COMPETITIVE ADSORPTION OF ARSENATE WITH PHOSPHATE, MOLYBDATE, SELENATE, AND SULFATE ON GOETHITE AND ZEROVALENT IRON (ZVI).

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ABSTRACT

A laboratory experiment, was carried out on synthetic goethite and zerovalent iron (ZVI) to study the competition between AsO_4^{3-} (10µg As mL^{-1})and PO_4^{3-}, SeO_4^{2-}, SO_4^{2-} and MoO_4^{2-} at different ratios (1:0, 1:1, 1:2 and 2:1) on the adsorption surfaces of the selected minerals. Obtained data showed that, at pH 7.0 a quantity of 2891 µg As g^{-1} goethite was adsorbed from the added As(V) (AsO_4^{3-}), with increasing the pH above 9.0 the adsorbed AsO_4^{3-} was decreased to be 1662 and 945 µg As g^{-1} goethite at pH 11.0 and 11.8 , respectively. On the other hand, the amount of adsorbed As(V) on ZVI recorded 23590 µg As g^{-1} at pH 4.0 and decreased to be 15620 and 983 µg As g^{-1} ZVI at pH 9.5 and 12.0, respectively. Adsorption of As(V) on both goethite and ZVI was decreased with increasing pH when As(V) was added alone or with PO_4^{3-} at As :P ratios of 1:0, 1:1 and 1:2.

However, more pronounced increases in AsO_4^{3-} adsorption was noticed when AsO_4^{3-} was added at 2:1 ratio as compared to PO_4^{3-} with all tested pH values. The adsorption affinity of goethite and ZVI to AsO_4^{3-} was affected largely by pH and arsenate concentration in the equilibrium solution. It could be mentioned that PO_4^{3-} could not compete well with arsenate on the specific sites of AsO_4^{3-} if its ratio to AsO_4^{3-} was less than 2:1. These results indicate that the preference of adsorption sites to AsO_4^{3-} was mainly affected by pH values and the concentration of associated oxyanions.

With respect to the competition between AsO_4^{3-} and SeO_4^{2-}, MoO_4^{2-} and SO_4^{2-}, obtained data also indicated that the adsorbed AsO_4^{3-} on both goethite and ZVI was decreased more at As:Se ratio of 1:2 as compared with other ratios. Selenate (SeO_4^{2-}) had competed with AsO_4^{3-} on the adsorption sites of both goethite and ZVI, and reduced the amount of adsorbed AsO_4^{3-} .Increasing the initial concentration of adsorbed As comparing with selenate or any other oxyanions alleviated the effect of competing oxyanions as indicated with As:Se ratio of 2:1. More than 95% of As(V)was adsorbed on both goethite and ZVI below pH 4.0 in single AsO_4^{3-} anion and binary with MoO_4^{2-} anion systems.

These data suggested that MoO_4^{2-} occupies a fraction of the pH- dependent As(V) adsorption sites on the studied minerals and there was another distinct fraction of sites had higher affinity for As MoO_4^{2-} at low pH. Obtained data also indicated that, the preference of the adsorbents to AsO_4^{3-} over SO_4^{2-} was declared when they added together.

Keywords: arsenate, competition, adsorption, pHospHate, molybdate, selenate, goethite and iron metal.

INTRODUCTION

Clay minerals, oxides and organic matter exert a strong preference for some anions in comparison to other anions, indicating the existence of chemical bonds between the surface and the specific anion. PHospHate has been the extensively studied anion that exhibits this specific adsorption (inner spHere complex) pHenomenon. Selenite (SeO_3^{2-})and arsenate (AsO_4^{3-}) are

adsorbed to oxides and soils through specific binding mechanisms (Rajan, 1979;Neal,*et al.* 1987b). Selenate (SeO_4^{2-}) and hexavalent chromium are only weakly bound to soil surfaces and are thus easily displaced by other anions. Balistrieri and Chao (1987) found the sequence of adsorption of anions onto oxidetobe:pHospHate=silicate=arsenate>bicarbonate/carbonate>citrate=selenite>molybdate>oxalate>fluoride=selenate>sulfate.

