# KINETICS OF ARSENITE AND ARSENATE DESORPTION FROM GOETHITE

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#### **ABSTRACT**

Arsenic is a toxin that can occur in the environment as a result of either natural processes or anthropogenic activities. The accumulation of arsenite and arsenate in soils and sediments threatens the health of plants, wildlife, and humans. Goethite can play an important role in controlling the concentration of soluble arsenic in pore water, by the formation of inner sphere surface complexes with arsenate and arsenite. Extraction, e.g., with phosphate, oxalate, and HCl has been suggested as a procedure to assess the amount and speciation of arsenic, yet desorption is not always quantitative. Arsenite and arsenate were equilibrated with goethite at low (0.02 mol kg<sup>-1</sup>) surface coverage and extracted with phosphate at P:As molar ratio of 100:1, as well as with 0.1M oxalate at pH values ranging from 1 to 13. Phosphate desorbed only 10-50% of the adsorbed arsenite, with the largest amount of arsenic desorbed at pH 4. At the same P:As ratio, phosphate extracted only 10-30% of adsorbed arsenate, with the greatest desorption at pH 1.5. Desorption of arsenite by phosphate at pH 5 was faster than that at pH 9 and reached an approximate maximum after 5 h. Desorption of arsenate was slow and increased gradually over the 200 h reaction time. Oxalate (0.1M) was able to extract from 1 to 22% of adsorbed arsenate at pH<5 in the dark. With exposure to light, 100% of adsorbed arsenate was extracted at pH <3, due to the photo-induced dissolution of the solid phase. At pH <4 and >10, a small proportion of arsenate was reduced to arsenite during the reaction with 0.1M oxalate. Arsenic speciation after the release of As(III) from goethite by 6M HCl was affected greatly by the reaction time and the exposure to light. As(III) was readily transformed to As(V) in the light in both oxalic acid (0.1M) and 2-6 M HCI. In the dark, oxidation of As(III) to As(V) was reduced but not totally eliminated.

Keywords: Arsenite, arsenate desorption, kinetics, goethite

#### INTRODUCTION

Arsenic is a potential toxin that can enter the environment in elevated levels naturally (Germani and Zoller, 1988; Bhumbla and Keefer, 1994; Kusnierova, 1994) and as a result of anthropogenic activities (Azcue and Nriagu, 1994; Mackie and Zdepski, 1998). Arsenic concentrations in drinking water supplies throughout the world, e.g., in Bangladesh (Dhar et al., 1997; Nickson et al., 2000; Chiu and Hering, 2000) have exceeded the As standard (50 µg /L). As(III) is usually considered to be more toxic than As(V) (NAS, 1977) and presence of As(III) and As(V) in different proportion in water supplies may produce different toxic effects. Therefore, measurement of total arsenic concentration is insufficient to assess the risk of As exposure in human populations. Studies of As speciation and transformations among species are essential to understanding the As behavior in the environment. Arsenic sorption, bioavailability and behavior in natural systems are largely

controlled by amorphous and crystalline Fe, Al and Mn hydroxides (Mok and Wai, 1994; Fujii and Swain, 1995).

Synthetic goethite (&FeOOH) has been selected as a model substrate for arsenate and arsenite adsorption principally because it can be synthesized under precisely controlled conditions as regular, well formed, small crystals of large surface area ( Parfitt et al., 1976). The adsorption/desorption of As is also very sensitive to pH and Eh conditions (Masscheleyn et al., 1991). Jones et al. (2000) indicated that rates of arsenic mobilization during reduction in soils are highly dependent on oxide surface area and arsenic surface coverage. Three different surface complexes exist on goethite for arsenate: a monodendate complex at very low coverages, both the monodentate and bidentate complexes at intermediate coverages, and predominantly the bidentate-binuclear complexes at very high coverages (Fendorf et al., 1997).

