1:2), PO<sub>4</sub> competed with AsO<sub>4</sub> and reduced its adsorption to 73%. At pH 5.5 and with As to P ratios of (1:0,1:1,1:2 and 2:1) the percentages of As adsorption were 100,95,54 and 97.5, while the corresponding percentages of As adsorption were 74,80,31.7 and 78.7 at pH 9.3 with the above mentioned As: PO<sub>4</sub> ratios, respectively. These results indicate that the preference of adsorption sites to As was mainly affected by pH values and the concentration of associated oxyanions.

#### **Arsenate and selenate.**

Results of competitive adsorption between As (V) and Se (IV) on goethite are shown in Table (35) and Fig. ( 17 ) in which adsorption of As (V) was decreased with increasing pH. when As (V) was added alone or with Se (IV) at As : Se ratio (1 : 0, 1 : 1 and 1:2). However, more pronounced increases in As (V) adsorption was noticed when As (V) was added at 2 : 1 As (V) : Se (IV) ratio. The affinity of goethite to As (V) was affected largely by pH and by As (V) concentration in equilibrium solution. At low pH values Adsorption of As (V) was decreased with increasing pH in the presence and absence of Se (IV). At 10 µg L<sup>-1</sup> initial concentration, As (V) surface coverage reached its maximum of 3119 µg g As (V) g<sup>-1</sup> goethite at pH 3 .0. and As: Se ratio of 1:0. At the same initial concentration of As (V), As was completely adsorbed on goethite below pH 4. Both As (V) and Se (IV) single anions displayed broad adsorption envelopes with pH range of 3.0 to 12. With As:Se ratio of 1:2 the adsorbed As was decreased more as compared with other ratios. These results are along with those of As adsorption envelopes reported on hydrous -Fe oxide by **Hsia et al (1994)** and on goethite by **Hingston et al . (1971)**.

Data of Table ( 35 ) and Fig. ( 17 ) reveal that at pH 4.0 and in the absence of Se (1:0 ratio ) arsenate was almost completely adsorbed by goethite. At the same pH value and with the ratios between As :Se of 1:1, 1:2, and 2:1 the adsorption values of As by goethite were 98%, 68.7 and 99%, respectively.

Thus selenate considerably competed with As on the adsorption sites and reduced the amount of As adsorbed on goethite to be 68.7%. Such decrease in As adsorption was greater than that obtained with  $\text{PO}_4$  under the same condition.

It means that selenate could be adsorbed on the same sites of arsenate and its reaction with binding sites may be similar to that of arsenate. At pH 5.5, arsenate was adsorbed by values of 100,96, 68 and 94% from As added with the tested As :Se ratio of 1:0, 1:1,1:2 and 2:1 respectively. The corresponding values of adsorbed As (V) with the above mentioned As:Se ratio and pH 9.3 were 74,61,34 and 56%, respectively. It could be noticed that increasing the initial concentration of As comparing with selenate or any other oxyanions alleviates the effect of competing oxyanions as indicated with As:Se ratio of 2:1.

#### **Arsenate and molybdate.**

Results of the competitive adsorption between As (V) and  $\text{MoO}_4$  on goethite are shown in Table ( 37 ) and Fig.( 17 ) Greater than 95% of As was adsorbed below pH 4.0 in single Mo anion and binary  $\text{MoO}_4$  anion systems on goethite. These data suggest that  $\text{MoO}_4$  occupies a fraction of the pH-dependent of As (V) adsorption sites on goethite and there is another distinct fraction of sites has higher affinity for As or  $\text{MoO}_4$  at low pH. Similar results were obtained by the competitive effect of

molybdate on arsenate adsorption on goethite, gibbsite, kaolinite, montmorillonite and illite (**Manning and Goldberg, 1996 a,b**)

#### **Arsenate and sulfate.**

Results of the competitive adsorption between As (V) and  $\text{SO}_4$  on goethite indicate that the competitive adsorption of As (V) and S on goethite which was studied using As: S ratios of 1: 0, 1:1, 1:2 and 2: 1 in the absence of S, adsorption of As (V) on goethite decreased with increasing pH. The preference of the adsorbent to As (V) over S was indicated when they added together as As (V) adsorbed was decreased with increasing pH with a slight deference as compared with no S addition. Up to pH 10.0 sulfate failed to compete with arsenate on As (V) adsorption sites considerably.

