

Combined Effect of Arsenic and Cadmium on the Transformation of Ferrihydrite into Crystalline Products

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Abstract: Ferrihydrite, prepared in the presence of different amount of As and Cd in the solution, was used to study the combined effect of As and Cd coexisted in the same system on the transformation of ferrihydrite into crystalline products at pH 8 and pH 12. The data showed that there was apparent interaction between As and Cd in the transformation process. At pH 8, the transformation product was hematite with 1% As and different percent Cd (mole fraction, so as the follows), but the size of particles formed with different amount of Cd was different. At pH 12, the transformation products varied from sole hematite with 1% As and less than 2% Cd to a mixture of hematite and goethite with more than and equal to 2% Cd, and the percentage of goethite in the transformation products increased with the increasing level of Cd in the system. XRD (X-ray diffraction) and chemical analysis data showed that almost all As and part of Cd initially present in the system were retained in the crystalline products. The presence of As increased the amount of Cd retained in the structure of iron oxide. SEM (Scanning Electron Microscope) examination showed that the presence of As and Cd also altered the morphology of crystalline products.

Key words: ferrihydrite; arsenic; cadmium; transformation; crystallization

Most metals such as cadmium, lead, copper, iron, nickel, chromium, zinc, and metalloids such as arsenic are harmful to many components of the ecosystem including zooplankton, phytoplankton even fish and mammals with high enough concentrations. Most mine effluents and industrial wastewater contain these metals and metalloids, the concentrations of them in wastewater have to be reduced to an acceptable level before being discharged to avoid environmental problems. Among various methods to control the concentrations of metals and metalloids, chemical precipitation reactions associated with coagulation-flocculation processes in engineering treatment system can decrease their concentrations to an adequate level [1]. In the coagulation-flocculation process for water treatment using iron salts, non-crystalline iron (III) hydroxide is precipitated from solution to remove contaminant elements by the mechanism of adsorption and coprecipitation. As a result of these treatment processes, chemical sludge is produced. The sludge has to be disposed properly to avoid secondary pollution. The landfill, which is the most widely proposed method for disposing this chemical sludge, is not sufficiently stable. Thus it is essential that the mechanisms which control the leaching behavior of metals and metalloids from water treatment sludge be understood so that the long-term environmental management of these waste solids be accom-

ished.

The solid formed during the precipitation-flocculation using iron salts is non-crystalline iron (III) hydroxide which usually known as ferrihydrite. It, with time, will transform into more crystalline products, usually including goethite and/or hematite through different mechanisms. That which transformation product predominates depends mainly on the pH of the system [2, 3]. Foreign ions also influence the nature of the transformation products and modify the crystal morphology. The effects of some ions on this process have been investigated. The organic ions include hydroxyl-carboxylic acids [4], sugars [5], humic acid [6], and cysteine [7]. The inorganic ions include Al [8], Mn [9], Si [10], Cu [11], Co [12], Zn [13], As [14] and Cd [15, 16]. Most ions investigated retard the transformation and suppress the formation of goethite in the transformation products. Most inorganic ions replace a proportion of Fe in the oxide structure.

Previous investigations focused on the effects of single foreign ion, but the effect of the coexistence of more than one ion should be more complicated and more relevant to nature system. There may also be interaction among ions when they coexist in the same system. The objective of this study is to investigate the combined effect of As and Cd coexisted in the same

system on the transformation of ferrihydrite into crystalline products at pH 8 and pH 12, at 70 °C.

1 Experiment Methods

All the chemicals used were AR (Merck). The solutions were prepared using Milli-Q water. The ferrihydrite was precipitated by slowly pumping 150 mL solutions of mixture of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 0.4 mol in total Fe, into 350 mL solutions of 0.6 mol NaOH containing different amount of dissolved $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ while vigorously stirring. The original solution compositions were chosen to give Cd/(Cd+Fe+As) and As/(Cd+Fe+As) in mole fractions 1% and/or 9%. After the mixing was completed, the pH of the suspensions was adjusted to 8 or 12 by means of 1 mol HNO_3 . The suspensions were held in closed polypropylene bottles of 500 mL in volume and the bottles were put into an oven at 70 °C for 28 day transformation. The bottles were shaken by hand every day.