Application of phosphate fertilizers has been shown to affect the mobility of arsenic in soils (Hiemstra and Riemsdijk ,1999). Excess of phosphate has been used to displacement As(III) or As(V) from sediments, fly ash, and soils, but the displacement is slow and often incomplete (Peryea, 1991). Digestion with 4 M HCl has been used to release As(III) and As(V) from lacustrine sediments.

The objectives of the current study are to evaluate: (1) the effect of pH on the desorption of arsenite and arsenate from goethite by phosphate and oxalate, (2) the kinetics of arsenite and arsenate desorption by phosphate and oxalate in dark and light conditions, and (3) possible changes in As speciation that can occur as a result of extraction with phosphate, oxalate and HCI.

#### MATERIALS AND METHODS

Goethite was synthesized according to the procedure of Schwertmann and Cornell (1991) and examined using X-ray diffraction analysis.

#### Desorption of As from goethite by phosphate Effect of pH

A goethite suspension (2g L<sup>-1</sup>) was reacted with As(III) or As(V) at a concentration of 20 mmol/kg (0.04 mmol L<sup>-1</sup>) in a 0.1M NaCl ionic strength buffer for 24 h at pH 7. Subsamples, 20 mL each, were taken by syringe and placed in 40 mL reaction vessels and phosphate was added to obtain the desire ratio between As and P (1:100). To the vessels which did not receive phosphate, deionized water was added. The pH of these subsamples was adjusted to be in the range of 1 to 13, and the samples were shaken for 24 h, centrifuged for 30 min at 10000 rpm and filtered through 0.2 \( \text{Dm} \) membrane filters. Arsenic concentration was measured using the hydride generation technique. With arsenate, a similar experiment was conducted, using the same conditions as with arsenite.

### Kinetics of As desorption from goethite by phosphate

Arsenite at low coverage (20 mmol/kg = 0.04 mmol L<sup>-1</sup>) was equilibrated with a goethite suspension (2g L<sup>-1</sup>) in a 0.1 M NaCl ionic strength buffer. The pH was adjusted to 5, and the reactants were stirred continuously for 24 h. Subsamples of 20 mL each were taken and placed in a 40-mL vessels, phosphate solution was added to give a final concentration of 4 mmol L<sup>-1</sup>, pH was adjusted again to 5, samples were shaken for different intervals, centrifuged for 30 min, filtered, and the pH was adjusted to 7.0 and kept at low temperature (2 °C) until As determination. Similar experiments were conducted with arsenite at pH 9 and arsenate at pH 5 and 9.

# Arsenite and arsenate desorption from goethite by 0.1 M oxalic acid Effect of pH

Arsenite (0.04 mmol L<sup>-1</sup>) was reacted with goethite (2 g L<sup>-1</sup>) in 0.1 M NaCl ionic strength buffer, at pH 7 for 24 h. Ten milliliter aliquots from the arsenite/goethite suspension were transferred to 40-mL vessels, 10 mL of 0.2M oxalic acid was added, pH was adjusted to obtain a range of values from pH 1 to 12, the vessels were shaken in the dark for 24 h, the supernatant was centrifuged and filtered, and the pH of the filtrate was measured. Arsenite and arsenate were measured by pH-selective hydridegeneration/atomic-absorption spectroscopy. An analogous experiment was conducted in the light. With arsenate, two similar experiments were conducted, using the same conditions as with arsenite.

# Kinetics of As desorption from goethite surfaces using 0.1 M oxalic acid (pH 1) under the light

Kinetics of As(III) desorption and oxidation at pH 1 under laboratory light conditions was evaluated in the presence and absence of 0.1M oxalic acid. Arsenite and arsenate (0.04 mmol L<sup>-1</sup>) were equilibrated individually in goethite suspension (2g L<sup>-1</sup>) at pH 7 in a 700 mL reaction vessel for 24 h. Ten milliliter aliquots of arsenite/goethite suspension were pipetted into 40 mL reaction vessels, then 10 mL of 0.2 M oxalic acid or deionized water was added, and the pH was adjusted to 1 using HCl. Vessels were shaken for different times and filtered through 0.2 µm membrane filters. Both As(III) and As(V) were determined using a pH-selective hydride-generation atomicabsorption procedure. Kinetics of As desorption from goethite surfaces using 0.1 M oxalic acid (pH 1) under the dark condition was tested through an experiment similar to that conducted under the light. Similar experiments were conducted with arsenate, using the same conditions as with arsenite.