The adsorption capacity for anions is however small relative to cation adsorption capacity of soils. Brouwere *et al.*(2004) suggested that $AsO_4^{3-}$is adsorbed to amorpHous oxides in soils and that sites of adsorption vary in their selectivity in respect of As and P. They proposed a two-site model of competitive AsO_4^{3-} -PO_4^{3-} (V) sorption in which amorpHous Fe and Al oxides represent the site capacity and the isotopically exchangeable As represents the adsorbed P. Jackson and Miller (2000) concluded that arsenite was extracted most efficiently by 0.5M PO_4^{3-} at low pH; however, amorpHous Fe oxide exhibited a strong affinity for AsO_2^- with a maximum of 18% of AsO_2^- extracted by 0.5M PO_4 at pH 2.8. Partial oxidation of AsO_2^- to AsO_4^{3-}occurred in all extractions where Fe oxide solid pHase was present, but only in the hydroxide extract in absence of Fe solid pHase. Addition of 0.1M PO_4 to extractants used for the dissolution of the amorpHous Fe oxide prevented the readsorption of $AsO_4^{3-}$and SeO_3^{2-} to goethite.

The aim of this work was to asses the competitive adsorption of (AsO_4^{3-},SeO_4^{2-}),(AsO_4^{3-},SO_4^{2-}),(AsO_4^{3-},PO_4^{3-}), and (AsO_4^{3-},MoO_4^{2-}) on goethite and zerovalent iron (ZVI).

MATERIALS AND METHODS

An experiment was carried out on a synthetic goethite (iron oxide,α-FeOOH) and zerovalent iron (fine powder of iron metal) to study the competition between As as AsO_4^{3-} (10µg As mL^{-1}) and Se, P, S, and Mo as SeO_4^{2-},PO_4^{2-}, SO_4^{2-}, or MoO_4^{2-}, respectively on the surfaces of the selected minerals under different pH values. Zerovalent iron is a neutral charge mineral, but it will be charged by positive and /or negative charges as a result of pH variation in the media (Raven *et al.*,1998).

Synthesis of goethite:

Goethite was synthesized in the lab. according to the procedure of Schwertmann and Cornell(1991) as follows: 100 mL of 1M Fe (NO_3)$_3$ freshly prepared, were poured into a 2L-polyethlene pottle, and 180 mL of 5 M NaOH were added rapidly with stirring to the pottle, 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 strring until the electrical conductivity of dialysis water became 6 µS/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 hot plate till the goethite was completely dissolved. The clear suspension was