These results were also consistent with the relative affinity of goethite surface to As (V), P, and Mo as its pH dependence and that affinity in most cases tended to be  $\text{P} = \text{As (V)} > \text{Mo}$  at neutral pH. Phosphate and As (V) appeared to compete for a similar set of surface sites at specific pH values, though there was an evidence that some sites were uniquely available for adsorption of either As (V) or P. These results are in agreement with those reported by **Manning and Goldberg. (1996)** in which arsenate and phosphate single –anion adsorption envelopes were similar with substantial adsorption occurring across a wide pH range, including pH values above the points of zero point of charge of iron oxides.

Arsenate, phosphate, and molybdate are tetrahedral oxyanions (**Cotton and Wilkinson, 1980**) that can compete for adsorption sites on soil mineral surfaces (**Murali and**

**Aylmore,1983).Hingston (1981)** estimated the mean areas occupied by the  $\text{AsO}_4$ ,  $\text{PO}_4$  and  $\text{MoO}_4$  tetrahedral on the goethite surface to be 0.61, 0.61 and 0.31  $\text{nm}^2$ , respectively.

When anions that protonate are present such as  $\text{H}_2\text{AsO}_4^-$  and  $\text{H}_2\text{PO}_4^-$ , an increase in pH results in an adsorption envelope that reflects the competition between the anion and surface sites for the decreasing presence of the proton (**Hingston et al., 1972**).

### **Cadmium**

With regard to Cd adsorption on goethite in a binary system containing Cd and Co at Cd : Co concentration ratios of 1:0,1:1,1:2 and 2:1 (Table 38 and Fig 19 ) Cd was adsorbed in small quantities at  $\text{pH} < 4.0$ . This may be attributable to the repulsion effect of the adsorbent sites on Cd and Co. Such repulsion effect may be ascribed to increasing the positive dependent charge at lower pH values. Then the adsorbed Cd was increased sharply with increasing  $\text{pH} > 4.0$  up to  $\text{pH} 7.0$  in the absence and presence of competing ion of Co. The highest adsorption of Cd was achieved with using 2:1 Cd: Co ratio while the lowest Cd adsorption occurred with using 1:1 Cd: Co .The pH envelopes study reveals that the quantities of adsorbed Cd were different and depended on Cd :Co ratio. At  $\text{pH} 4.0$  and with 1:0,1:1, 1:2 Cd:Co ratios the adsorbed Cd percentages recorded the following values 28,16,40 and 4.5. However appreciable quantities of Cd were adsorbed with  $\text{pH} 5.5$  and 1:0,1:1and 1:2 Cd : Co ratios as compared with values obtained at  $\text{pH} 4.0$  At  $\text{pH} 9.3$  the adsorption of Cd was independent from Cd :Co ratios as it recorded almost 100% with all tested ratios These results are in agreement with those reported by **Dzombak and Morel (1990)**















#### **4.2.3.2.Zerovalent iron.(ZVI)**

##### **Arsenate and phosphate.**

Results of competitive adsorption between As (V) and  $\text{PO}_4$  on zerovalent iron (ZVI) are shown in Fig (18) and Table (39), adsorption of As was decreased with increasing pH with very slight differences between the amounts adsorbed on zerovalent iron (ZVI) in particular when As (V) was added alone or with P, Se, Mo and S, at As : Se , P, Mo and S (1 : 0,1:1,1:2 and 2 : 1).

However, more pronounced increases in As (V) adsorption was noticed when As was added at 2: 1 As: Se, P, Mo and S ratios. The affinity of ZVI to As (V), Se, P and Mo was affected largely by pH and by As concentration in the equilibrium solution.