### Kinetics of As desorption from goethite surfaces using 2M HCI

Arsenite (0.04 mmol L<sup>-1</sup>) was reacted with goethite (2g L<sup>-1</sup>) in 0.1 M NaCl for 24 h at pH 7. To 150 mL of the As(III)/goethite suspension, 150 mL of 4M HCl was added and subsamples (10 mL each) were taken at different times and filtered. The concentrations of As(III) and As(V) in the filtrate were measured using the pH-selective hydride-generation atomic-absorption procedure. A parallel experiment was conducted using arsenate, under the same experimental conditions as with arsenite.

### Release and oxidation of arsenite from goethite by 6 M HCI

As (III) (0.04 mmol L<sup>-1</sup>) was reacted with goethite (2g L<sup>-1</sup>) in the dark at pH 7 for 24 h. Then 10 mL of 12 M HCl was added to 10 mL As(III)/goethite suspension in a 40 mL vessel, and the mixture was shaken in the dark or in the light for 2 or 12 h. Samples were filtered through 0.2  $\mu$ m membrane filter, and As(III) and As(V) were determined.

### RESULTS AND DISCUSSION

Effect of phosphate on As desorption

Arsenic was added to the goethite suspension at a low-coverage rate of 0.02 mmol g<sup>-1</sup> to ensure a complete adsorption on goethite surfaces.

Effect of pH.

In the absence of phosphate, As desorption was greatest at the pH extremes, e.g., pH 1 (28%) and pH 12.5 (35%) (Fig. 1). Between pH 4 and 9 arsenic desorption by water (without P) was negligible. In the presence of phosphate, with increasing pH the percentage of desorbed As decreased from 55% (pH 1) to 13% (pH 9), above which there was a dramatic increase in As desorption. But at all pH values, no more than approximately 55% of the original As (III) was desorbed.

Arsenate was adsorbed completely at pH <9 in the absence of phosphate (Fig. 2). Phosphate had the greatest affect on As(V) desorption at pH 1 (30%) and As desorption decreased with increasing the pH up to pH 9 (10%). Above pH 9, the desorption of As(V) increased to approximately 45% at pH 12.5 in presence of phosphate. At each pH, the amount of desorbed arsenate was less than the corresponding amount of desorbed arsenite, as described above. 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 (55%) was achieved with using phosphate and arsenite at pH 1. Yet the desorption of arsenite or arsenate by phosphate was not complete, such incomplete desorption may be a attributable to the formation of bionuclear adsorption complexes of As(III) and As (V) on goethite surfaces which restrict the rate of desorption (Sun and Doner ,1996, and Fendorf et al. ,1997).

Kinetics of As desorption by phosphate

Arsenite desorption at pH 5 increased sharply and reached its maximum (74%) after 5 h (Fig. 3). At pH 9 the desorption increased and reached the maximum (23%) after 10 h. Arsenite desorption at pH 5 was higher than that at pH 9. In case of arsenate (Fig. 4), desorption of As(V) increased gradually with increasing time of equilibrium (0-200 h), and the amount of As(V) desorbed at pH 5 was greater than that desorbed at pH 9. After 192 h of reaction, the desorption of arsenate at pH 5 and 9 were 55 and 35%, respectively. At pH 5 the amount of desorbed arsenite by phosphate was higher than that of arsenate during the reaction time (0-200h). This may be because As(III) does not sorb as strongly as As(V) at low As surface coverage (Pierce and Moore, 1982). Since As(III) is less strongly sorbed than As(V) to a variety of sorbents, arsenic is generally more mobile in arsenite than in arsenate.