transferred quantitively to a 50-mL volumetric flask and brought to volume using deionized water. From that solution one mL was taken and diluted to a 100 mL using deionized water. Iron was measured in the last solution using Atomic Absorption Spectroscopy (Perkin Elmer 3300).The concentration of goethite in the final suspension was 32 gL^{-1}. 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).
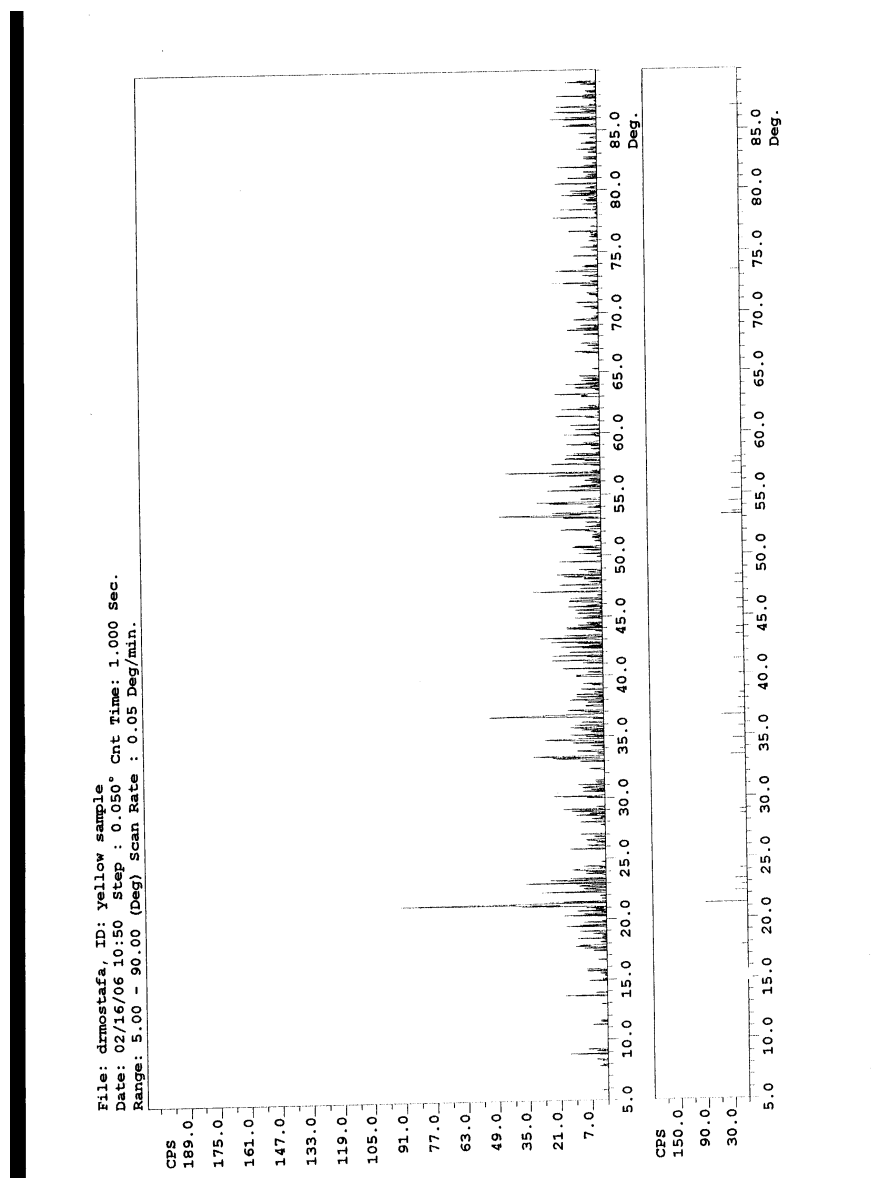

Fig.(1) X-ray diffraction analysis of the synthesized goethite.

Competitive adsorption:

A portion of 2.5 mL goethite suspension or 0.01g zerovalent-iron was shaken with distilled water which was added to complete the volume to be 25 mL, then the pH was adjusted to be in the range of 3.0 to 12.0. The suspension was prepared at one of three different ratios(1:0, 1:1, 1:2, or 2:1), of As as AsO_4^{3-}(10μg As mL^{-1}) to the previous mentioned oxyanions in the presence of 0.1M of NaCl as a back ground electrolyte. The reaction vessels were shaken for 4 h, centrifuged for 30 min at 3000 rpm, and the supernatants were filtrated. The pH in the filtrates was measured, and arsenic was determined using Inductively Coupled Plasma Spectrometry (Plasma JY Ultima).

RESULTS AND DISCUSSION

Competitive adsorption of arsenate with pHospHate, molybdate, selenate, or sulfate on goethite and zerovalent iron (ZVI).
Goethite.
Arsenate and pHospHate.