After 28 days, the suspensions were filtered under vacuum using 0.45 μm millipore nylon filter media. The retained solids were extracted by shaking for 30 min with 0.4 mol HCl; at a solid/solution ratio of 0.1 g solid per 100 mL to remove untransformed ferrihydrite [5]. The solids from this extraction were dried at 50 °C. X-ray diffraction (XRD) patterns were obtained using a Nicolet Diffractometer with $\text{CuK}\alpha$ radiation. The proportions of goethite and hematite in the crystalline products were estimated by comparison with a series of standards made by mixing known amounts of synthetic goethite and hematite. The ratio of the height of 110 peak of goethite to the sum of the height of 104 peak of hematite and the height of 130 peak of goethite was used for this estimation.

The adsorbed and coprecipitated As and Cd in the flocs were determined by analyzing the residue content of As and Cd in the filtrate using ICAP/AES Spectrophotometer. The percentage of adsorbed and coprecipitated As and Cd is expressed as $(x(\text{As}_s) - x(\text{As}_r)) / x(\text{As}_s)$ and $(x(\text{Cd}_s) - x(\text{Cd}_r)) / x(\text{Cd}_s)$, where $x(\text{As}_s)$ and $x(\text{Cd}_s)$ were the concentration (mg/L) of As and Cd added originally and $x(\text{As}_r)$ and $x(\text{Cd}_r)$ were the residue concentration (mg/L) of As and Cd in the filtrate. The extent of transformation was expressed as the ratio $x(\text{Fe}_s) / x(\text{Fe}_t)$, where $x(\text{Fe}_s)$ is the 0.4 mol HCl soluble iron and $x(\text{Fe}_t)$ is the total iron in a sample. The degrees of As and Cd retained in the crystalline products were expressed as $n(\text{As}) / ((n(\text{As}) + n(\text{Cd}) + n(\text{Fe})))$ and $n(\text{Cd}) / ((n(\text{As}) + n(\text{Cd}) + n(\text{Fe})))$ respectively, where $n(\text{As})$, $n(\text{Cd})$, and $n(\text{Fe})$ were the mole numbers of As, Cd, and Fe in the crystalline products. The total amount of Cd and Fe in the crystalline products was measured by

ICAP/AES Spectrophotometer after dissolving the crystalline product in 12 mol HCl. The total amount of As was measured by using Neutron Activation Analysis (NAA).

The Scanning Electron Microphotographs (SEM) of crystalline products were obtained using a Philips 515 Scanning Electron Microscope operating at 20.0 kV. For SEM examination the samples were dehydrated at 110 °C for 2 h, and after that the samples were dispersed in pure methanol with ultrasonic treatment and finally were filtered with 0.1 nuclepore filter and coated with Pt.

2 Results and Discussions

2.1 Adsorption and coprecipitation of arsenic and cadmium

The results of adsorption and coprecipitation of As and Cd by ferrihydrite at pH 8 and pH 12 with different amount of As and Cd initially in the system was shown in table 1.

Table 1 Percentage of adsorbed and coprecipitated As and Cd by ferrihydrite at different pH and initial amount of As and Cd

pH	Initial amount (mole fraction) %		Adsorbed and coprecipitated %	
	As	Cd	As	Cd
8	1	1	100.0	100.0
	1	9	100.0	100.0
	9	1	99.9	100.0
	9	9	99.9	100.0
12	1	1	91.3	100.0
	1	9	97.8	100.0
	9	1	56.9	88.2
	9	9	66.7	96.8