In the absence of P, adsorption of As on zerovalent iron (ZVI) increased gradually with increasing pH, at pH 4.3 almost  $24960 \mu\text{g As g}^{-1}$  of the added As was adsorbed, while at pH 9.0 value of  $875 \mu\text{g As g}^{-1}$  was adsorbed. The preference of the adsorbent to As over P was indicated when they added together as As (V) adsorbed amount was decreased gradually with increasing pH with slight differences as compared with no P addition. However, As (V) was more affected by P and the amount of adsorbed As recorded  $23590 \mu\text{g As g}^{-1}$  at pH 4.0 and As: P ratio of 1:1, decreased to  $15620 \mu\text{g As g}^{-1}$  at pH 9.5 and decreased sharply with increasing pH to achieve  $983 \mu\text{g As g}^{-1}$  at pH 12.0. Results of competitive adsorption between As (V) and P on (ZVI) are shown in Fig (17) and indicated that adsorption of As (V) was decreased with increasing pH when As (V) was added alone or with P at low As : P ratio (1 : 0,1:1 and 1 : 2).

However, more pronounced increases in As (V) adsorption was noticed when As (V) was added at 2: 1 As: P ratio. The affinity of ZVI to As (V) was affected largely by pH and by As (V) concentration in equilibrium solution. At the  $10 \mu\text{g mL}^{-1}$  starting concentration, As (V) surface coverage reached maximum of  $24960 \mu\text{g Asg}^{-1}$  on ZVI at pH 4.3 Fig (17)

At  $10 \mu\text{g As mL}^{-1}$  as starting concentration, As (V) was 100% adsorbed on (ZVI) below pH 7. Both As (V) and P single anions displayed broad adsorption envelopes with almost 100% adsorption of As (V) below pH 6 and 98% with As: P ratio (1:1) and decreased with As: P ratio of 1:2.

Phosphate and As (V) appeared to compete for a similar set of surface sites, though there was evidence that some sites were uniquely available for adsorption of either As (V) or  $\text{PO}_4$ . The results obtained revealed that at pH 4.3 As was almost completely adsorbed when its ratios with  $\text{PO}_4$  were 1:0 (100%), 1:1 (98%) and 2:1 (66%), while only 45% of As was adsorbed with As: $\text{PO}_4$  ratio of (1:2). It could be mentioned that  $\text{PO}_4$  could not compete with arsenate on the specific sites of As if its ratio to As was  $>2:1$ .

At a ratio of As: $\text{PO}_4$  (1:2),  $\text{PO}_4$  competed with  $\text{AsO}_4$  and reduced its adsorption to 67%. At pH 5.5 and with As to P ratios of (1:0, 1:1, 1:2 and 2:1) the percentages of As adsorption were 100, 94, 36 and 82, while the corresponding percentages of As adsorption were 16, 62, 38.5 and 34 at pH 9.3 with the above mentioned As:  $\text{PO}_4$  ratios, respectively. These results indicate that the preference of adsorption sites to As was mainly affected by pH values and the concentration of associated oxyanions.

These results corroborate the results of **Manning and Goldberg (1996)**.

Arsenate, phosphate, and molybdate are tetrahedral oxyanions (Cotton and Wilkinson,1980) that can compete for adsorption sites on soil mineral surfaces (**Murali and Aylmore,1983**).**Hingston(1981)** estimated the mean areas occupied by the  $\text{AsO}_4$ ,  $\text{PO}_4$  and  $\text{MoO}_4$  tetrahedral on the goethite surface to be 0.61, 0.61 and 0.31  $\text{nm}^2$ , respectively.

#### **Arsenate and selenate.**

Results of competitive adsorption between As (V) and Se (IV) on (ZVI) are shown in Table 40 and Figs (18 ). Adsorption of As (V) was decreased with increasing pH, when As (V) was added alone or with Se (IV) at low As : Se ratio (1 : 0, 1 : 1 and 1:2). However, more pronounced increases in As (V) adsorption was noticed when As (V) was added at a ratio of 2 : 1 As (V) : Se (IV). The affinity of goethite to As (V) was affected largely by pH and by As (V) concentration in equilibrium solution. The highest As (V) adsorption was noticed with As (V) : Se (IV) ratio of 2 : 1 particularly at low pH values. Adsorption of As was decreased with increasing pH in the presence and absence of Se (IV).

At the  $10 \mu\text{g mL}^{-1}$  initial concentration, As (V) surface coverage reached maximum of  $24960 \mu\text{g As (V) g}^{-1}$  on (ZVI) at pH 4.3. Fig ( 18). At the  $10 \mu\text{g mL}^{-1}$  As (V) (initial concentrate) As (V) was adsorbed 100% on (ZVI) below pH 4. Both As (V) and Se (IV) single anions displayed broad adsorption envelopes with 98% adsorption of As (V) below pH 5.5 and As: Se (IV) ratio of 1 : 1 and decreased to be 1.5% at pH 8.0.