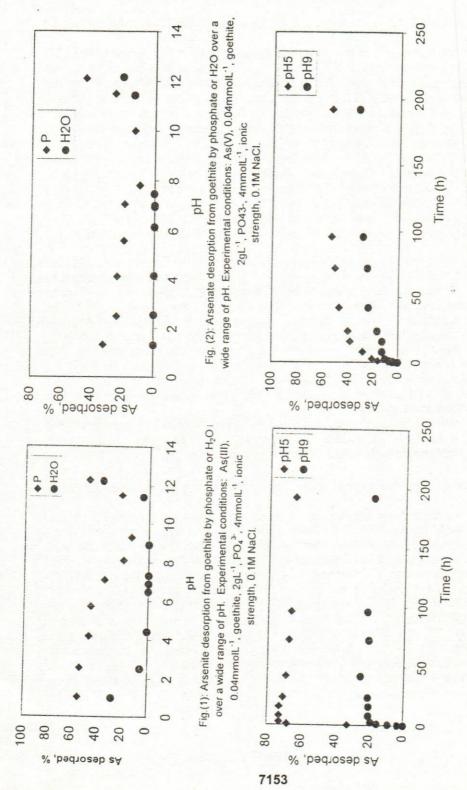


Fig.(4): Kinetics of arsenate desorption from goethite by phosphate. Experimental conditions: As(V), 0.04 mmolL<sup>-1</sup>, goethite, 2gL<sup>-1</sup>, PO43-, 4mmolL<sup>-1</sup>, ionic strength, 0.1M NaCl.

Fig. (3): Kinetics of As(III) desorption from goethite by phosphate. Experimental conditions: As(III), 0.04 mmolL<sup>-1</sup>, goethite, 2gL<sup>-1</sup>, PO43., 4mmolL<sup>-1</sup>, ionic strength, 0.1M NaCI

### Desorption Of As From Goethite Surfaces By 0.1m Oxalic Acideffect Of Ph

With reaction in the dark (Fig.5), As(V) desorption ranged from 23% (pH 1) to negligible (pH 5 to 9) to 18% (pH 11). Transformation to As(III) was negligible at all pH values. These results indicated that 0.1M oxalate was not an effective extractant of As(V) in the dark. It was proposed that the inhibition of reductive dissolution of iron oxides by binuclear complexes formed with oxyanions [As(V)] is due to the greater energy required to remove metal ions from the crystal lattice (Eick et al., 1999).

With reaction in the light (Fig. 6), almost 100% of the original As(V) was desorbed at pH <3; however, almost 10% of the As(V) was converted to As(III). Under these conditions of extraction, the goethite was almost totally dissolved. With increasing pH values, the As desorption decreased to 8% (pH 4) and negligible (pH 6 to 8), and then increased again to 10% (pH 10.5) and 85% (pH 11). Above pH 10, there was appreciable conversion of As(V) to As(III)

With reaction in the dark (Fig. 7) at pH 1.5, the desorbed As(III) was oxidized to As(V). While at pH 2 almost 50 % of liberated As(III) oxidized to As(V). These are very different results than those obtained with ferrihydrite (Jain and Loeppert, 2000), where As(III) was not converted to As(V) under similar conditions. These differences in result indicate that the goethite surface might have influenced the oxidation of As(III) to As(V) in the dark. This result agrees with the result of Sun and Doner (1998) in which goetite surface played an important role in As(III) oxidation. Oxidation of As(III) to As(V) was happened only at pH less than 3. The As(III) was not transformed to As(V) at pH 4, and with increasing pH from 4 to 9 the quantity of desorbed As(III) decreased sharply.

With reaction in the light (Fig. 8), there was total oxidation of the desorbed As(III) to As(V) over the pH range of 1.5-12. The release of As decreased from 84% (pH 1) to 8% (pH 4) to negligible (pH 5-10.5).

