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# **Biomimetic and Bio-Inspired Catalytic System for Arsenic Detoxification: Bio-Inspired Catalysts with Vitamin-B<sub>12</sub> Cofactor**

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## **1. Introduction**

The developments in science and technology in the twenty-first century are required to be environment-friendly. Therefore, the new fields of biomimetic chemistry or bio-inspired chemistry are expected to receive considerable attention, since scientific and technological developments based on biomimetic or bio-inspired chemistry will be environment-friendly. The reactions occurring in living organisms are highly efficient and do not cause any wastage. The development of processes that mimic biological processes has been termed biomimetics. Biomimetics involves a wide range of studies including the development of new materials and new reactions based on self-assembly or molecular recognition. Biomimetic chemistry is a new field of chemistry aimed at realizing the excellent functions such as self-assembly or molecular recognition of living organisms by utilizing an artificial substance or a combination of artificial substances. For mimicking highly selective biological reactions that proceed under mild conditions in a flask, mimicking the action of enzymes is one of the most important objectives.

Bio-inspired chemistry is a field of chemistry that is aimed at creating materials that mimic biological systems such as biological molecules, cells, or their assemblies, and formulating new ideas using these materials. The methods based on bio-inspired chemistry are superior to the hitherto known methods of material development that involved studying and mimicking certain biological functions, and therefore, it is expected that novel materials will be synthesized by employing the methods based on bio-inspired chemistry. By adopting the functional expressions in biological systems and the concepts of material science, research in the field of bio-inspired chemistry aims to realize technologies that will have a wider range of applications than the biological functions. It is expected that novel technology based on biomimetic chemistry or bio-inspired chemistry will be human- and environment-friendly. In this study, we have developed a novel detoxification process to remove inorganic arsenic. This process involves converting arsenic into nontoxic arsenobetaine by methylation; a bio-inspired catalyst that is a vitamin-B<sub>12</sub> derivative was used to carry out the methylation, depending on the intended meaning.

## 2. Arsenic detoxification

### 2.1 Toxicity of arsenic compounds

Inorganic arsenic compounds are carcinogenic and are acutely and chronically toxic. Arsenic is widely distributed in the natural environment (Nickson, 1998), and it is expected to have an adverse impact on humans and the environment. According to the results of a survey, many people in the world (mainly in Asia) are suffering from poisoning due to naturally occurring arsenic, e.g., arsenic found in ground water (Chowdhury, 1999; Sun, 2004).

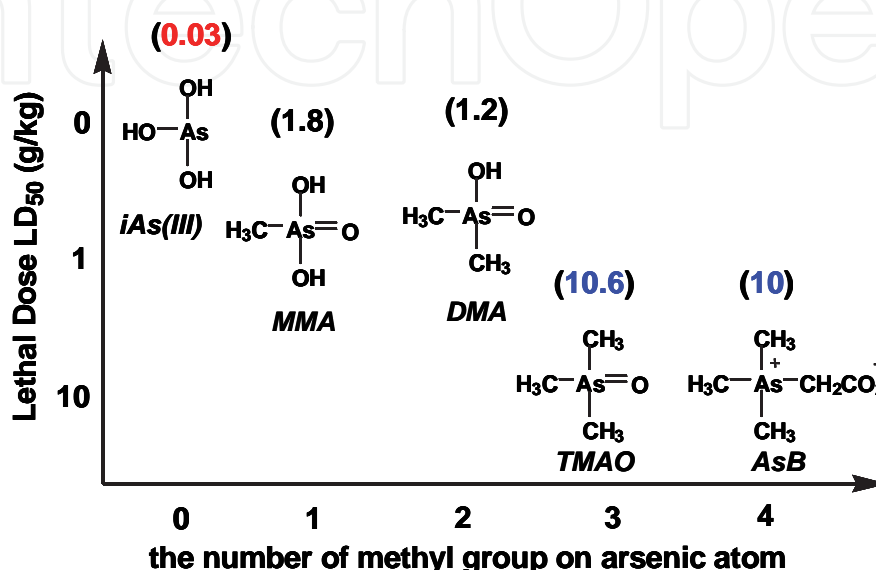


Fig. 1. The toxicity of arsenic compounds and their chemical structure. iAs(III): arsenite, MMA: methylarsonate, DMA: dimethylarsinate, TMAO: trimethylarsine oxide, AsB: arsenobetaine.

The toxicity of arsenic compounds is strongly dependent on their oxidative states and chemical structures. In the case of heavy metals such as mercury and lead, organic metal compounds such as methyl mercury and alkyl lead compounds are known to be more toxic than their corresponding inorganic counterparts (Craig, 2003). However, arsenic compounds are an exception: organic arsenic compounds are generally less toxic than their inorganic counterparts (Fig. 1). In particular, the acute toxicity of the trimethylarsenic compound arsenobetaine [AB,  $\text{Me}_3\text{As}^+\text{CH}_2\text{CO}_2^-$ ; (trimethylarsonio) acetate; Mouse oral LD<sub>50</sub>, 10 g kg<sup>-1</sup>] is about 1/300 of that of trivalent inorganic arsenic compound arsenite [iAs(III), arsenic trioxide,  $\text{As}_2\text{O}_3$ ; Mouse oral LD<sub>50</sub>, 0.03 g kg<sup>-1</sup>] (Kaise, 1985).

A substantial amount of arsenobetaine exists in fish and shellfish, and it is stable under normal conditions. It is internationally recognized to be a nontoxic, naturally occurring arsenic compound as it has low affinity for body tissues and is excreted rapidly from the body when ingested (Vahter, 1983).

### 2.2 Biological system

In the marine ecosystem, inorganic arsenic is biologically methylated and is concentrated as arsenobetaine in fish and shellfish via the food chain. This biological methylation is said to proceed in a stepwise manner: the pentavalent arsenic compound [As(V)] is first reduced by a reducing enzyme to the trivalent arsenic compound [As(III)], which then undergoes

oxidative methylation by a methyltransferase (via an alternate reaction, Fig. 2, Challenger, 1945, Edmonds & Francesconi, 1987; Edmonds, 2000).

### 2.3 Enzymatic system

It has been reported that many enzymes are involved in the conversion of inorganic arsenic compounds to arsenobetaine (Thomas et al., 2004); however, enzymes that are directly involved in the biosynthesis of arsenobetaine have not been isolated (Edmonds & Francesconi, 1981) (Fig. 2).

### 2.4 Non-enzymatic system

S-adenosylmethionine (SAM) and methylcobalamin (CH<sub>3</sub>B<sub>12</sub>), a derivative of vitamin B<sub>12</sub>, have been previously proposed as coenzymes of methyltransferase for the methylation of arsenic compounds. In addition, reduced glutathione (GSH) is proposed as the coenzyme of the reducing enzyme. The methylation of inorganic arsenic using GSH and SAM as a methyl donor can only be accomplished in the presence of an enzyme extracted from biological sources. In contrast, when methylcobalamin is used as the methyl donor, the methylation of inorganic arsenic in the presence of GSH can be accomplished even when an apoenzyme is absent. Thus, the methylation of arsenic with methylcobalamin as the methyl donor can be carried out using fewer and more readily available compounds than the methylation with SAM as the methyl donor.