These results are in agreement with those on hydrous Fe oxide (**Hsia et al., 1994**) and goethite (**Hingston et al., 1971**).

Data of Table ( 40 ) and Fig ( 18 ) reveal that at pH 4.0 and in the absence of Se (1:0 ratio ) arsenate was almost completely adsorbed by ZVI. At the same pH value and with the ratios between As :PO<sub>4</sub> of 1:1, 1:2, and 2:1 the adsorption values of As by ZVI were 98%, 98% and 94%, respectively.

Thus selenate has appreciably competed with As on the adsorption sites and reduced the amount of As adsorbed on ZVI. Such decrease in As adsorption was greater than that obtained with PO<sub>4</sub> under the same condition.

It means that selenate could be adsorbed on the same sites of arsenate and the complex with binding sites may be similar to that of arsenate. At pH 5.5, arsenate was adsorbed by the following values 98%, 97%, 93% and 94% with the tested As :Se ratios, respectively. The corresponding values of adsorbed As with the tested As:Se ratios and at pH 9.3 were 3.5, 1.5, 13 and 47%, respectively. It could be noticed that increasing the initial concentration of As comparing with selenate or any other oxyanions alleviates the effect of competing oxyanion as indicated with As:Se ratio of 2:1. These results corroborated the results of (**Sposito ,1984; Goldberg and Glaubig,1988**) in which oxyanion adsorption commonly decreases as the pH increases.

#### **Arsenate and molybdate.**

Results of competitive adsorption between As (V) and MoO<sub>4</sub> on ZVI (Table 41 and Fig. 18 ) reveal that more 95% of Mo was adsorbed below pH 4.0 in single Mo anion and binary

As (V) Mo anion systems on (ZVI). These data suggest that As (V) occupies a fraction of the pH-dependent Mo adsorption Sites on (ZVI) and there is another distinct fraction of sites has higher affinity for Mo then As (V) at low pH. Similar results were obtained by the competitive effect of molybdate on arsenate adsorption on goethite, gibbsite ,kaolinite, montmorillonite and illite. (**Manning and Goldberg, 1996 a,b**) Arsenate, phosphate, and molybdate are tetrahedral oxyanions (**Cotton and Wilkinson,1980**) that can compete for As (V) adsorption sites on soil mineral surfaces (**Murali and Aylmore,1983**).

#### **Arsenate and sulfate.**

Results of competitive adsorption between As (V) and  $\text{SO}_4$  on ZVI. (Table 42 and Fig. 18 ) The competitive absorption of As (V) and S on (ZVI) was studied using As: S ratios of 1: 0, 1:1, 1:2 and 2: 1. In the absence of S, adsorption of As (V) on (ZVI) decreased with increasing pH.

The preference of the adsorbent to As (V) over  $\text{SO}_4$  was indicated when they added together as As (V) adsorption was decreased with increasing pH with slight deference as compared with no S addition.

#### **Cadmium**

With regard to Cd adsorption on ZVI in a binary system containing Cd and Co at Cd : Co concentration ratios of 1:0,1:1,1:2 and 2:1 (Table 43 and Fig.19), Cd was adsorbed in small quantities at  $\text{pH} < 4.0$  This may be attributable to the repulsion effect of the adsorbent sites to Cd and Co, the repulsion effect may be ascribed to increasing the positive dependent charge at lower pH values. Then the adsorbed Cd was



increased sharply with increasing pH > 4.0 up to pH 7.0 in the absence and presence of competition ion (Co). The highest adsorption of Cd was achieved with using 2:1 Cd: Co ratios while the lowest Cd adsorption occurred with using 1:1 Cd:Co ratio. The pH envelopes study reveals that the quantities of adsorbed Cd were different and depended on Cd :Co ratio. At pH 4.0 and with 1:0, 1:1, 1:2 Cd:Co ratios the adsorbed Cd percentages recorded the following values: 14, 47, 8.9 and 25%. However appreciable quantities of Cd were adsorbed with pH 5.5 at 1:0, 1:1, 1:2 and 2:1 Cd : Co ratios as compared with values obtained at pH 4.0. At pH 9.3 the adsorption of Cd was independent from Cd :Co ratios as it recorded almost 100% with all tested ratios. These results are in agreement with all tested ratios and with those reported by **Dzombak and Morel (1990)** for a fairly complete compilation.

