The data showed that all As and Cd added was adsorbed or coprecipitated at pH 8, almost independent of initial amount of As and Cd in the range investigated. But at pH 12, the uptake of As and Cd by ferrihydrite was dependent on the amount of As and Cd in the system. When 1 % As (mole fraction, so as the follows) was initially present in the system, all Cd added was taken up by ferrihydrite, but the percentage of As taken by ferrihydrite varied from 91.3% to 97.8% with 1% and 9% Cd respectively initially in the system. When 9% As was present, the uptake of As and Cd by ferrihydrite decreased. When 1% Cd was present in the system, 56.9% As and 88.2% Cd initially present were taken up. When 9% Cd was present, 97.8% Cd and 66.7% As were taken up. This showed that there was an interaction between As and Cd in the uptake by ferrihydrite at pH 12. The percentage of As taken up by ferrihydrite

increased with increasing the level of Cd in the system, while the percentage of Cd taken up decreased with increasing the level of As in the system.

Matthew [17] and Belzile [18] have studied the adsorption of arsenate on ferrihydrite and found that the amount of arsenate taken up by ferrihydrite decreases continually with increasing the pH and concentrations of arsenate. The same law was found in our investigation. But the presence of Cd increased the uptake of As at pH 12. This may be because the presence of Cd altered the surface properties of particles of ferrihydrite and made it absorb more As.

2.2 Transformation products

The percentage of Fe transformed into crystalline products and transformation products after 28 day transformation at 70 °C was shown in **table 2**. The percentage of transformed Fe and transformation products depends on the pH values and the amount of As and Cd initially present in the system.

Table 2 Transformation products at different pH values and different amount of As and Cd after 28 day transformation

pH	Initial amount (mole fraction) / %		Transformed iron / %	Transformation products
	As	Cd		
8	1	1	99.0	Hematite
	1	9	93.0	Hematite
	9	1	<1.0	Amorphous
	9	9	<1.0	Amorphous
12	1	1	100.0	Hematite
	1	9	84.0	Hematite+goethite
	9	1	<1.0	Amorphous
	9	9	<1.0	Amorphous

At pH 8, with 9% As in the system, the transformation products remained amorphous, but with 1% As, the transformation product was sole hematite. The percentage of transformed Fe varied with the amount of Cd in the system, from 99.0% with 1% Cd to 93% with 9% Cd. Ferrihydrite transformed into a mixture of goethite and hematite at pH 8 if no foreign ions exist in the system [3, 16]. The research work has proved that the presence of Cd suppressed the formation of goethite at pH 8, but with 1% Cd, the formation of goethite can not be suppressed completely [16]. In this study the formation of goethite is suppressed completely with 1% Cd and 1% As in the system. This means that the presence of As also suppresses the formation of goethite at pH 8.

At pH 12, the transformation products remained

amorphous with 9% As in the system. When 1% As was present in the system, the transformation products depended on the amount of Cd present in the system. Only hematite was formed with 1% Cd initially present, but a mixture of hematite and goethite was formed with 9% Cd. This seemed to mean that the presence of Cd increased the formation of goethite at pH 12. In order to investigate the detail effect of Cd, the experiments with different amount of Cd while the amount of As in the system kept a constant at 1% were carried out at pH 12. The results were shown in **table 3**. The data

Table 3 The transformation products with different amount of Cd present at pH 12 after 28 day transformation

Initial amount (mole fraction) / %		Transformed iron / %	Transformation products
As	Cd		
1	0	100.0	Hematite
1	1	100.0	Hematite
1	2	100.0	Hematite
1	4	99.0	Hematite+goethite (15%)
1	6	98.0	Hematite+goethite (45%)
1	9	84.0	Hematite+goethite (65%)

showed that the compositions of transformation products varied with the amount of Cd present in the system. The transformation products were mainly hematite when less than or equal to 2% Cd, but a few rods like goethite particles can be seen in SEM photograph. The percentage of goethite in transformation products increased with the increasing level of Cd in the system. When 9% Cd was present, a mixture containing 65% goethite was formed. This proved that the presence of Cd decreased the suppressing effect of As on the formation of goethite at pH 12. The data in table 3 also showed that the increasing level of Cd present in the system also retarded the transformation process.