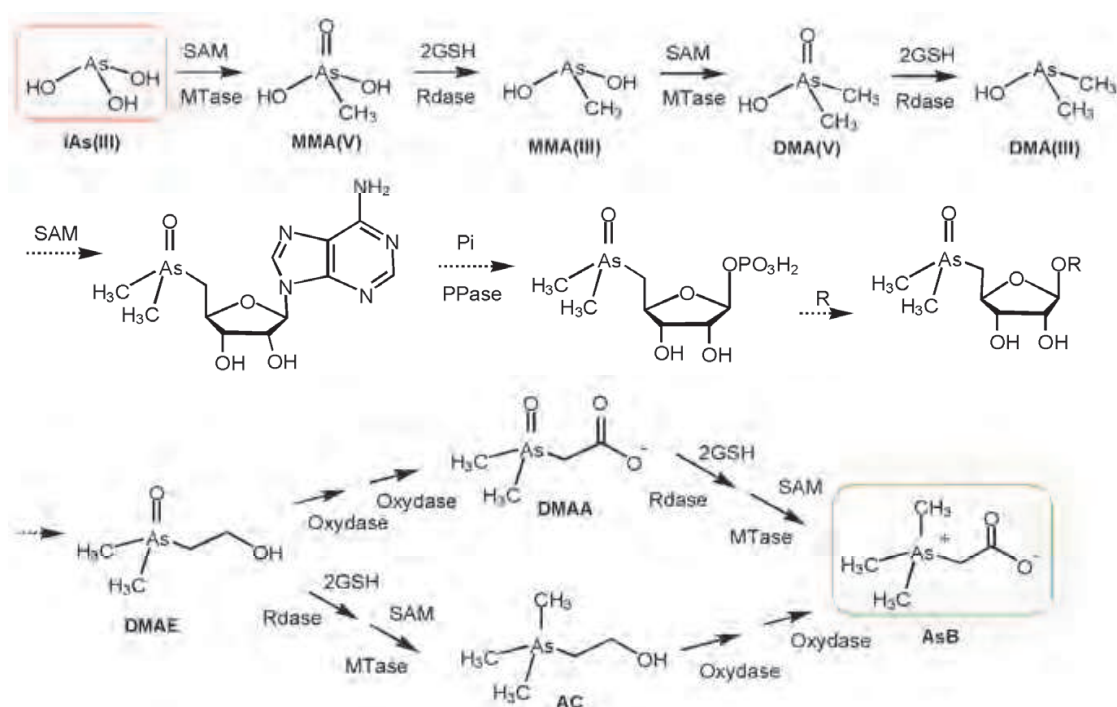


Fig. 2. Estimated biosynthetic path-ways of arsenobetaine in marin food chain system. SAM: S-adenosyl methionine, GSH: glutathione (reduced), MTase: methyltransferase, Rdase: reductase, Pi: inorganic phosphate, PPase: protein phosphatase, iAs(III): arsenite, MMA(V): methylarsonate, DMA(V): dimethylarsinate, DMA(III): dimethylarsonite, DMAE: dimethylarsinoyl ethanol, DMAA: dimethylarsinoyl acetate, AC: arsenocholine, AsB: arsenobetaine.

## 2.5 Organic synthesis

Synthetic methods for obtaining arsenobetaine from inorganic arsenic by using organic solvents have been proposed (Ismail & Toia, 1988; Moore & Ehman, 1977). The synthesis of trimethylarsine by treating arsenic trioxide with trimethylaluminum or with a Grignard reagent has been reported. However, it is difficult to handle these reagents in industrial-scale synthesis of arsenobetaine. Alkylaluminum is a water-reactive substance, and Grignard reagents become inactive in water. Since many incidents of environmental pollution caused by inorganic arsenic are reported in papers on water treatment of ground water etc., it is necessary to design a reaction system suitable for aqueous solutions.

## 3. Biomimetic system for arsenic detoxification

A biological path-way involves the three-step food chain system consisted of chlorella, artemia and shrimp (Nakamura et al., 2006) (Fig. 3). We have examined a biomimetic system with the aim of methylating inorganic arsenic in mild, aqueous solutions using naturally occurring compounds and without using any organic solvents. By allowing the natural derivative of vitamin B<sub>12</sub>, methylcobalamin, and the natural derivative of amino acid, GSH, to react with arsenic trioxide, trimethylarsine oxide (TMAO), which is an important intermediate in the synthesis of arsenobetaine, was obtained in an aqueous solution; a stoichiometrical high yield and high selectivity were achieved (Nakamura et al., 2008a, 2008d). The reaction also proceeded when GSH was replaced with cysteine, a simpler amino acid. TMAO reacted with iodoacetic acid in the presence of GSH in a mild, aqueous solution to produce arsenobetaine quantitatively. This reaction also proceeded when GSH was replaced with cysteine.

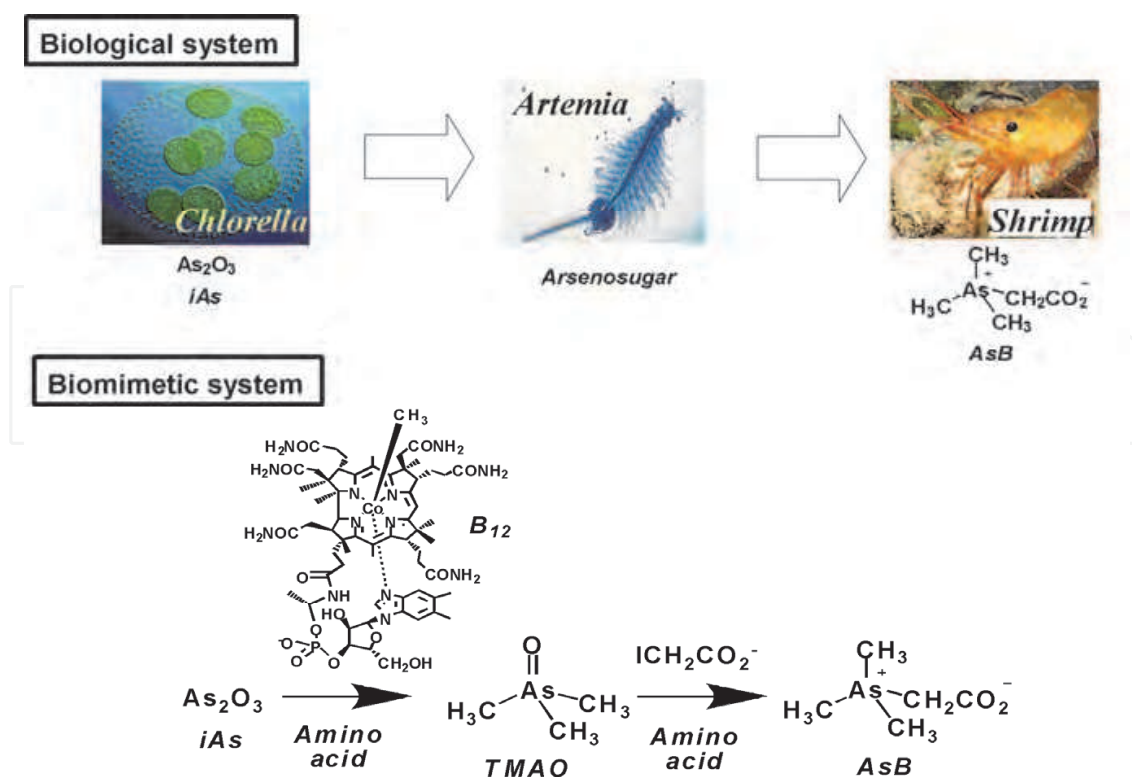


Fig. 3. Biological and biomimetic synthetic path-ways of arsenobetaine.