#### **4.2.4.Experment IV: Kinetics of arsenic adsorption.**

##### **4.2.4.1.goethite.**

Knowledge of reaction kinetics at the solid liquid interface is extremely important in understanding the adsorption/desorption processes controlling As solubility and bioavailability in soil and water systems.

With low concentration of initial arsenic in solution equivalent to  $10 \mu\text{g As mL}^{-1}$  arsenate adsorption at pH 5.0 increased very fast in the first 2 min. of the reaction and a portion of 99% of the added As was adsorbed (Fig 20. and Table 44), then, adsorption reaction proceeded gradually and slowly to reach 99.9.% of the added As after 1.0 h. of the reaction initiation.

At pH9, arsenate adsorption was more faster with increasing time from 0.0 to 40 min. with low initial As concentration. Such faster As(V) adsorption may be due to the formation of monodentate complex with  $\text{Fe}^{3+}$  atoms of goethite surface.

A linear monodentate arrangement of arsenate must form on a goethite surface functional group that is singly coordinated to central Fe atoms. The formation of monodentate complex at very low coverage was confirmed by EXAFS results (Waychunas et al., 1993, and Fendorf et al., 1997).

It could be concluded that, with low initial As concentration, the adsorption of As (V) on goethite was rapid and more than 99.6% and 96.6 of the added As was adsorbed within 4 min. at pH 5 and 9, respectively. Similar results were

obtained by **Abd El- Haleem (2001)** who found that adsorption of As(V) at pH 5.0 and 8.0 was almost similar under the low coverage of As(V). Data of As sorbed by unit weight of goethite ( $q$ ,  $\mu\text{g of As g}^{-1}$ ) and equilibrium As concentration  $c$ ,  $\mu\text{g As mL}^{-1}$ ) were highly fitted to linear form of Langmuir and Frundlich adsorption isotherms equations.. the slight decrease in As(V) adsorption occurred with time could be attributable to the release of OH<sup>-</sup> ion from goethite surface by ligand exchange with arsenate which increase pH. Ligand exchange involves the substitution of an oxyanions species (**Rajan, 1976,1979; parfitt et al., 1975**). The ligand exchange process can alter the pH of the system by increasing the concentration of OH<sup>-</sup> ions, which in turn, can compete with P and As for surface complexation sites ( **Rajan and Fox, 1975;Hingston, 1981;Gebhardt and Coleman, 1974; Barrow,1974**).Oxyanion adsorption commonly decreases as the pH increases not only because the presence of OH<sup>-</sup> ions but also because of the increase in negative charge of adsorbing surface (**Sposito, 1984; Goldberge and Glauding, 1988**).When anions that protonate are present, such as  $\text{H}_2\text{AsO}_4^-$  an increase in pH results in an adsorption envelopes that reflects the competition between the anion and surface sites for the decreasing presence of the proton (**Hingston et al. 1972**). Similar results on Ferrihydrite were reported by **Raven et al. (1998)** with equilibrium arsenite concentration adsorption at pH 9 being greatly higher than at pH 5.

#### **4.2.4.2.Zerovalent iron. (ZVI)**

With low concentration of initial arsenic in solution equivalent to  $10 \mu\text{g As mL}^{-1}$  arsenate adsorption at pH 5.0 increased very fast in the beginning of the reaction and a portion

of 100% of the added As was adsorbed (Fig. 20 and Table 44). Then, adsorption reaction proceeded gradually to keep 100.% of the added As adsorbed at the end of the reaction.

At pH 9, arsenate adsorption was faster with increasing time from 0.0 to 10 h. with low initial As concentration. However, at pH 5 adsorption of arsenate was faster and complete than adsorption of arsenate at pH 9.0. This may be due to the formation of monodentate complex with Fe<sup>3+</sup> atoms of goethite surface.

A linear monodentate arrangement of arsenate must form on a goethite surface functional group that is singly coordinated to central Fe atoms.

The formation of monodentate complex at very low coverage was confirmed by EXAFS results (**Waychunas et al., 1993, and Fendorf et al., 1997**).