The formation of goethite or hematite from ferrihydrite is believed to be through different mechanisms. The formation of hematite includes aggregation and rearrangement of ferrihydrite; the formation of goethite includes dissolution and reprecipitation of iron oxide in the solution [2]. The presence of As in the system suppresses the formation of goethite by hindering the dissolution of ferrihydrite. The mechanism is believed to be similar to that of hydroxy-carboxylic acids in which the ferrihydrite is stabilized by linking of two or more units of ferrihydrite per anion and a network of particles resisted to both aggregation and dissolution is formed [14]. The research work has proved that the presence of Cd does not suppress the formation of goethite at pH 12 [13]. In this study the coexistence of Cd with

As in the system decreased the suppressing effect of As on the formation of goethite. This may be because that the presence of Cd reduced the ability of As linking the ferrihydrite particles and made the dissolution of ferrihydrite possible, so goethite was able to form. The more Cd was present in the system, the weaker was the ability of As linking ferrihydrite particles.

2.3 Retaining of arsenic and cadmium in crystalline products

The chemical analysis of crystalline products showed that both As and Cd were retained in them. The results were shown in **table 4**. The data showed that only part of Cd initially present was retained in the crystalline products, more Cd was retained at pH 12 than at pH 8. With 1% Cd initially present in the system, the mole fraction of Cd in crystalline product was only 0.43% at pH 8, but this value increased to 0.53% at pH 12. With 9% Cd, the content of Cd in the crystalline products increased from 2.09% at pH 8 to 4.43% at pH 12. This proved that Cd was more easily retained at pH 12 than at pH 8.

Table 4 The content of As and Cd remained in the crystals with different amount of As and Cd initially in the system and at different pH values

pH	Initial amount (mole fraction) / %		Mole fraction in the crystals / %	
	As	Cd	As	Cd
8	1	1	1.02	0.43
	1	9	1.08	2.09
	1	0	0.91	0.00
	1	1	1.03	0.53
12	1	2	0.98	1.39
	1	4	1.05	3.37
	1	6	1.05	4.23
	1	9	1.04	4.43

The data also showed that almost all As initially present was retained in the crystalline products independent of pH values. Some researchers [14, 18, 19] have studied the adsorption of arsenate on ferrihydrite and found that it is difficult to evince that arsenic was incorporated into the structure of ferrihydrite. Only Fox [20, 21] proposed that dissolved arsenate and phosphate concentrations in surface waters are controlled by the formation of a solid solution with ferric arsenate or phosphate and ferrihydrite as end member phase. The experimental results presented here suggested that the solid solution containing As and Cd is formed. Both As and Cd was incorporated in the structure of iron oxide because XRD examination of crystalline products showed no other phases than hematite and goethite in the

transformation products. How arsenic was retained in the crystalline products was not very clear because As and Cd were retained at the same time in most crystalline products. Cd can be retained in the structure of goethite or hematite had been proved [16]. There might be interactions between As and Cd and the presence of Cd made As be retained in the crystalline products more easily in some way.

2.4 Morphology of transformation products

SEM of the transformation products formed at different pH values and with different amount of As and Cd initially present was shown in **figure 1**. The pH values at which the transformation was carried out and the amount of As and Cd in the system influenced the compositions of the transformation products, the shape and the size of crystalline particles.

(1) The effect of pH values.

When 1% As and 1% Cd were present in the system, the transformation product was only hematite. The shape of particle of hematite crystals was long ellipsoidal with a length of about 0.5 μm at pH 8 (figure 1 (a)). But thicker and more ellipsoidal particles were formed at pH 12 (figure 1 (d)). The thickness of particles formed at pH 12 was as about twice as that of particles formed at pH 8. This suggested that the conditions at pH 12 were more favorable for the growth of hematite than that at pH 8 when low level of As and Cd was present in the system.