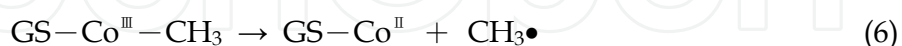
Electron spectrum analysis revealed that methylcobalamin had been reduced by GSH to a Co(II) species. It was suggested that the active methyl group thus produced was involved in the methylation of arsenic.

Three possible mechanisms (involving a carbonium ion, a radical, or a carbanion) for the methyl transfer from methylcobalamin to arsenic can be postulated:

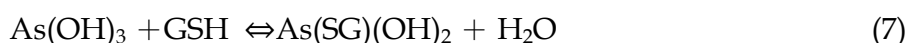


If the reaction were to proceed via the mechanism involving a carbonium ion, the methyl transfer to iAs(III) would produce monomethylarsenic acid [MMA(V)]. However, MMA(III) was produced first. It has been proposed that in the model reaction of methionine synthetase, a carbonium ion is involved in the methyl transfer from methylcobalamin to a thiol group. However, under the reaction conditions in this study, methyl transfer to the thiol group of GSH was not observed. Therefore, a mechanism other than that involving a carbonium ion had to be proposed. It has been reported that methyl transfer from methylcobalamin to a heavy metal such as mercury, lead, and palladium occurs via a nucleophilic attack of carbanion on the positively charged metal ion. Arsenic belongs to the same group as phosphorus, and arsenous acid, like phosphorous acid, exists as an anion in aqueous solutions. The attack of carbanion on an anionic species is considered energetically unfavorable. Therefore, we concluded that the methyl transfer proceeds via a mechanism other than that involving a carbanion.

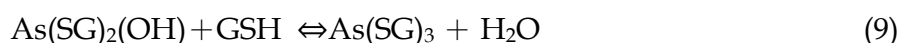
Electron spectrum analysis revealed that Co<sup>III</sup>-CH<sub>3</sub> reduced to Co<sup>II</sup> in the presence of GSH via a GSH-coordinated species (Nakamura et al, 2009). These reactions can be represented by chemical equations (4)–(6). First, the sulfur in GSH coordinates with cobalt to form a C-Co-S species [equation (4)], which is deprotonated to form a thiolate-type GSH-coordinated species [equation (5)]. It is suggested that the trans effect of this complex promotes the homolytic cleavage of the cobalt-carbon bond [equation (6)]. We consider that the methyl radical produced is transferred to arsenic.



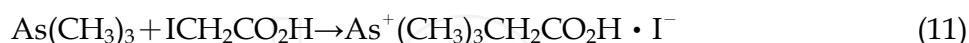
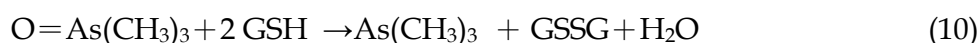
Arsenic compounds are reduced by GSH (As<sup>V</sup>→As<sup>III</sup>). In addition, arsenic compounds are known to form arsenic-GSH conjugates [equations (7)–(9)]. It has been reported that these arsenic-GSH conjugates act as substrates for arsenic methyltransferase when SAM is used as a coenzyme. It is believed that GSH plays an important role in the reductive activation of methylcobalamin and also in the conversion of arsenic to As<sup>III</sup> or a conjugated species that is an active species for methyl transfer.







The synthesis of arsenobetaine (AsB) from TMAO in the presence of GSH was carried out under mild, aqueous conditions.



The mechanisms for these reactions [equations (10) and (11)] are explained as follows: TMAO undergoes two-electron reduction by GSH to form trimethylarsine; then, arsenobetaine is produced when the lone-pair electrons in the arsenic of trimethylarsine are transferred to the positively charged  $\alpha$ -carbon of iodoacetic acid.

#### 4. Bio-inspired catalytic system for arsenic detoxification

A bio-inspired catalysis system was developed (Fig. 4). Photoirradiation of an aqueous solution of arsenic(III) trioxide in the presence of methylcobalamin causes a photochemical methyl transfer to produce methylated arsenic (Nakamura et al., 2008a; Nakamura & Hishinuma, 2009). It is known that the photoirradiation of methylcobalamin induces homolytic cleavage of the Co-C bond to produce a Co(II) species and a methyl radical [ $\text{Co}(\text{III})-\text{CH}_3 \rightarrow \text{Co}(\text{II}) + \text{CH}_3\cdot$ ] (Nakamura et al., 2008e). We speculate that the methyl radical thus produced is used in the methylation of arsenic in the above reaction (Nakamura et al., 2009). A catalytic cycle will be realized if a super-nucleophilic Co(I) species is produced through the reduction of Co(II) [ $\text{Co}(\text{II}) + e^- \rightarrow \text{Co}(\text{I})$ ], followed by the production of Co(III)-CH<sub>3</sub> through the oxidative methylation of this Co(I) species by a methyl donor [ $\text{Co}(\text{I}) + \text{CH}_3^+ \rightarrow \text{Co}(\text{III})-\text{CH}_3$ ]. Because the photochemical methylation of arsenic is known to proceed with visible light irradiation, the development of a photochemical reduction system that also realizes a catalytic cycle is desirable. It has been shown that the excited electrons in a conductor produced by the photoirradiation of titanium oxide act as good reducing agents. The reduction potential is estimated to be between +0.5 and -1.5 V (vs SHE) or -0.65 V (vs SHE at pH 9) (Hoffman et al., 1995). Because the oxidation/reduction potential of vitamin B<sub>12</sub> for Co(II)/Co(I) is in the range -0.50 to -0.61 V (vs SHE) (Kim & Carraway, 2002; Lexa & Saveant, 1983), if appropriate conditions are chosen, it will be possible to construct a system in which Co(II) is reduced to Co(I) by the photoexcited electrons of titanium oxide (Nakamura et al., 2008a, 2008c). Furthermore, it is known that Co(I) is a super-nucleophilic species, which will react with a methyl donor such as methyl *p*-toluene sulfonate to produce Co(III)-CH<sub>3</sub> (Krautler, 1984). Thus, it should be possible to realize a catalytic cycle by combining these three elementary reactions (Nakamura, 2010a, 2011a).

A system consisting of vitamin B<sub>12</sub>, titanium oxide, and a methyl donor was used to examine the transfer of a methyl group to arsenic trioxide (Fig. 4 B). UV irradiation and the presence of vitamin B<sub>12</sub> and a methyl donor were necessary for the methylation reaction to proceed. The yield (based on vitamin B<sub>12</sub>) of this methylation reaction was over 10,000% (Nakamura, 2008b). In this study, the methylcobalamin, GSH, and cysteine used for carrying out detoxification to remove inorganic arsenic were derivatives of natural products. In addition, the detoxification reaction proceeded in mild, aqueous solution, and organic solvents were not required. Thus, this method can be considered to be human- and environmentally friendly.