It could be concluded that, with low initial As concentration, the initial adsorption of As (V) on ZVI was rapid with 100% and 99.7% of the added As was adsorbed within 10 min. at pH 5 and 9 respectively. With arsenate at pH 5, adsorption rate was rapid initially and 100% of total As added was adsorbed in the first 10 h., whereas, an approximate adsorption of 98.7% of the total As added occurred at pH 9.0.













#### **4.2.5. Experiment V :Desorption of arsenic and cadmium from soils by DTPA.**

##### **4.2.5.1.Soil**

##### **Arsenic**

While most studies in environmental soil chemistry have focused on the adsorption or sorption of ions and molecules on soils, the desorption process is also extremely important. 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 desorbed,i.e.,the reactions appear to be irreversible. Such apparent irreversible is commonly referred to as hysteresis or nonsingularity.

Desorption of As (V) from soil was tested and obtained data are presented in Table (47)

Desorped As ( $\mu\text{g g}^{-1}$ ) from loamy soil by DTPA solution increased gradually with increasing initial As (V) concentration (Table 48 and Fig. 21).The highest desorption increases were attained with increasing initial As(V) concentration from 10 to 30, and from 60 to 90  $\mu\text{g mL}^{-1}$ .Increasing initial As (V) concentration from 60 to 80  $\mu\text{g mL}^{-1}$  in solution resulted in a moderate increase in As desorption. However, a slight increase in the desorbed As was observed with increasing its initial concentration from 30 to 60 and from 90  $\mu\text{g As mL}^{-1}$ .

Desorbed As % was computed for each initial concentration, the highest desorption percentages, i.e., 39.0, 39.4

and 40.5 % were accompanied with initial concentrations of 90,30 and 80  $\mu\text{g As mL}^{-1}$ , respectively.

Concerning clay loam soil, the highest increase in desorbed As was noticed with increasing the initial As concentration from 20 to 30,70 to 80  $\mu\text{g As mL}^{-1}$ . However, moderate increases were observed with increasing the initial As concentration from 10 to 90  $\mu\text{g As mL}^{-1}$  (Table 49). The highest desorption percentages were observed with the low coverage of As which was accompanied with the low initial As concentration, i.e., almost 43.7 and 39.3% of adsorbed As were desorbed using DTPA solution when the initial As concentration were 70 and 80  $\mu\text{g As mL}^{-1}$ , respectively.

### **Cadmium**

Desorption of Cd from soils is shown in Tables (50-51) and illustrated in Fig (22). Desorped Cd from loamy soil increased with increasing the initial concentration of Cd and the highest desorption increases were attained with increasing initial Cd concentration from 10 to 20  $\mu\text{g Cd mL}^{-1}$ .

Desorped Cd % was computed for each initial concentration and the highest desorption percentages, i.e., 51.9 and 55 % were accompanied with initial concentration of 10 and 20  $\mu\text{g Cd mL}^{-1}$ , respectively.

Concerning clay loam soil, a sharp increase in desorped Cd was noticed with increasing the initial Cd concentration from 10 to 40  $\mu\text{g Cd mL}^{-1}$  followed by gradual increases with increasing initial Cd concentration from 10 to 80  $\mu\text{g Cd mL}^{-1}$ . The highest desorption percentages were observed with the low coverage of Cd which was accompanied with low initial Cd

concentration i.e., almost 59.0 and 60 of adsorbed Cd were desorbed using DTPA solution, this result is in agreement with **Papadopoulos and Rowell (1988)** showed that the  $\text{CaCO}_3$  surface has a high affinity for Cd. Also, **Renella et al. (2004)** showed that Cd mobility was reduced mainly by adsorption on carbonates **Hela et al. (1996)** concluded that Cd adsorbed on calcareous soil was partially irreversible. .... The high values of desorbed Cd from clay loam soil could be due to its high content of clay,  $\text{CaCO}_3$ , and O.M. These results stand in well agreement with those of **Sposito, (1989)**.

#### **4.2.5.2 Effect of phosphates on arsenic desorption from goethite.**

Arsenic was added to the goethite suspension at a low-coverage rate of  $10 \mu\text{g As mL}^{-1}$  to ensure a complete adsorption on goethite surfaces at pH 5.0 and pH 9.0 (Fig. 23 ). Arsenate was adsorbed completely at pH <9 in the absence of phosphate.

