

Title: Arsenic in the groundwater environment

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Abstract: Arsenic is a metalloid which can exist in various allotropes, finding its importance in semiconductors industry, pesticides, insecticides and as well as a wood preservative. Arsenic contamination of groundwater is a serious problem faced by all over the world. The chemistry of arsenic in aquatic system is quite complicated as the element may exist in any of the four stable oxidation states (+5, +3, 0,-3), but in this paper we have focused on As(III) and As(V). This paper aims to focus on the sources of As and understanding the geochemical reaction of arsenic in the underground environment. It will also focus on identifying the dominant species of arsenic in groundwater at different pH condition by plotting the log C - pH diagrams, and its adsorption, precipitation for removal from Water and status of Arsenic pollution in Bangladesh.

Introduction

Of the available fresh water sources, Ground water is the very promiseable source for drinking water and as well as for irrigation and industrial processes. Due to rapid industrialization, urbanization and globalization, we concentrated on the demand of the public, not on the sustainable development, for the betterment of the future. A highly populated, developing country like India, its ultimate aim is to provide food security, water security, and employment security not on the sustainable development, so it negotiates.

During the early to mid-1900, the indiscriminate use of arsenical pesticides has led to the extensive contamination of soils worldwide. The contaminated site exists throughout worldwide. The presence of arsenic in the environment may be due to both natural and anthropogenic sources.

As having an atomic number 33 with an outer electronic configuration $4s^2 4p^3$ considered in the periodic table as metalloid. In most of the times As behaviour is similar to the orthophosphate ion in the aerated systems. However As is more mobile than P, whereas phosphorous changes its valence state (Walsh et al., 1977). Arsenic shows no sign to validate it has been an essential component for biological processes. The toxicity of arsenic compounds depends on a number of factors, including the chemical forms it present:

inorganic As forms are more toxic than organic, and As (III) is more toxic than arsenate, As (V) (World Health Organization, 1981).

In India, major parts of Ganga delta downstream side of Rajmahal hills in West Bengal and other low lying areas of Bangladesh is identified as the Arsenic contaminated area, which is due to the soil nature. Moreover due to excessive abstraction of groundwater which leads to entrainment of oxygen in the groundwater which in turn oxidizes the pyrite and arsenopyrite and arsenic reaches water also by reductive dissolution of ferric-oxyhydroxide that contains sorbed arsenic. The problem of As contamination in West Bengal and Bangladesh has been considered devastating, since a major portion of population is at high risk.

In soil both the As forms such as arsenate and arsenite predominantly presents. While the toxic form arsenite is mobile in water and arsenate adsorbed on to the soil surface. Arsenic is mainly transported in the environment by water. In oxygenated water, arsenic usually occurs as arsenate, but under reducing conditions, for instance, in deep well-waters, arsenites predominate. In water, the methylation of inorganic arsenic to methyl- and dimethyl arsenic acids is associated with biological activity. Human exposure of As is mainly via food intake, with smaller contribution from air and drinking

water. Normal As concentration in human whole blood and urine has been reported to be about 100 and 15µg/L (Fowler, 1977). Conjunctivitis, hyperkeratosis, melanosis, cancer of the skin and lungs have been reported as the most commonly observed diseases of As exposure.

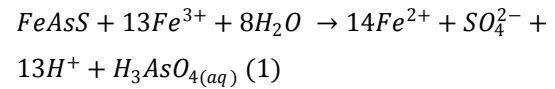
With greater public awareness of As poisoning in human and animal nutrition, both the governments showing interest in formulating guidelines and remediation technologies for mitigating As-contaminated ecosystems.

Arsenic sources and speciation

Natural sources

The toxic metalloid arsenic is found worldwide as in trace quantities within the subsurface. About 99% of Arsenic is found in rocks (Bhumbla & Keefer., 1994). The distribution of As in the soil is mainly depending on the nature of the parent material it is derived (E. Smith et al., 1998). It is reported that As mainly appears in the form of sulphides in association with the sulphides of ores of silver, lead, copper, nickel, antimony and cobalt (WHO, 2000). It mostly exists in either the arsenopyrite (FeAsS), realgar (AsS), or orpiment (As₂S₃) forms (Newman et al., 1998). The introduction of As in the environment mainly because of the weathering action and erosion of these sediments (Bhumbla & Keefer., 1994).