Thus, we have succeeded in developing a safe and efficient method for the conversion of extremely poisonous inorganic arsenic to arsenobetaine, which is a nontoxic, natural, organic arsenic compound. The conversion can be carried out in mild, aqueous solutions, and we expect that this method for arsenic detoxification using natural products will find applications in various fields (Nakamura, 2010b, 2011b), including water treatment.

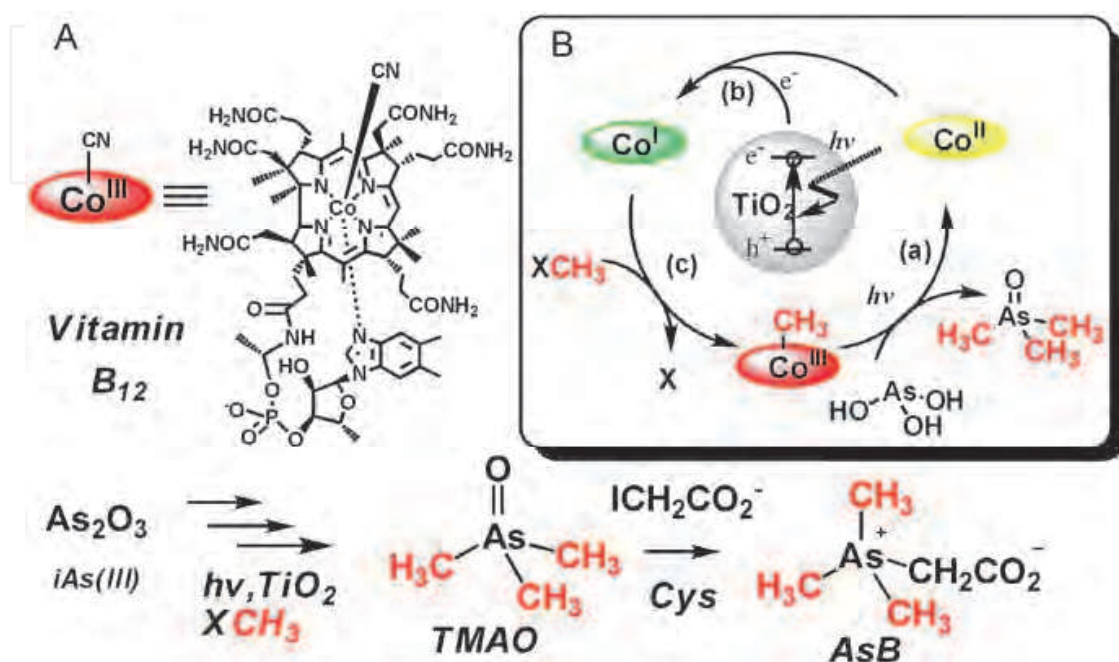


Fig. 4. Photo-sensitive bio-inspired catalytic system with vitamin B<sub>12</sub>. A: synthesis of arsenobetaine (AsB) by using bio-inspired catalytic system with vitamin B<sub>12</sub>. B: estimated reaction mechanism of catalytic system with vitamin B<sub>12</sub> for methyl transfer from methyl donor to arsenic. XCH<sub>3</sub>: methyl donor, hv: photoirradiation.

## 5. Application of arsenic detoxification system

### 5.1 Water treatment

The Annual Report of the World Economic Forum (Davos Forum), held in January 2009, warned that “the world is heading toward water bankruptcy,” and that “in less than 20 years the economic web will collapse if we continue to waste and overuse water.” In fact, more than 70 major rivers that supply water for agricultural or drinking purposes in various parts of the world are on the verge of drought crises (Samans & Waughray, 2009). Furthermore, it is feared that a lack of water resources may reduce the cultivated acreage by an equivalent of about 30% of the land used worldwide in grain production. With regard to the environment, although global warming has received the most attention recently, the biggest environmental issue for mankind is actually the shortage of water, a problem with which we will soon be faced. Among the problems related to water, pollution by inorganic arsenic is a very serious issue globally. The prolonged ingestion of groundwater contaminated with inorganic arsenic in the natural environment is causing the number of patients with arsenic poisoning to increase, especially in Southeast Asia and South America. The arsenic detoxification system using a biomimetic or bio-inspired catalyst has the potential to provide a fundamental solution for the treatment of arsenic-contaminated water



(Fig. 5). Several treatment methods have been proposed for obtaining arsenic-free drinking water from arsenic-contaminated water by the removal of arsenic. These methods include the evaporation method, the filtering method, the adsorption method using adsorbents, the coprecipitation method, membrane treatments using reverse osmotic pressure (RO) membranes, and so on. Although these methods can provide arsenic-free water by removing or transferring inorganic arsenic from the water, there is no safe and efficient way of treating the inorganic arsenic collected when using the above procedures. In the evaporation method, a high concentration of inorganic arsenic remains in the residue after evaporation. In the case of the filtering or adsorption methods, a high concentration of inorganic arsenic remains in the packing or adsorbents, and used reverse-cleaning liquids contain high concentrations of arsenic. Coprecipitation with iron or other species produces a large amount of waste containing inorganic arsenic. The treatment using the reverse osmotic membrane produces a highly concentrated inorganic arsenic solution, for which there is no appropriate treatment method. As described above, the materials generated by these conventional methods, which contain high concentrations of inorganic arsenic, can cause secondary pollution and generate arsenic-contaminated water if they are not properly managed (Fig. 5).