Phosphate had the greatest effect on As (V) desorption from goethite at pH 3.0 (31.6%) and As desorption was slightly increased with increasing the pH up to 7.0 (33%). Above pH 7.0, the desorption of As (V) increased to approximately (70.6%) at pH 12. In presence of phosphate in a concentration 100 times as arsenate, and at pH (9) phosphate had the greatest effect on As (V) desorption at pH 3 (43.7 %) and As desorption increased with increasing the pH up to 7.0 (46%). Above pH 7, the desorption of As (V) increased to a approximately 75.5 % at pH 12.

The obtained results indicated that desorption of As is very sensitive to pH condition. Similar results were obtained by









**Masscheleyn et al. (1991).** The highest desorption percentage (76 %) was achieved with using phosphate at pH 5.0. Yet the desorption of arsenate by phosphate was not complete, such incomplete desorption may be attributable to the formation of bionuclear adsorption complexes of As (V) on goethite surfaces which restrict the rate of desorption (**Sun and Doner,1996; Fendorf et al., 1977; Abd El-Haleem,2002**).

The sorption of AsO<sub>4</sub> (or PO<sub>4</sub>) on goethite and gibbsite decreased with increasing the initial PO<sub>4</sub>/AsO<sub>4</sub> (molar ratio) up to 2.0. However, PO<sub>4</sub> inhibited AsO<sub>4</sub> sorption more on gibbsite than on goethite, whereas AsO<sub>4</sub> prevented PO<sub>4</sub> sorption more on goethite than gibbsite (**Violante et al., 2002**) Arsenate adsorption on amorphous Fe oxide (**Jain and loeppert, 2000**), goethite, gibbsite (**Hingston et al.,1971; Manning and Goldbrg, 1996a**), kaolinite, montmorillonite, and illite (**Manning and Goldberg, 1996b**) was significantly reduced the presence of competing phosphate concentrations. Arsenite adsorption by amorphous Fe oxide was also reduced the presence of competing phosphate concentrations although some sites exhibited considerably higher selectivity for arsenite than for phosphate (**Jain and Loeppert,2000**)

#### **4.2.3. Effect of sulphate on Arsenate desorption on goethite.**

Data illustrated in Fig. ( 23 ) show that sulfate has no appreciable effect on As(V) desorption at pH 3.0 (0.34%) and As desorption was negligible with increasing the pH up to 7.0 (0.34). Above pH 7, the desorption of As (V) increased to approximately (59.8%) at pH 12.0. While at pH 9.0 the desorption of As(V) by sulphate showed almost the same results of those at pH 3.0 to 7.0. Similar results were obtained by



(Wilkie and Hering, 1996 and Jain and Loeppert,2000).Arsenate adsorption on alumina (Xu et al., 1988) and arsenite adsorption on amorphous Fe oxide were reduced by competing sulfate concentrations,although to a lesser degree than by competing phosphate concentrations. (Wilkie and Hering, 1996; Jain and Loeppert,2000)

#### **4.2.5.2 Effect of molybdate on arsenate desorption on goethite.**

Results of Fig (23) indicate that molybdate has the greatest effect on As (V) desorption at pH3.0 (32%) and As desorption was decreased with increasing the pH up to pH 7.0 (0.10%) Above pH 7.0, the desorption of As (V) increased to approximately (58.9%) at pH 12.0 in presence of molybdate at initial concentration ratio of 100:1 ( $\text{MoO}_4:\text{PO}_4$ ) and at adsorption pH 5.0. At adsorption pH of 9.0, Fig ( 23 ) reveals that molybdate showed the greatest effect on As (V) desorption at pH3.0 (43.2%) and As desorption decreased with increasing the pH up to 8.0 (6.23%) above pH 8,the desorption of As (V) increased to approximately (64.4%) at pH 12.0.