The mobility of arsenate in soils depends on several factors including redox potential, soil mineralogy, pH, and the presence of other oxyanions that compete with As(V)(AsO_4^{3-}) for soil retention sites. The effects of pH and competing anions on the adsorption of arsenate AsO_4^{3-} on goethite were investigated.The competitive adsorption of AsO_4^{3-} and PO_4^{3-} on goethite versus pH was studied using As : P ratios of 1:0,1:1 and 1:2 as presented in Fig. (2)

In the absence of PO_4^{3-}, adsorption of AsO_4^{3-} on goethite was slightly decreased with increasing pH. At pH 7.0 a quantity of 2891 µg As g^{-1} goethite was adsorbed, while at pH 8.0 the adsorbed As (V) was decreased to be 2881 µg As g^{-1} goethite followed by a sharp reduction with increasing the pH above pH 9.0 to be 1662 and 945 µg As g^{-1} goethite at pH 11.0 and 11.8, respectively.

The preference of the adsorbent (goethite) to AsO_4^{3-} over PO_4^{3-} was indicated when they were added together (at a ratio of 1:1 As:P), as the amount of As (V) adsorbed was decreased gradually with increasing pH with slight differences as compared with no P addition at pH> 5.84. However, arsenate was more affected by pHospHate and the amount of adsorbed arsenate being 2678 µg As g^{-1} goethite at pH 6.0, decreased to 2190 µg As g^{-1} goethite at pH 7.0 and decreased sharply with increasing pH to achieve 975 µg As g^{-1} goethite at pH 11.2.

Data of the competitive adsorption between AsO_4^{3-} and PO_4^{3-} on goethite which are shown in Fig (2) indicate that adsorption of As (V) was decreased with increasing pH when AsO_4^{3-} was added alone or with PO_4^{3-} at As : P ratios of l : 0,1:1 and 1 : 2. However, more pronounced increases in AsO_4^{3-} adsorption was noticed when AsO_4^{3-} was added at 2: 1 As: P ratio with all tested pH values.

The affinity of goethite to AsO_4^{3-} was affected, to large extent, by both pH and AsO_4^{3-} concentration in equilibrium solution. The lowest AsO_4^{3-}

adsorption was noticed with As: P ratio of 1 : 2 particularity at the high pH values.

At the initial concentration of 10 µg As L^{-1}, arsenate surface coverage reached a maximum of 3119 µg As g^{-1} goethite at pH 3.0 as shown in Fig. (2), at that initial AsO_4^{3-} concentration, AsO_4^{3-} was almost completely adsorbed on goethite below pH 4.0 in the absence of PO_4^{3-}. Both AsO_4^{3-} and PO_4^{3-} when added as single anions displayed broad adsorption envelopes with 100% adsorption of AsO_4^{3-} below pH 4.0 and 98% at ratio of 1:1 As: P.

Fig.(2).Competitive adsorption of AsO_4^{3-} and PO_4^{3-},SeO_4^{2-},SO_4^{2-} or MoO_4^{2-} on goethite as a function of pH. Experimental conditions: As: P, Se ,S or Mo (1:0,1:1,2:1and 1:2), ionic strength buffer, 0.1M NaCl.

The results obtained revealed that at pH 4.0 AsO_4^{3-} was almost completely adsorbed when its ratios with of As:P were 1:0 (100%),1:1 (98%) and 2:1 (99%), while only 73% of AsO_4^{3-} was adsorbed with As:P ratio of (1:2). It could be mentioned that PO_4^{3-} could not compete well with arsenate on the specific sites of AsO_4^{3-} if its ratio to AsO_4^{3-} was less than 2:1.

At a ratio of As:P (1:2), PO_4^{3-} competed with AsO_4^{3-} 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 AsO_4^{3-} 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 at the some above mentioned As: P ratios, respectively. These results indicated that the preference of adsorption sites to As was mainly affected by both pH values and the concentration of associated oxyanions.

Arsenate and selenate.