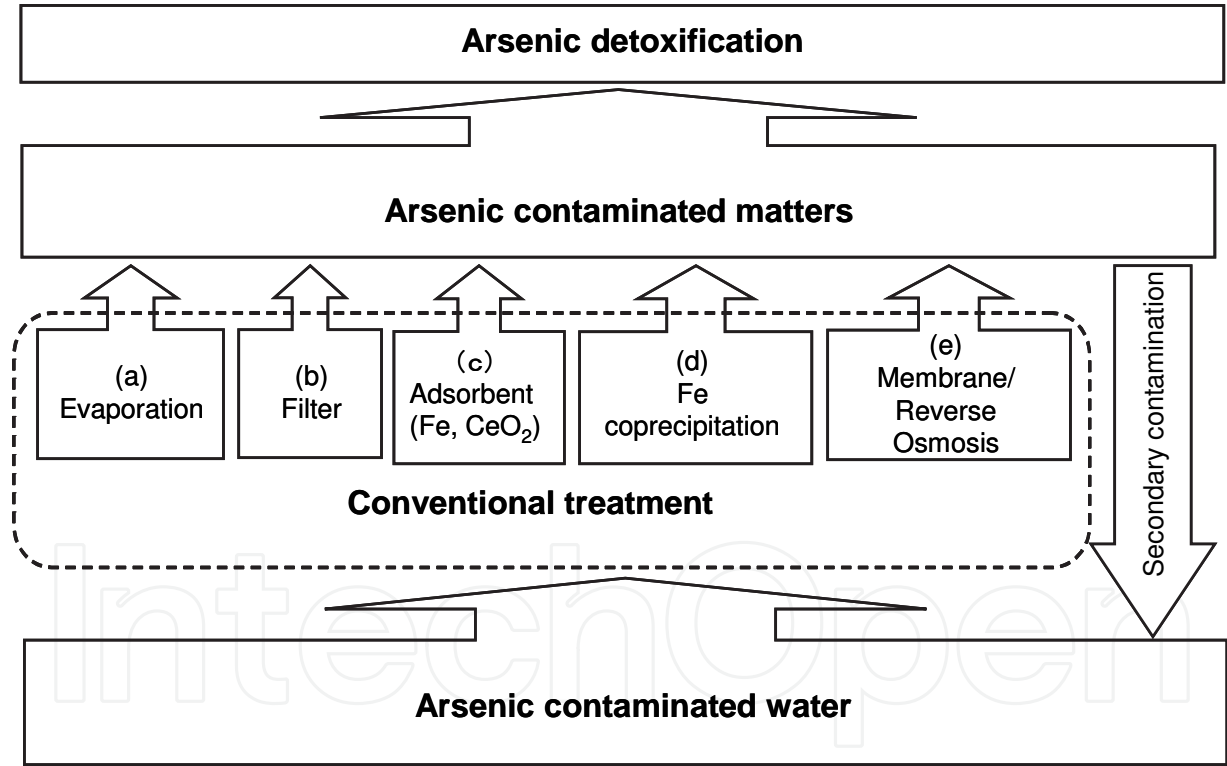


Fig. 5. Flowchart of the proposed treatment of arsenic contaminated water by a combination of conventional methods and arsenic detoxification technology.

For the prevention of such secondary pollution, it is desirable to treat the inorganic arsenic safely using a detoxification system (Fig. 5). The treatment processes for an inorganic arsenic detoxification technology using biomimetic or bio-inspired catalysts are as follows (Fig. 6): (a) arsenic-contaminated water with concentration exceeding 0.01 mg As/L, which is the criterion for drinking water stipulated by the WHO Guidelines for Drinking-Water Quality (WHO, 2008), is treated using the conventional methods (b) ; (c) drinking water with a

concentration below 0.01 mg As/L is obtained; (d) this reaction converts the inorganic arsenic to nontoxic arsenobetaine; (e) the arsenobetaine thus obtained is stored or disposed of in accordance with the appropriate laws and regulations. The detoxification processes are described in detail as follows: (f) if the removed inorganic arsenic is of high concentration or solid, it is treated directly, and if the concentration is low, a solution with high inorganic arsenic concentration is obtained through a concentration process; (g) the inorganic arsenic thus obtained is converted to arsenobetaine by the biomimetic method using vitamin B<sub>12</sub>, amino acids and iodoacetic acid; (h) the arsenobetaine (desired product), vitamin B<sub>12</sub>, and amino acids are separated by chromatography; (i) the arsenobetaine is evaporated to dryness, and stored in a container; (j) the separated vitamin B<sub>12</sub> and amino acids are retreated, and (k) reused for the next detoxification reaction. Because arsenobetaine is stored separately in a container, there is no risk of secondary pollution. These processes enable the sustainable treatment of arsenic-contaminated water.

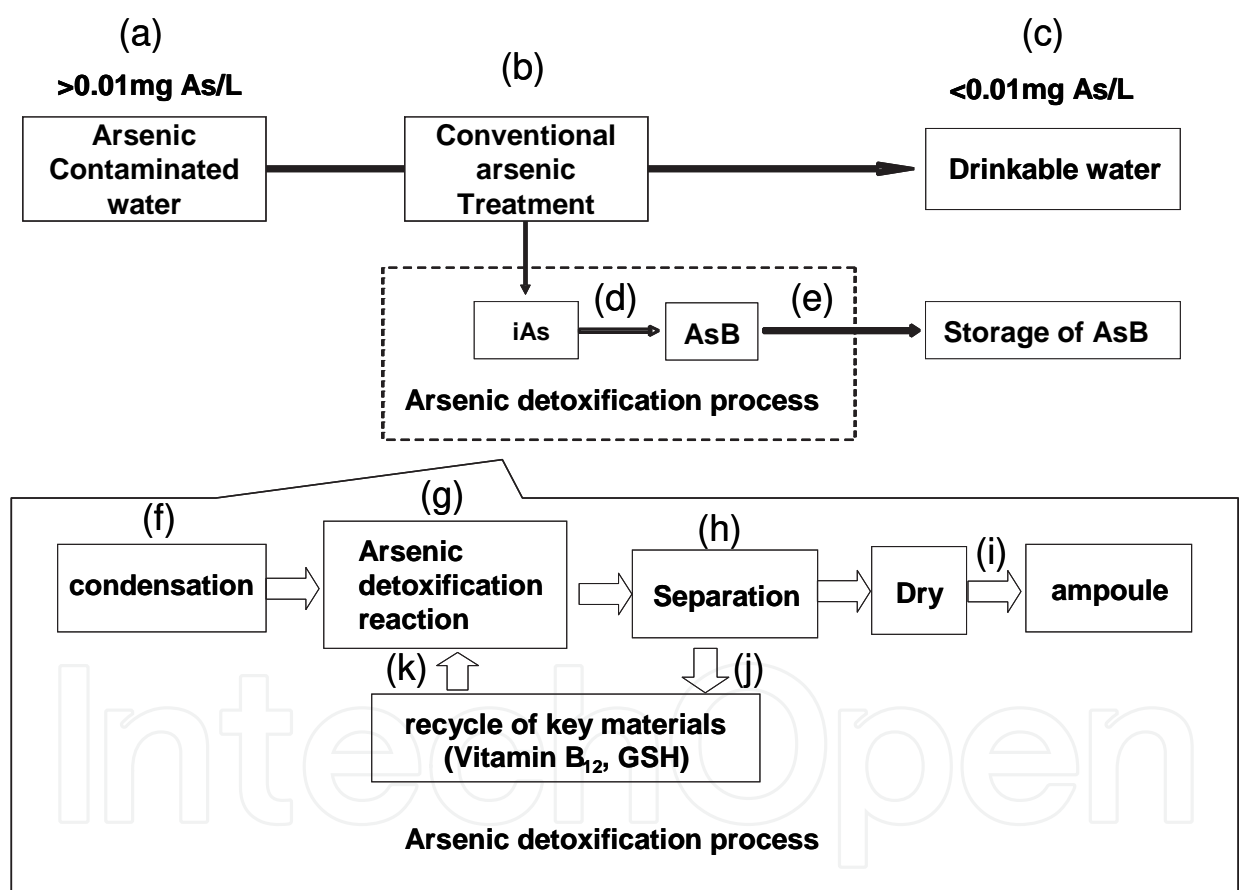


Fig. 6. Flowchart of the proposed treatment of arsenic contaminated water by a combination of conventional methods and arsenic detoxification process.

Using the biomimetic method, we conducted the detoxification of arsenic-contaminated groundwater (Fig. 6) containing arsenic at a concentration of 0.2 mg As/L, which is 20 times the concentration stipulated in the WHO Guidelines (WHO, 2008). In the natural environment, inorganic arsenic exists as a pentavalent species (arsenic acid) (Fig. 7). The arsenic-contaminated groundwater was purified by the evaporation method, and the residue obtained in this process was successfully converted to arsenobetaine by the

biomimetic detoxification system (Fig. 8). To date, we have succeeded in carrying out the biomimetic detoxification of arsenic acid in amounts equivalent to 10 m<sup>3</sup>/day of water with a concentration of 0.03mg As/L (which exceeds the WHO Guidelines) (Fig. 9).