## Kinetics of As desorption from goethite surfaces by 0.1M oxalic acid (pH 1).

Kinetics of As(III) desorption and oxidation at pH 1 in the light were determined with and without 0.1M oxalic acid. In the presence of oxalate (Fig. 9), As(III) concentration decreased sharply with increasing time from 10 min to 5 h; however, a corresponding increase in As(V) concentration was observed with time. These trends are attributable to the role of oxalic acid in the reductive dissolution of goethite in the presence of light, which is accompanied by As(III) oxidation to As(V). After 24 h of the reaction 77% of As(III) was desorbed and totally oxidized to As(V). In the absence of oxalic acid (Fig. 10), the release of As(III) was high initially during the period of dissolution of the Fe oxide, but then the desorbed As concentration decreased as the dissolution of oxide ceased and the As(III) was readsorbed. In the absence of oxalic acid, there was no evidence of oxidation of As(III) to As(V).

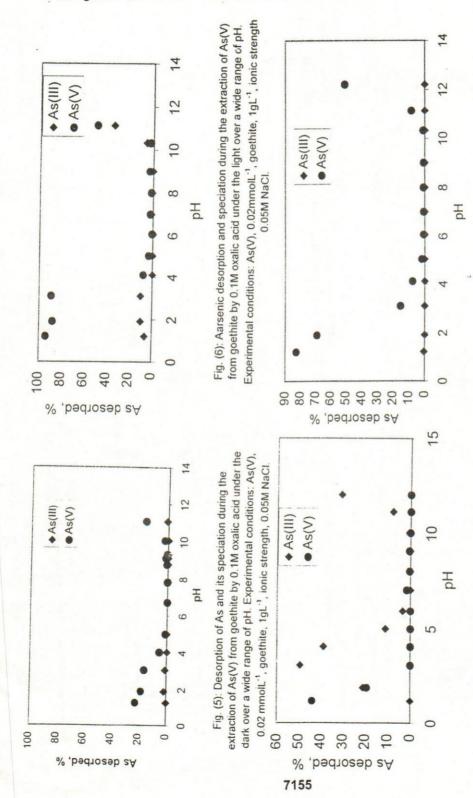
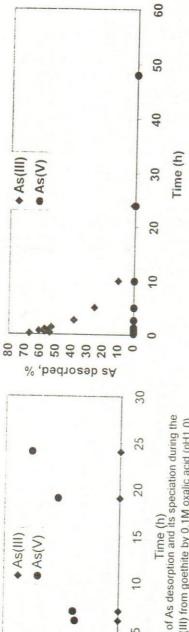


Fig.(8): Arsenic desorption and its speciation during the extraction of As(III) from goethite by 0.1M oxalic acid under the light over a wide range of pH. Experimental conditions: As(III), 0.02 mmolL<sup>-1</sup>, goethite, 1gL<sup>-1</sup>, and ionic strength, 0.05M NaCI.

Fig. (7): As desorption and its speciation during the extraction of As(III) from goethite with 0.1M oxalic acid under the dark over a wide range of pH. Experimental conditions: As(III), 0.02 mmolL<sup>-1</sup>, goethite, 1gL<sup>-1</sup>, ionic strength, 0.05M NaCI.

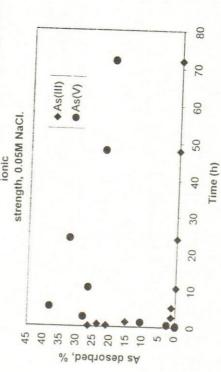


100 80 09 40 20

As desorbed, %

Fig. (9): Kinetics of As desorption and its' speciation during the under the light. Experimental conditions: As(III), 0.02mmolL-1, extraction of As(III) from goethite by 0.1M oxalic acid (pH1.0) goethite, 1gL-1, ionic

strength, 0.05M NaCl.



**♦** As(III) As(V)

1.0)under the light. Experimentalconditions: As(V), 0.02mmolL<sup>-1</sup>, goethite,1gL<sup>-1</sup>, and ionic strength, 0.05M NaCI.

30

20

10

20

30

As desorbed,

0

10

Time (h) 15

Fig.( 12 ): Kinetics of As desorption and its speciation during the extraction of

As(III) from goethite with 2M HCI. Experimental conditions: As(III), 0.02mmolL<sup>-1</sup>, goethite, 1gL<sup>-1</sup>, and ionic strength, 0.05 M NaCl.