The introduction of As in the water through the decomposition of arsenopyrite according to the following mechanism (Rimstidt et al., 1994)



The studies revealed that the under reducing conditions As (III) is predominantly present in the underground water. Now researchers also claimed that the high withdrawal of ground water also causes the release of arsenic in the groundwater (Masscheleyn et al., 1991).

The natural content of As in the soil with a mean of 5-6 mg As kg⁻¹ of soil with a range from 0.1-40 mg As kg⁻¹ of soil (Walsh et al., 1977; Tamaki & Frankenberger 1992). Natural waters having the concentration with a range from <0.5 µg L⁻¹ to >12000 µg L⁻¹ (Schrieber et al.2003; Wang & Mulligan 2004). Usually ground waters having more concentrations of As than surface waters. Several factors such as geo-physical, geo-chemical processes, biological processes including oxidation of As-sulphides and desorption of As from oxides, leaching of As from sulphides, geothermal waters, reductive dissolution of As containing oxides (Schrieber et al.2003; Wang & Mulligan 2004). As concentrations found in the ground water samples of Bangladesh & West Bengal also varies from 0.03-0.75 mg/L with a mean value of 0.41 mg/L (H.M. Anawar et al., 2003) and around 35 million

people are drinking ground water containing As of this much concentrations daily.

Anthropogenic sources

Anthropogenic activities that introduce As in the environment are majorly classified into three categories. Industrial activities, mining and other sources. Industrial activities including glass manufacturing, cosmetics, fireworks, Cu-based alloys (E. Smith et al., 1998). The ores such as Pb, Zn, Cu containing As as a major component. Consequently contamination of the atmosphere, soil, ground water happens due to the smelting operations of these metals and also from mine dumps. Other sources such as fly ash from coal fired power plants, agricultural activities, wood preservatives, tannery wastes, agricultural activities (E. Smith et al., 1998). Besides direct release of As into the air from coal fired power plants, the left over ash is also containing high concentrations of As which is being landfilled and also leaching of As from ash is also a major problem. More than 65,000 acres of land being used for storage of these fly ash in India (V.C. Pandey et al., 2011). Indian bituminous coal is containing 22.3-62.5 ppm (V.C. Pandey et al., 2011). Arsenic as sodium arsenate was used as a pesticide in the treatment of animal hides. In 20th century arsenical pesticides in the form of lead arsenate (PbAsO_4), calcium arsenate (CaAsO_4), magnesium arsenate (MgAsO_4),

zinc arsenate (ZnAsO_4) and zinc arsenite ($\text{Zn}(\text{AsO}_2)_2$) were used all over the world in agriculture fields which upon leaching increased the concentration in the surface as well as ground waters and now it was totally eliminated (E. Smith et al., 1998).

As speciation

Knowledge on As speciation gains momentum since both toxicity and mobility of As are closely related to its chemical form (S. Dorban et al., 2006). As can be found in environment as a variety of inorganic and organic compounds in soils. Usually inorganic arsenic compounds are present as +5 and +3 oxidation states as arsenate and arsenite.

The trivalent arsenic forms exist as arsenous acid (As_2O_3), arsenious acid (HAsO_2), arsenite (H_2AsO_3^- , HAsO_3^{2-} , AsO_3^{3-}) ions, arsenic trichloride (AsCl_3), arsenic sulphide (AsS_3), and arsine (AsH_3). Pentavalent As commonly occurs as arsenic pentoxide (As_2O_5), orthoarsenic acid (H_3AsO_4), metaarsenic acid (HAsO_3), and arsenate (H_2AsO_4^- , HAsO_4^{2-} , AsO_4^{3-}) ions.

The presence of different forms of organic As, as monomethylarsonic acid [MMA, $\text{CH}_3\text{AsO}(\text{OH})_2$], dimethylarsenic acid [DMA, $(\text{CH}_3)_2\text{AsO}(\text{OH})$], trimethylarsine oxide [$(\text{CH}_3)_3\text{AsO}$], methyl arsine (CH_3AsH_2), dimethyl arsine [$(\text{CH}_3)_2\text{AsH}$] and trimethyl arsine [TMA, $(\text{CH}_3)_3\text{As}$] has also been

observed in contaminated water (Gao and Burau, 1997).