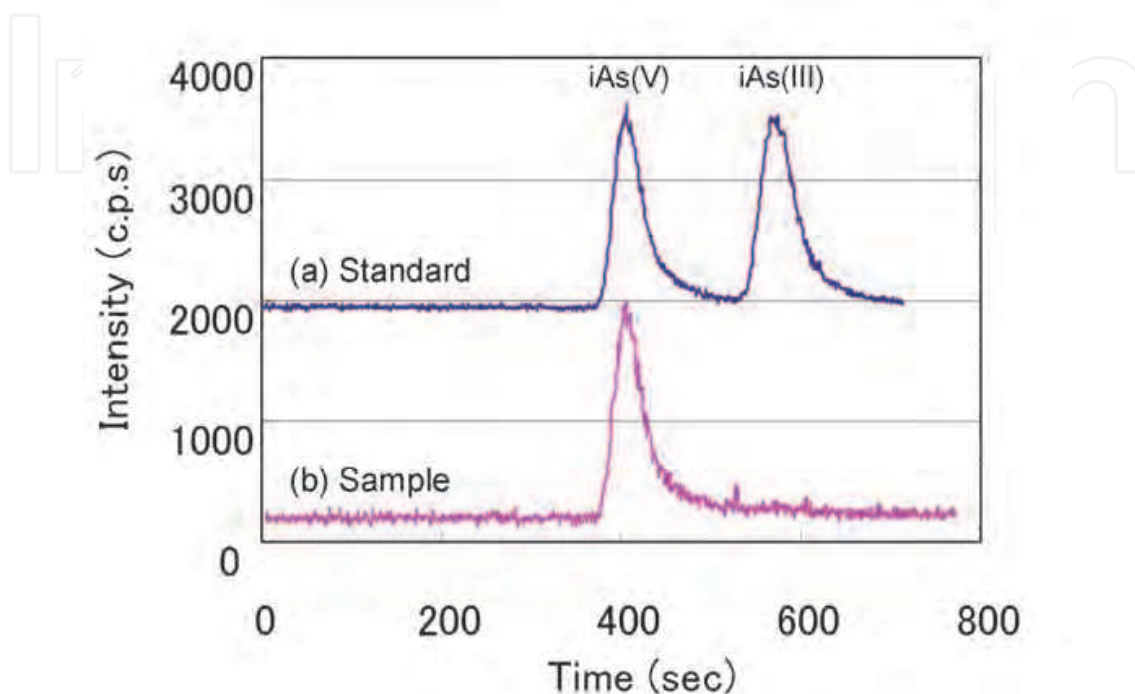


Fig. 7. ICP-MS chromatogram. (a) Standard solution of iAs(III) and iAs(V). (b) Arsenic contaminated ground water.

A comparison of the conventional and detoxification treatments of arsenic is shown in Table 1. When treatment methods other than the detoxification method are used, the arsenic species remains as the extremely poisonous inorganic arsenic, and is unchanged during the treatment; thus, secondary pollution is a concern. The detoxification method is applicable to both trivalent and pentavalent inorganic arsenic (biomimetic system). On the other hand, treatment methods using activated alumina, manganese dioxide, coagulation-sedimentation, and so forth are not applicable to trivalent arsenic, which needs to be first converted to pentavalent inorganic arsenic by an oxidizing agent. With regard to the space needed for the treatment of arsenic waste, the detoxification method enables the volume of arsenic-containing waste to be minimized through the isolation of arsenobetaine (photographs in Fig. 9). On the other hand, the adsorption and coagulation-sedimentation methods require adsorbents or coagulation-sedimentation agents in amounts that are hundreds of times larger than the volume of the arsenic treated. Thus, the volume of these inorganic-arsenic-containing treatment agents becomes more than hundreds of times greater than that of the original inorganic arsenic. The proposed arsenic detoxification technology can be used alone or in combination with the conventional technologies in the field of water treatment (Fig. 5, Table 1).

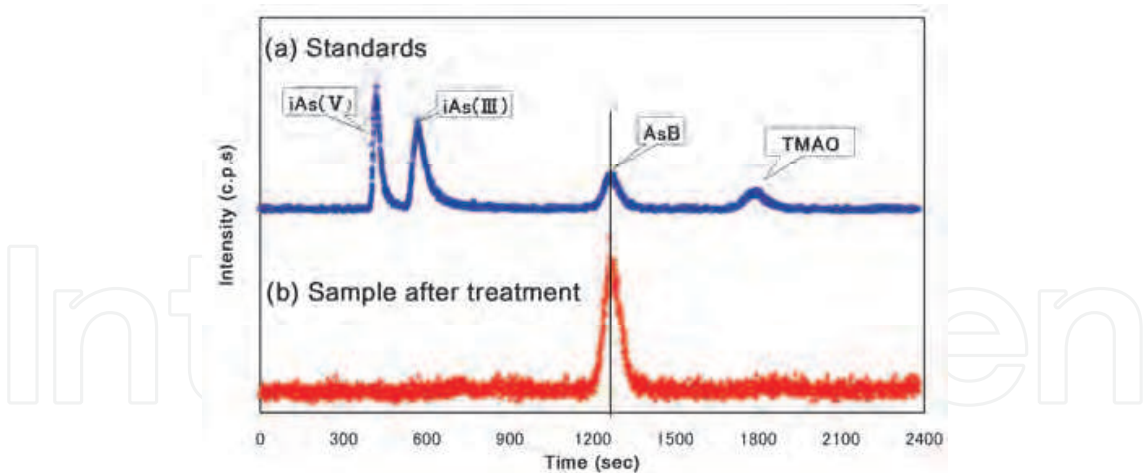


Fig. 8. Inductively-coupled plasma mass spectrometer (ICP-MS) chromatogram. (a) Standard solution of iAs(III), iAs(V), AsB and TMAO. (b) Sample after treatment of detoxification.

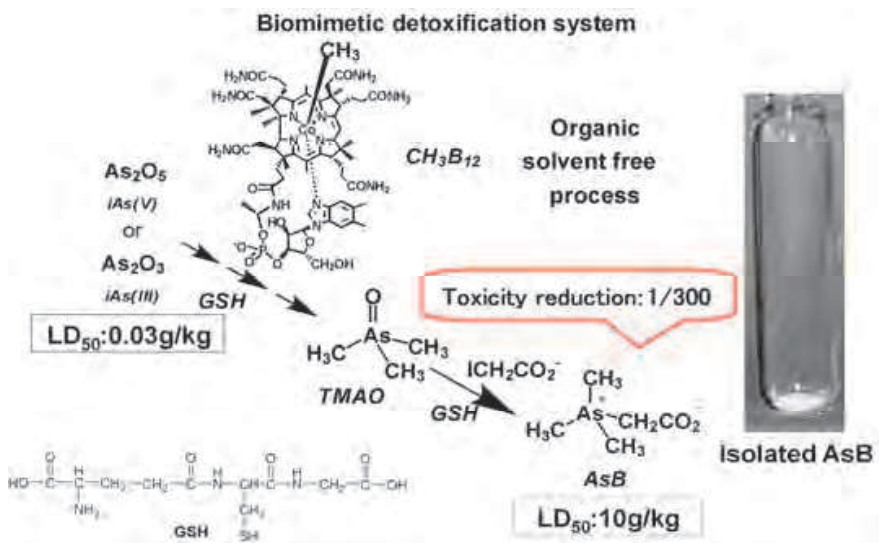


Fig. 9. An isolated arsenobetaine transformed from iAs(V) by using a biomimetic detoxification system.