Results of competitive adsorption between AsO_4^{3-} and SeO_4^{2-} on goethite are shown in Fig. (2) which reveals that adsorption of AsO_4^{3-} was decreased with increasing pH. when AsO_4^{3-} was added alone or with SeO_4^{2-} at As : Se ratios of (l : 0, l : l and 1:2). However, more pronounced increases in AsO_4^{3-} adsorption was noticed when AsO_4^{3-} was added at 2 : 1 As : Se ratio. The affinity of goethite to AsO_4^{3-} was affected largely by both pH and AsO_4^{3-} concentration in equilibrium solution. Adsorption of AsO_4^{3-} was decreased with increasing pH in the presence as well as in absence of SeO_4^{2-}. At 10 µg As L^{-1} initial concentration, AsO_4^{3-} surface coverage reached a maximum of 3119 µg As g^{-1} goethite at pH 3 .0 and As: Se ratio of 1:0. At the same initial concentration of arsenate, AsO_4^{3-} was completely adsorbed on goethite below pH 4. Both AsO_4^{3-} and SeO_4^{2-} single anions displayed broad adsorption envelopes with pH range of 3.0 to 12. With As:Se ratio of 1:2 the adsorbed AsO_4^{3-} 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).

Fig. (2) reveals 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 at ratios between As :Se of 1:1, 1:2, and 2:1 the adsorption values of AsO_4^{3-} by goethite were 98%, 68.7 and 99%, respectively.

Thus selenate considerably competed with AsO_4^{3-} on the adsorption sites and reduced the amount of AsO_4^{3-} adsorbed on goethite to be 68.7%. Such decrease in As adsorption was greater than that obtained with PO_4^{3-} under the same condition. This 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 AsO_4^{3-} added at As :Se ratios of 1:0, 1:1,1:2 and 2:1, respectively. The corresponding values of adsorbed AsO_4^{3-} 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 AsO_4^{3-} 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 AsO_4^{3-} and MoO_4^{2-} on goethite are shown in Fig.(2). More than 95% of AsO_4^{3-} was adsorbed below

pH 4.0 in single Mo anion and binary MoO_4^{2-} anion systems on goethite. These data suggest that MoO_4^{2-} occupies a fraction of the pH-dependent AsO_4^{3-} adsorption sites on goethite and there is another distinct fraction of sites has higher affinity for AsO_4^{3-} or MoO_4^{2-} at low pH. Similar results were obtained by the competitive effect of molybdate and arsenate adsorption on goethite, gibbsite ,kaolinite, montmorillonite and illite (Manning and Goldberg, 1996 a,b)

Arsenate and sulfate.

Results of the competitive adsorption between AsO_4^{3-} and SO_4^{2-} on goethite indicated that the competitive absorption of AsO_4^{3-} and SO_4^{2-} on goethite which was studied using As: S ratios of 1: 0, 1:1, 1:2 and 2: l, in the absence of SO_4^{2-}, adsorption of AsO_4^{3-} on goethite decreased with increasing pH. The preference of the adsorbent to AsO_4^{3-} over SO_4^{2-} was indicated when they were added together as AsO_4^{3-} adsorbed was decreased with increasing pH with a slight difference as compared with no SO_4^{2-} addition. Up to pH 10.0, sulfate failed to compete with arsenate on AsO_4^{3-} adsorption sites considerably.

These results were also consistent with the relative affinity of goethite surface to AsO_4^{3-}, PO_4^{3-}, and MoO_4^{2-}.Affinity in most cases tended to be PO_4^{3-} = AsO_4^{3-} > MoO_4^{2-} at neutral pH. PHospHate and arsenate 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 AsO_4^{3-} or PO_4^{2-}. These results are in agreement with those reported by Manning and Goldberg (1996 a) which revealed that arsenate and pHospHate single –anion adsorption envelopes were similar with substantial adsorption occurring across a wide pH range, including pH values above the 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 AsO_4^{3-}, PO_4^{3-} and MoO_4^{2-} tetrahedra on goethite surface are 0.61, 0.61 and 0.31 nm^2,respectively.