When 1% As and 9% As were present in the system, the different transformation products were formed at different pH values. Only hematite was formed at pH 8 (figure 1 (b)), but a mixture of hematite and goethite with 65% goethite was formed at pH 12 (figure 1 (h)). The shape of hematite crystals was also altered, from about 0.1 μm ellipsoidal particles formed at pH 8 (figure 1 (b)) to about 0.1 μm hexagonal ones formed at pH 12 (figure 1 (h)). The shape of particles of goethite was rod-like crystal with a length of about 1 μm .

(2) Effect of the amount of As and Cd in the system.

The different transformation products were formed with 1% As and different amount of Cd in the system. The transformation product was only hematite with different amount of Cd at pH 8, but the size of particles was different. The length of ellipsoidal particles formed with 1% Cd (figure 1 (a)) was as about five times as that of particles formed with 9% Cd (figure 1 (b)). This showed that the presence of Cd interfered with the growth of hematite crystals at pH 8. At pH 12, the presence of different amount of Cd altered the compositions and shape of particles of the transformation pro-

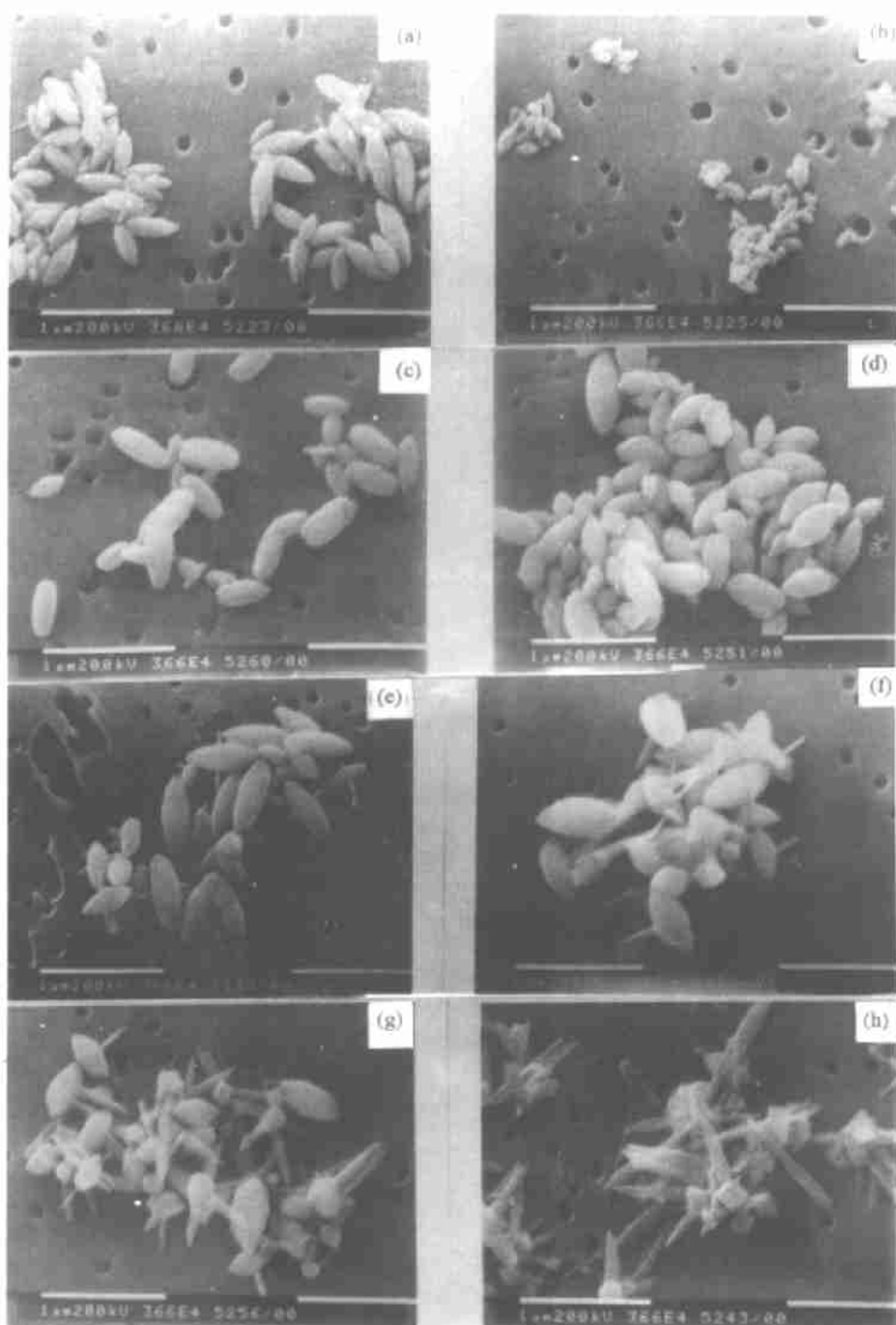


Figure 1 Scanning electron micrographs of transformation products with different As and Cd initially present in the system and at different pH values. The transformation period was 28 days at 70 °C. A 30 min extraction with 0.4 mol HCl was used to remove the amorphous material. The rod-like particles were goethite and other particles were hematite.

(a) 1% As and 1% Cd present at pH 8, product was: hematite; (b) 1% As and 9% Cd present at pH 8, product was: hematite; (c) 1% As and 0% Cd present at pH 12, product was: hematite; (d) 1% As and 1% Cd present at pH 12, product was: hematite; (e) 1% As and 2% Cd present at pH 12, product was: hematite and a little goethite; (f) 1% As and 4% Cd present at pH 12, product was: hematite 85%, goethite 15%; (g) 1% As and 6% Cd present at pH 12, product was: hematite 55%, goethite 45%; (h) 1% As and 9% Cd present at pH 12, product was: hematite 35%, goethite 65%.

ducts. When Cd was absent in the system, only hematite was formed (figure 1 (c)). When 1% Cd was present, some ellipsoidal particles were formed (figure 1 (d)). A few thin rod-like goethite particles were formed