Fig. (11). Kinetics of As desorption and its speciation during the extraction of As(V) from goethite by 0.1M oxalic acid (pH

00 06 80 70 09 50 40

Experimental conditions: As(III), 0.02mmol L-1, goethite, 1g L-1, and

extraction of As(III) from goethite with HCI (pH 1.0) under the light. Fig. (10): Kinetics of As desorption and its speciation during the

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Arsenate desorption from goethite surfaces by 0.1M oxalic acid (pH 1) under the light is shown in Fig. (11). The release of As(V) was increased sharply and reached the maximum (90%) at 6 h. Increasing time over 6 h did not increase the released As(V). There was no evidence of reduction of As(V) to As(III).

Kinetics of As desorption from goethite surfaces by 2 M HCI

In the case of arsenite, appreciable As(III) was released to the solution, particularly in the first hour (Fig. 12). The concentrations of As(III) decreased sharply with increasing time of desorption. The decrease in As(III) concentration was accompanied with an increase in As(V) concentration, indicating the transformation of As(III) to As(V) in the light under these acidic conditions. The gradual decrease in total dissolved As with time indicates the gradual readsorption of the initially desorbed As.

In the case of arsenate (Fig. 13), As (V) concentration in the equilibrium solution increased sharply in the first 40 min. and gradually with increasing time of desorption over 40 min. The rate of release and amount of desorbed As from the solid phase in case of As(III) were higher than in the corresponding case with As(V). This result could be partially attributed to the

negative effect of As(V) on goethite dissolution.

Release and oxidation of As(III) from goethite surfaces by 6 M HCI

With 2h reaction in the light and dark (Fig.14), 80 % of adsorbed As(III) was released as a result of reductive dissolution of solid phase, and the oxidation of As(III) to As(V) was higher in case of light as compared with the dark. In case of light about 48 % of the released As was oxidized to As(V). However, in case of dark 39 % of released As was converted to As(V). With 12 h reaction in the light approximately 90 % of adsorbed As (III) was released and totally oxidized to As(V). With reaction in the dark for 12 h, As release approached completion, but approximately 40 % of the As(III) was converted to As(V).

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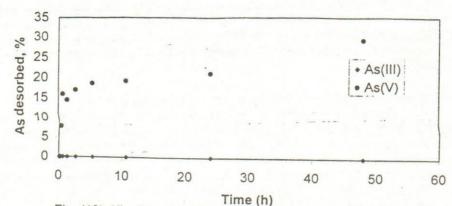


Fig. (13): Kinetics of As desorption and speciation during the extraction of As(V) from goethite by 2M HCl under the light. Experimental conditions: As(V), 0.02mmol L<sup>-1</sup>, goethite, 1gL<sup>-1</sup>, ionic strength, 0.05 M NaCl.

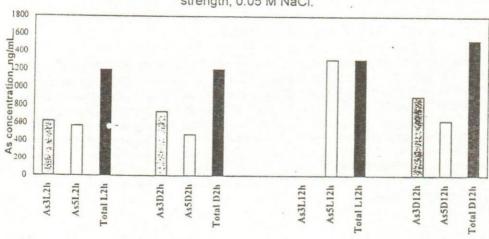


Fig. (14): Arsenite release and oxidation during the extraction with 6 M HCI after 2 and 12 h under the light and dark conditions. Experimental conditions:As(III), 0.02 mmolL<sup>-1</sup>, goethite, 1gL<sup>-1</sup> ionic strength, 0.05M NaCI.