When anions that protonate are present such as $H_2AsO_4^-$ and $H_2PO_4^-$, 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).

Zerovalent iron (ZVI)

Arsenate and pHospHate.

Results of competitive adsorption between AsO_4^{3-} and PO_4^{3-} on zerovalent iron (ZVI) are shown in Fig (3). Adsorption of AsO_4^{3-} was decreased with increasing pH with very slight differences between the amounts adsorbed on zerovalent iron (ZVI) in particular when AsO_4^{3-} was added alone or with PO_4^{3-}, SeO_4^{2-}, MoO_4^{2-} and SO_4^{2-}, at As : Se , P, Mo or S (1 : 0,1:1,1:2 and2 : l).

However, more pronounced increases in AsO_4^{3-} adsorption was noticed when As was added at 2: 1 As: Se, P, Mo or S ratio. The affinity of

ZVI to AsO_4^{3-}, SeO_4^{2-}, PO_4^{3-} and MoO_4^{2-} was affected largely by pH and by As concentration in the equilibrium solution.

In the absence of PO_4^{3-}, adsorption of AsO_4^{3-} on zerovalent iron (ZVI) decreased gradually with increasing pH, at pH 4.3 almost 24960 µg As g^{-1} of the added As was adsorbed, while at pH 9.0 value of 875 µg As g^{-1} was adsorbed. The preference of the adsorbent to AsO_4^{3-} over PO_4^{3-} was indicated when they were added together as AsO_4^{3-} adsorbed amount was decreased gradually with increasing pH with slight differences as compared with no PO_4^{3-} addition. However, AsO_4^{3-} was more affected by PO_4^{3-} and the amount of adsorbed AsO_4^{3-} recorded 23590 µg As g^{-1} at pH 4.0 and As: P ratio of 1:1, decreased to 15620 µg As g^{-1} at pH 9.5 and decreased sharply with increasing pH to achieve 983 µg As g^{-1} at pH 12.0. Results of competitive adsorption between AsO_4^{3-} and PO_4^{3-} on (ZVI) are shown in Fig (3) and indicated that adsorption of AsO_4^{3-} was decreased with increasing pH when AsO_4^{3-} was added alone or with PO_4^{3-} at low As : P ratio (I : 0,1:1 and 1 : 2). However, more pronounced increases in AsO_4^{3-} adsorption was noticed when AsO_4^{3-} was added at 2: 1 As: P ratio. The affinity of ZVI to AsO_4^{3-} was affected largely by pH and by AsO_4^{3-} concentration in equilibrium solution. At the 10 µg mL^{-1} starting concentration, AsO_4^{3-} surface coverage reached maximum of 24960 µg Asg^{-1} on ZVI at pH 4.3 Fig (3)

At 10 µg As mL^{-1} as a starting concentration, AsO_4^{3-} was 100% adsorbed on (ZVI) below pH 7. Both AsO_4^{3-} and P single anions displayed broad adsorption envelopes with almost 100% adsorption of AsO_4^{3-} below pH 6 and 98% with As: P ratio (1:l) and decreased with As: P ratio of 1:2.

PHospHate and AsO_4^{3-} appeared to compete for a similar set of surface sites, though there was evidence that some sites were uniquely available for adsorption of either AsO_4^{3-} or PO_4^{3-}. The results obtained revealed that at pH 4.3 As was almost completely adsorbed when its ratios to PO_4^{3-} were 1:0 (100%),1:1 (98%) and 2:1 (66%), while only 45%of As was adsorbed with As:P ratio of (1:2). It could be mentioned that PO_4^{3-} could not compete with arsenate on the specific sites of AsO_4^{3-} if its pHospHorus ratio to As was >2:1.