when 2% Cd was present in the system, but the amount of goethite must be less than 5% because it could not be detected by XRD. The compositions and the shape of particles of the transformation products kept changing

continually with the increasing level of Cd in the system. Some hexagonal particles of hematite were formed when 4% Cd was present in the system (figure 1 (f)). When 9% Cd was present, only small hexagonal hematite particles (about 0.1–0.2 μm) were formed and no ellipsoidal particles were found (figure 1 (h)). The amount of goethite increased from less than 5% with 2% Cd to 65% with 9% Cd (figure 1 (h)). The particle size of goethite also increased with increasing level of Cd in the system. This showed again that the presence of Cd in the system was favorable for the formation of goethite.

3 Conclusions

(1) The presence of As and Cd strongly retarded the transformation of ferrihydrite into crystalline products at pH 8 and pH 12 at 70 °C, and there were interactions between As and Cd in their effects on the transformation of ferrihydrite and the transformation products. The retarding effect of As was much stronger than that of Cd. No transformation takes place after 28 days transformation when 9% As was initially present in the system.

(2) The presence of 1% As suppressed the formation of goethite at both pH 8 and pH 12 leading to a transformation product consisting of only hematite. The presence of different amount of Cd with As in the same system did not affect the composition of the transformation products but affected the size of the transformation products at pH 8. The presence of different amount of Cd with As lead to the formation of goethite and the amount of goethite in the transformation products varied from less than 5% with 2% Cd to 65% with 9% Cd at pH 12.

(3) The chemical analysis and XRD examination data showed that almost all As added in this research is retained in the crystalline products, but only part of Cd added was retained. More Cd is retained at pH 12 than at pH 8.

(4) The presence of As and Cd also altered the morphology of crystalline products. The particle size of hematite formed with 1% As and 1% Cd was much bigger

than that of hematite formed with 1% As and 9% Cd at pH 8. The shape of hematite altered from ellipsoidal particles with low level of Cd present to hexagonal ones with high level of Cd, the size of them also decreased. The particle size of goethite increased with increasing the level of Cd in the system.

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