Method	Property		
	Detoxification capability	Space needed for waste storage	Note
Arsenic detoxification	Yes	Minimal	Applicable for iAs(III) and iAs(V)
Adsorbent	No	Large	Interfering substance: Phosphate (Li et al., 2011)
Filter	No	Med-large	Oxidant needed for iAs(III)
Reverse osmosis membrane	No	Medium	Fouling substance
Coprecipitation	No	Large	Oxidant needed for iAs(III)

Table 1. Comparison of arsenic detoxification system and conventional arsenic treatment systems.

5.2 Recycling technologies of rare metals

Amid the growing awareness of the need to save resources and energy globally, we are strongly required to change our current mass-consumption society to a sustainable circulatory society. From the viewpoint of resource security and environmental conservation, the recycling of rare metals is of utmost importance. GaAs semiconductors have been used for the production of cell phones, electronic information equipment, light-emitting diodes (LEDs), and solar cells, which are essential for the realization of a low-carbon society. The consumption of GaAs is expected to increase with the future development of society. In view of resource security, gallium recycling is crucial for securing a stable supply of the rare metal gallium. On the other hand, environmental destruction has been progressing with the mining of gallium and the manufacture of gallium products; therefore, in terms of the conservation of the environment, the development of an environmentally friendly recycling technology is very important. In addition, health damage from the arsenic associated with the recycling of gallium from GaAs semiconductors has been reported. Given this background, the development of technologies that allow the safe treatment of arsenic in processes for arsenic recycling is required. Therefore, we applied our environmentally friendly arsenic detoxification technology to the recycling of gallium from GaAs semiconductors (Fig. 10) (Nakamura et al., 2008f, 2010b, 2011b).

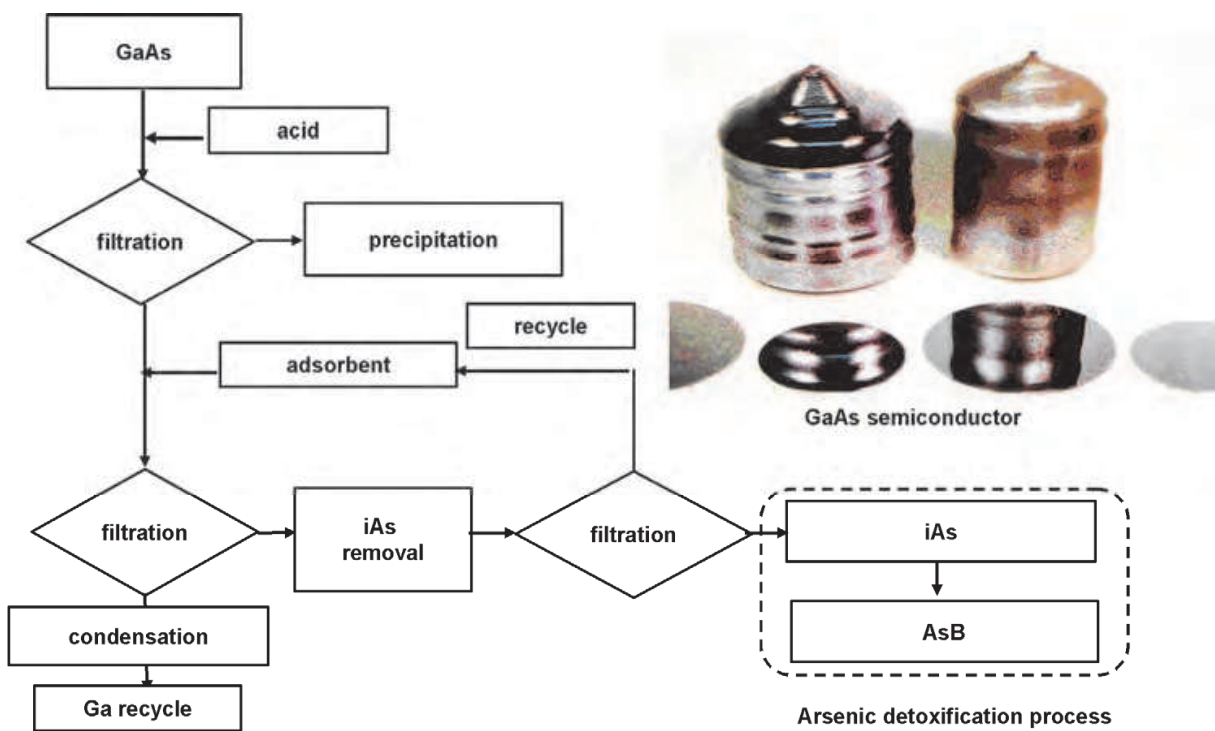


Fig. 10. Process of recycling of gallium and detoxification of arsenic from GaAs semiconductor using biomimetic arsenic detoxification system.

Here, we explain the recycling of the gallium from GaAs semiconductors and the detoxification of arsenic (Fig. 10). GaAs semiconductors are dissolved in acid, and inorganic arsenic is removed by an arsenic-specific adsorbent to recover the gallium. The adsorbent is treated with alkali to dissociate the arsenic. The arsenic thus obtained is biomimetically



detoxified and converted to arsenobetaine. The adsorbent from which the arsenic has been dissociated is reusable. Thus, it is possible to recover valuable gallium from waste GaAs semiconductors, and at the same time to treat the hazardous arsenic safely with this detoxification method.

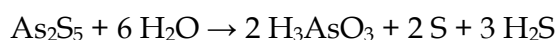
### 5.3 Detoxification of arsenic from abandoned chemical weapons

Many of the chemical agents used in chemical weapons contain arsenic. Chemical weapons produced by the old Japanese army, as well as foreign chemical weapons, such as Clark I (DA, diphenyl chloroarsine) and Clark II (DC, diphenyl cyanoarsine) of Germany, adamsite of Poland, and lewisite of Russia contain arsenic compounds. The development of a safe and efficient technology for the disposal of such chemical weapons using chemical agents is required (SCJ, 2006).

Various methods have been proposed for the treatment of arsenic in chemical weapons. For example, methods such as (1) recovering arsenic as arsenic sulfide by incineration treatment in a sulfur burner (SCJ, 2006), (2) solidifying or insolubilizing arsenic using solidifiers such as cement, and (3) treating by heating at 800–1100°C in a rotary kiln have been reported.