At a ratio of As:P (1:2), PO_4^{3-} competed with AsO_4^{3-} 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 AsO_4^{3-} adsorption were 100,94,36 and 82,while the corresponding percentages of AsO_4^{3-} adsorption were 16,62,38.5 and 34 at pH 9.3 with the above mentioned As: P ratios, respectively. These results indicate that the preference of adsorption sites to AsO_4^{3-} was mainly affected by pH values and the concentration of associated oxyanions.

Arsenate and selenate.

Results of competitive adsorption between AsO_4^{3-} and SeO_4^{2-} on (ZVI) are shown in Fig (3). Adsorption of AsO_4^{3-} was decreased with increasing pH, when AsO_4^{3-} was added alone or with SeO_4^{2-} at low As : Se ratio (I : 0, l : l and 1:2). However, more pronounced increases in AsO_4^{3-} adsorption were noticed when AsO_4^{3-} was added at a ratio of 2 : 1 As: Se. The affinity of goethite to AsO_4^{3-} was affected, to a large extent, by both pH and AsO_4^{3-} concentration in equilibrium solution. The highest AsO_4^{3-} adsorption was noticed with As : Se ratio of 2 : 1 particularity at low pH values. Adsorption of

AsO_4^{3-} was decreased with increasing pH in the presence and absence of SeO_4^{2-}.

At the 10 µg mL^{-1} initial concentration, AsO_4^{3-} surface coverage reached maximum of 24960 µg As g^{-1} on (ZVI) at pH 4 .3, and its adsorption was 100% at pH <4 (Fig.,3). Both AsO_4^{3-} and SeO_4^{2-} single anions displayed broad adsorption envelopes with 98% adsorption of AsO_4^{3-} below pH 5.5 and As: Se 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 Fig (3) revealed that at pH 4.0 and in the absence of SeO_4^{2-} (1:0 ratio, As:Se) arsenate was almost completely adsorbed by ZVI. 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 ZVI were 98%, 98% and 94%, respectively.

Fig.(3).Competitive adsorption of AsO_4^{3-} and PO_4^{3-}, SeO_4^{2-},SO_4^{2-} or MoO_4^{2-} on zerovalent iron as a function of pH. Experimental conditions: As:P,Se,S or Mo (1:0,1:1,2:1and 1:2), ionic strength buffer, 0.1M NaCl

Thus, selenate has appreciably competed with AsO_4^{3-} on the adsorption sites and reduced the amount of AsO_4^{3-} adsorbed on ZVI. Such decrease in AsO_4^{3-} adsorption was greater than that obtained with PO_4^{3-} 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 AsO_4^3 as compared that of 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 AsO_4^{3-} and MoO_4 on ZVI Fig. (3) revealed that more than 95% of MoO_4^{2-} was adsorbed below pH 4.0 in single Mo anion and binary AsO_4^{3-} - MoO_4^{2-} anion systems on (ZVI). These data suggest that AsO_4^{3-} occupies a fraction of the pH-dependent Mo adsorption sites on (ZVI) and there is another distinct fraction of sites has higher affinity for MoO_4^{2-} than AsO_4^{3-} 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 AsO_4^{3-} adsorption sites on soil mineral surfaces (Murali and Aylmore,1983).

Arsenate and sulfate.

Results of competitive adsorption between AsO_4^{3-} and SO_4^{2-} on ZVI were presented Fig. (3) The competitive absorption of AsO_4^{3-} and SO_4^{2-} on (ZVI) was studied using As: S ratios of 1: 0, 1:1, 1:2 and 2: l. In the absence of S, adsorption of AsO_4^{3-} on ZVI decreased with increasing pH.

The preference of the adsorbent to AsO_4^{3-} over SO_4^{2-} was indicated when they were added together as AsO_4^{3-} adsorption was decreased with increasing pH with slight difference as compared with no SO_4^{2-} addition.

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الإدمصــاص التنافسـى للارسـنك مــع الفوسفات،المولبيدات،السـلينات والكبريــت علـى الجيوثايت والزيروفالنت أيرن.