Similar results were obtained by the competitive effect of molybdate on arsenate adsorption on goethite, gibbsite ,kaolinite, montmorillonite and illite. (Manning and Goldberg, 1996 a,b)







#### **4.2.5.3 Effect of phosphate on arsenic desorption from zerovalent iron.**

Arsenate was initially adsorbed at pH 5.0 and 9.0 in the absence of phosphate (Fig. 24 ) phosphate had the greatest effect on As (V) desorption at pH 3.0 (10.1%) in case of pH 5.0. As desorption decreased with increasing the pH up to pH 7.0 (7.08%). Above pH 7.0, the desorption of As (V) increased to approximately (48.1%) at pH 12.0 in presence of phosphate and initial adsorption pH of 5.0, while at the initial adsorption pH of 9.0 phosphate had the greatest affect on As (V) desorption at pH 3.0 (23.5%) and As desorption decreased with increasing the pH up to 7 (22.09%). Above pH 7.0, the desorption of As(V) increased to approximately 55.7% at pH 12.0 in presence of phosphate and arsenate at a concentration ratio of (100:1).

#### **4.2.5.3. Effect of sulphate on arsenic desorption from zerovalent iron.**

Arsenate was initially adsorbed at pH 5.0 and 9.0 in the absence of sulphate (Fig. 24 ), sulphate had not affected on As (V) desorption at pH 3.0 as lowest As quantities were desorbed (0.28%) and As desorption did not change with increasing the pH up to 9.0 (0.08%). Above pH 9.0, the desorption of As (V) increased to approximately (45.5%) at pH 12.0 in presence of sulphate and at initial pH of 5.0. While at pH 9.0 sulphate showed the lowest effect on As (V) desorption at pH 3.0 (0.93%) and As desorption decreased with increasing pH up to pH 8.0 (1.79%). Above pH 8.0, the desorption of As(V) increased to approximately (65.8%) at pH 12.0 in presence of sulphate to arsenate at concentration ratio of (100:1).

#### 4.2.5.3. Effect of molybdate on arsenic desorption from zerovalent iron.

Arsenate was firstly adsorbed at pH 5.0 in the absence of molybdate (Fig. 24) and extracted by molybdate which declared the greatest effect on As (V) desorption at pH 3.0 (33.2%) and As desorption decreased sharply with increasing the pH up to 7.0 (0.00). Above pH 7.0, the desorption of As(V) increased to approximately (39.9%) at pH 12.0 in presence of molybdate and initial adsorption pH of 5.0. As(V) was initially adsorbed at pH 9.0 and extracted by molybdate which revealed the greatest effect on As(V) desorption at pH 3.0 (51.93%) and As desorption decreased with increasing the pH up to pH 7.0 (1.30%). Above pH 7.0, the desorption of As(V) increased to approximately (55.8%) at pH 12.0. in presence of molybdate at a concentration ratio of (100:1,  $\text{MoO}_4\text{:As}$ ).

Desorption of As (V) by phosphate, sulphate and molybdate was highly dependent on pH. The maximum As desorption at the low and high pH values, but in no case achieved greater than (70-75%), (59.9-66%) and (59-64%) in case of using phosphate, sulphate and molybdate on goethite at pH 5.0 and 9.0 respectively. Also As desorption was at its maximum 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 on Ferrihydrite at pH 5.0 and 9.0 respectively (**Loeppert and Jain 2000**). As well as As desorption was at the maximum at low and high pH values, but in no case achieved greater than (48.1-55.7%), (45.4-65.8%) and (39.9-55.8%) in case of presence phosphate, sulphate and molybdate on zerovalent iron at pH 5.0 and 9.0 respectively.

These results are in agreement with those reported by **Hiemstra and Riemsdijk (1999)** in which application of phosphate fertilizer has been shown to affect the mobility of arsenic in soils. Excess of phosphate has been used to displace As (V) from sediments, fly ash, and soils, but the displacement is slow and often incomplete (**Peryea, 1991**).

It could be concluded that  $\text{SO}_4^{=}$  ions failed to extract or replace arsenate adsorbed on Goethite and Zerovalent iron (ZVI) in a pH range of 3.0 to 8 under the initial adsorption pH values of 5.0 and 9.0. At pH < 6.0 and > 9.0 both of phosphate and molybdate were able to extract appreciable quantities of As initially adsorbed on goethite and (ZVI) at pH values of 5.0 and 9.0 and they can be used as extracts for adsorbed As, except in the case of As adsorbed at pH 5.0 on (ZVI), where phosphate did not succeed to extract appreciable quantities of the adsorbed As at pH ranged from 3.0 to 9.0.