### CONCLUSIONS

Desorption of As(III) and As(V) by phosphate was highly dependent on pH, it increases mostly at pH <10 and decreases at pH >10. In the cases of both As(III) and As(V), desorption was at the maximum at low and high pH values, but in no case achieved greater than 60% of the initially adsorbed As. Minimum desorption was observed at approximately pH 9-10 (arsenite) and pH 8 (arsenate). Arsenite desorption at pH 5 and 9 increased sharply and reached its maximum within 10 h. In case of arsenate, the desorption increased gradually with increasing reaction time up to 200 h. The amount of As(V) desorbed at pH 5 (55%) was greater than that desorbed at pH 9 (35%). In general, 0.1M oxalate was not effective in desorbing arsenate at pH 4-10 and the extracted quantities are less than the corresponding quantities with phosphate. Arsenic speciation after the release of As(III) from goethite by 6M HCI was affected greatly by the reaction time and the exposure to light. As(III) was readily transformed to As(V) in the light in both oxalic acid and 2-6 M HCI. In the dark, oxidation of As(III) to As(V) was reduced but not totally eliminated.

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حركية عكس الإدمصاص للزرنيخايت والزرنيخات من الجوثايت. على أحمد عبدالحليم\*، ر.ه. . لوبرت\*\* و ل.ر.هوسنر \*\*
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الزرنيخ عنصر سام يمكن تواجده في البيئة كنتيجة للعمليات الطبيعية أو للنشاط الإنساني وتراكم الزرنيخايت والزرنيخات في التربة والرواسب يهدد صحة النبات والحياة البريــة وحيــاة الإنسان ويمكن أن يلعب الجوثايت (أكسيد حديديك مراهد) دورا هاما في التحكم في تركيز وذوبان الزرنيخ في الماء وذلك بتكوين معقدات سطحية داخلية مع الزرنيخايت والزرنيخات، والاستخلاص بواسطة الفوسفات والأوكسالات وكذلك حمض الهيدروكلوريك قد اقترح كاجراء لتقييم الكمية المستخلصة وكذلك صور الزرنيخ ولكن عكس الإدمصاص ليس دائما كاملاً. تم اتزان الزرنيخايت والزرنيخات مع الجوثايت عند تركيز أولى منخفض ( ٠,٠٢ مــول / كجم جوثايت ) وتم الإستخلاص بواسطة الفوسفات الذي أخسيف بنسبة ١٠٠ فوسفات : ١ زرنيخ وكذلك بواسطة ٠,١ مولر أوكسالات عند رقم حموضة يتــراوح مــابين ١٣ ١ ولقــد وجــد أن الفوسفات حررت من ١٠-٥٠% من الزرنيخايت المدمصة وكانت أكبر كمية للزرنيخ المتحررة عند PH ٤. وعند نفس النسبة بين الفوسفات والزرنيخ استخلص الفوسفات من ١٠-٣٠% من الزرنيخات المدمصة مع أقصى استخلاص عند PH. وجد أن عكس الإدمصاص للزرنيخايت بواسطة الفوسفات عند pH ٥ كان أسرع منه عند pH ٩ ووصل الى أقصاه بعد خمس ساعات، بينما عكس ادمصاص (تحرر) الزرنيخات كان بطيئا واستمر ٢٠٠ ساعة من بدايــة التفاعــل وكانت الأوكسالات ( ٠,١ مولر ) قادرة على استخلاص من ١-٢٢ % من الزرنيخات المدمصة عند pH أقل من ٥ في الظلام ومع التعرض للضوء ١٠٠٠% مـن الزرنيخـات المدمصـة قـد استخلص عند pH أقل من ٣ وهذا يعزي الى انحلال الطور الصلب للجوثايت الناتج عن تأثير الضوء. عند pH أقل من ٤ وأكبر من ١٠ وجد أن جزء صغير من الزرنيخات قد اختــزل الــي الزرنيخايت خلال التفاعل مع الأوكسالات.

تأثرت صور الزرنيخ بعد تحرر الزرنيخايت من الجوثايت بواسطة حمض الهيدروكلوريك ٦ مولر بزمن التفاعل والتعرض للضوء، وتحولت الزرنيخايت الي زرنيخات في الضوء مع كل من حمض الأوكساليك ٠٠١ مولر وحمض الهيدروكلوريك ٢-٦ مولر .تناقصت أكسدة الزرنيخايت الي زرنيخات في الظلام ولكنها لم تستبعد كلية .