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أجريت تجربة معملية على كل من معدنى الجيوثايت وبرادة الحديد النقية عديمة الشحنة لدراسـة التنـافس بـين الزرنيخـات (10ميكروجرام/ملـل)وكـل مـن الفوسفات ،السـلينات،المولبيدات والكبريت بنسب مختلفة (1:صفر،1:1، 1:2، 2:1) وذلك على أسطح إدمصاص المعادن المختارة . وقد أظهر البيانات المتحصل عليها أنه عند رقم ال pH 7 كانت كمية الزرنيخ المدمصة على الجيوثايت من الكمية الكلية المضافة هى 2891 ميكروجرام /جرام جيوثايت ومع زيادة ال pH عن 9 انخفضت الكمية المدمصة لتكون 1662، 945 ميكروجرام /جم جيوثايت عند ال pH 11، 18 على الترتيب . على الجانب الأخر كانت كمية الزرنيخ المدمصة علـى بـرادة الحديد النقيـة 23590 ميكروجرام /جم برادة حديد عند pH 4 ، وانخفضت لتكون 15620 و 983 ميكرو جرام /جرام عند 9.5pH و12 على الترتيب .انخفض ادمصاص الزرنيخ على كل مـن الجيوثايـت او بـرادة الحديد بزيادة رقم ال pH سواء عند اضافة منفردا او مع مجموعه الفوسفات بالنسب المختلفة المذكورة سابقاً .إلا أنه لوحظ أنه يوجد زيادات واضحـه فى ادمصـاص الزرنخيات عندما اضيفت بنسبة 2:1 مقارنه بالفوسفات عند كل قيم ال pH المختبرة. تأثرت القدرة الادمصاصية للجيوثايت وبرادة الحديد النقية كثيرا برقم pH وكذلك تركيز الزرنيخ فى المحلول المتزن . ولقد لـوحظ أن مجموعه الفوسفات لم تنافس جيداً الزرنيخـات علـى مواقـع الادمصـاص الخاصـة بالزرنيخـات عندما كانت نسبتها للزرنيخ اقل من 2:1 . توضح النتائج المتحصل عليها ان افضليه ادمصاص الزرنيخات على المواقع الادمصاصية للمعادن المدروسه تاثيرا كثيرا بقيم ال pH وتركيز الاكاسيد الانيونية المرافقة لهـا .امـا بالنسبة للتنافس بـين الزرنخيـات والسـلينات والمولبيدات والكبريتـات فقد اظهـرت النتائج المتحصل عليها ايضا ان الزرنخيات المدمصة على كل مـن الجيوثايت وبـرادة الحديد تناقصت اكثر عندما كانت نسبه الزرنيخ :السلينوم 2:1 مقارنه بالنسب الاخرى .نافست السلينات الزرنخيات على مواقع ادمصاص كل مـن الجيوثايت والزيروفالنت ايرن وادت الـى نقص كميـة الزرنخيـات المدمصة .وقد ادت الزيادة الى تركيز الزرنخيات فى بدايه التجربه مقارنـه بالسيلنيوم او اى انيون اخر من الايونات المدروسه الى تناقص التاثير التنافسى لها على مواقع الادمصاص . ادمص اكثر من 95% من الزرنيخات المضافة على كل من الجيوثايت وبرادة الحديد عند pH اقل من 4.00 سواء عند اضافتها بمفردها او مع المولبيدات وتشير النتائج الى ان المولبيدات تشغل جزء من مواقع الادمصاص الناتجه عن تغير فى رقم الحموضـه (pH) والموجـودة على المعادن المدروسـة ، وانـه يوجد جزء اخر من المواقع له قدرة عاليـه علـى الارتبـاط بالزرنيخ او المولبيدات عند قيم ال pH المنخفضة . اظهرت النتائج المتحصل عليها ان الافضليه لادمصاص الزرنيخات عن الكبريتات على المواقع الادمصاصية للمعادن المدروسة قد ظهرت عند اضافتها معا .