The problems associated with the individual methods above are as follows:

1. In the method to recover arsenic as arsenic sulfide by incinerating the abandoned chemical weapons in a sulfur burner, the resultant arsenic sulfide (As<sub>2</sub>S<sub>5</sub>) is readily hydrolyzed to arsenous acid (H<sub>3</sub>AsO<sub>3</sub>), sulfur (S), and hydrogen sulfide (H<sub>2</sub>S) by hot water. In other words, this process generates extremely poisonous arsenous acid and hydrogen sulfide gas:



2. In the solidification or insolubilization method, the large amount of cement necessary for the treatment poses a problem. An additional issue is that there has been a report describing the seeping of arsenic out of the cement, so that, using the insolubilization method, the concentration of arsenic in the soil cannot be controlled below the value stipulated in the Environmental Quality of Standards of Soil Pollution. From the viewpoint of long-term stability, cement is poorly resistant to alkali and acid; this causes extremely poisonous inorganic arsenic to seep out readily.
3. A treatment method involving heating a mixture of mainly plastic-containing industrial waste and organic arsenic-contaminated waste at 800–1100°C in a rotary kiln has been reported. In this method, because the waste is heated at a very high temperature, the sublimation of the generated inorganic arsenic (sublimation point of arsenous acid = 135°C) and its pyrolysis (decomposition point of arsenic acid = 315°C) become problematic. Air pollution and environmental pollution can be caused, and there is a risk of the workers being exposed to and poisoned by inorganic arsenic.

To solve these problems, we applied our biomimetic system to the detoxification of the arsenic from chemical weapons. The residue left after the explosive treatment of abandoned chemical weapons was treated with acid to extract all of the inorganic arsenic (Fig. 11). Insoluble materials were removed by filtration. The filtrate was subjected to the proposed biomimetic detoxification treatment, and arsenobetaine was successfully isolated after column chromatography of the resultant. All the arsenic from the abandoned chemical weapons treated in this way was detoxified by conversion to arsenobetaine. The volume of arsenic-containing waste was reduced by a factor of about 25 by this conversion to and isolation as arsenobetaine (Fig. 11).

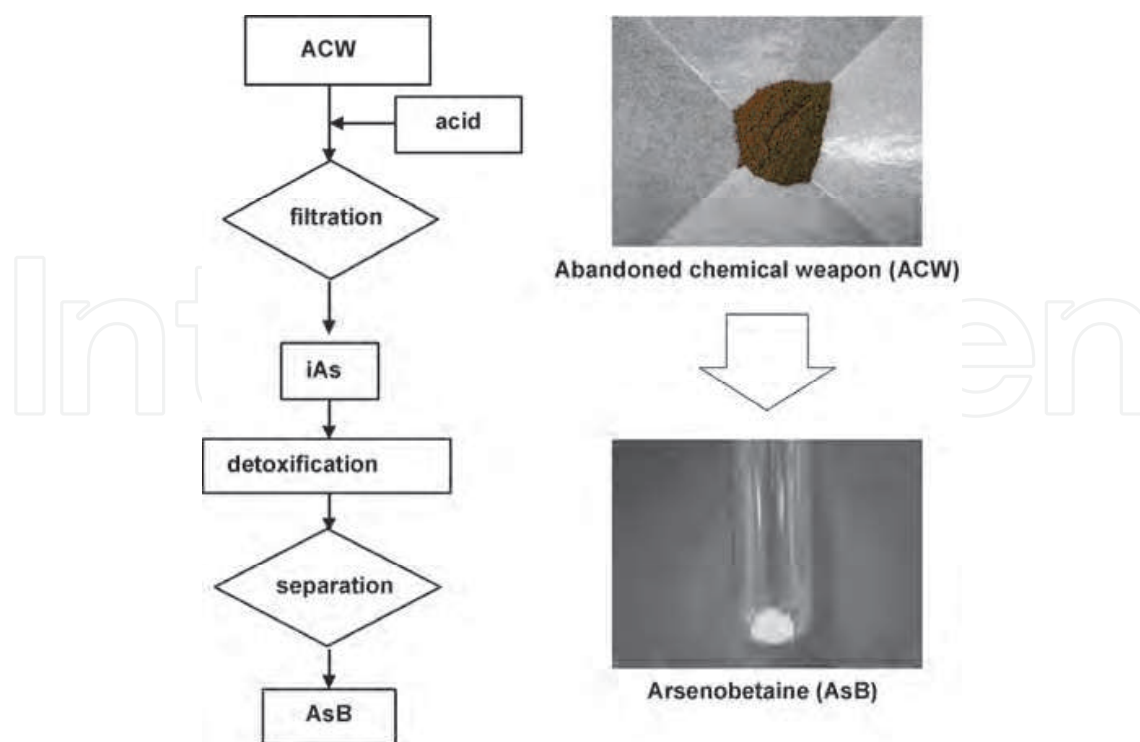


Fig. 11. Process for the detoxification of abandoned chemical weapons, the pulverized abandoned chemical weapons actually used, and the synthesized and isolated arsenobetaine.

## 6. Conclusion

We have succeeded in designing a vitamin-B<sub>12</sub>-containing biomimetic or bio-inspired catalytic system, and in constructing a system in which a catalytic cycle is realized. This catalytic system, which utilizes the naturally occurring biological materials vitamin B<sub>12</sub> and amino acids or the naturally occurring inorganic material titanium oxide, with water as the solvent, is safe and environmentally friendly. We have demonstrated that inorganic arsenic in arsenic-contaminated groundwater can be detoxified by using this biomimetic or bio-inspired catalyst. In conventional methods, inorganic arsenic is removed or moved in its original form, and the toxicity of the inorganic arsenic remains unchanged, so secondary pollution is a problem. In the present treatment method, the toxicity of arsenic per se can be removed, and thus it is expected that this technique will contribute to solving the problem of arsenic-contaminated groundwater globally. To contribute to the realization of a circulatory society, we also applied this biomimetic or bio-inspired catalytic system to the recycling of rare metals. The gallium from GaAs semiconductors was recovered, and the arsenic from the semiconductors was shown to be detoxified. In the detoxification treatment of inorganic arsenic from abandoned chemical weapons, arsenobetaine was successfully produced and isolated. The vitamin-B<sub>12</sub>-containing biomimetic or bio-inspired catalytic system provides a safe and efficient water-treatment system that proceeds smoothly under mild aqueous conditions. This system is expected to find applications in various fields in the future.

## 7. Acknowledgements

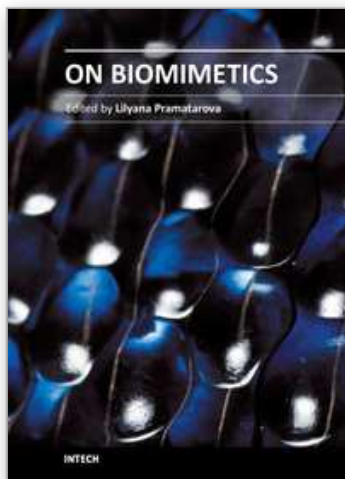
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Bio-mimicry is fundamental idea – How to mimic the Nature™ by various methodologies as well as new ideas or suggestions on the creation of novel materials and functions. This book comprises seven sections on various perspectives of bio-mimicry in our life; Section 1 gives an overview of modeling of biomimetic materials; Section 2 presents a processing and design of biomaterials; Section 3 presents various aspects of design and application of biomimetic polymers and composites are discussed; Section 4 presents a general characterization of biomaterials; Section 5 proposes new examples for biomimetic systems; Section 6 summarizes chapters, concerning cells behavior through mimicry; Section 7 presents various applications of biomimetic materials are presented. Aimed at physicists, chemists and biologists interested in biomineralization, biochemistry, kinetics, solution chemistry. This book is also relevant to engineers and doctors interested in research and construction of biomimetic systems.

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