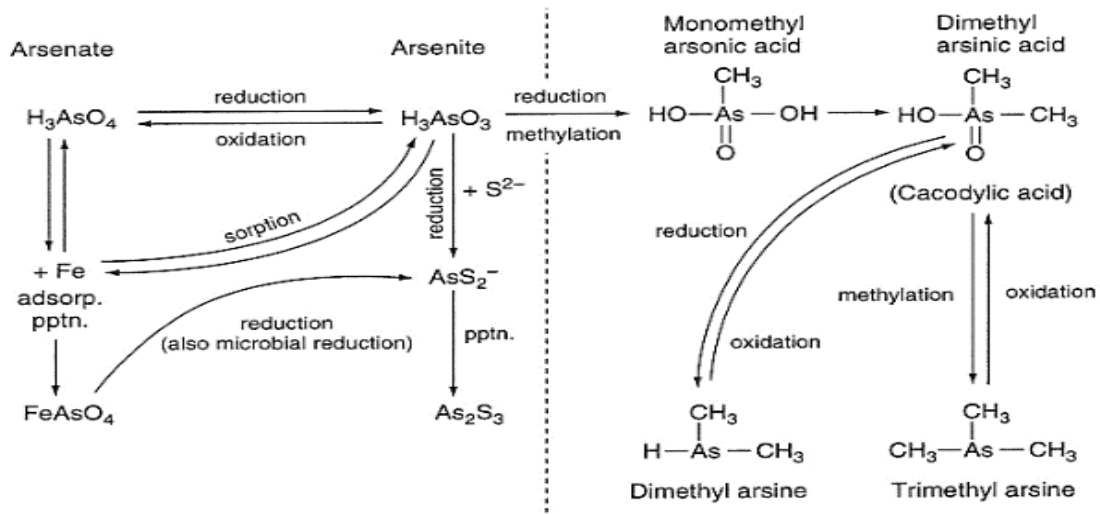


Fig. 1 (Reproduced) Simplified transformation pathways of Arsenic in the environment (Prokasha et.al., 2005)

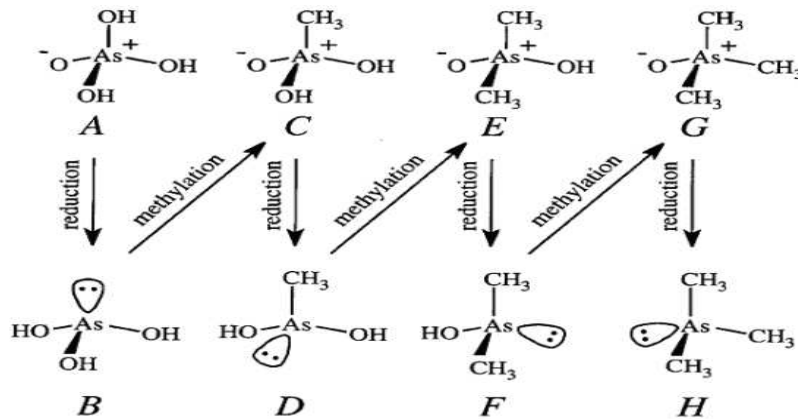
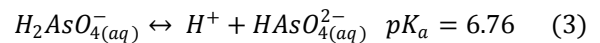
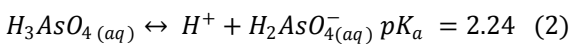
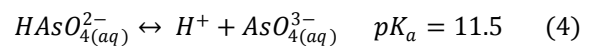


Fig. 2 (Reproduced) Challenger mechanism for the transformation of arsenate from trimethylarsine (A) arsenate; (B) arsenite; (c)methylarsonate; (D) methylarsonite;(E)dimethylarsonate; (F) dimethylarsinite; (G) trimethylarsine oxide;(H) trimethylarsine. (Alexander Poser, 2006).

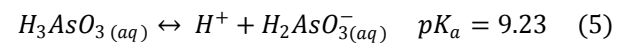
Geo chemical reactions of arsenic



The equilibria for Arsenic acid (As^V) in aqueous solutions are given below



The equilibria for Arsenic acid (As^{III}) in aqueous solutions are given below



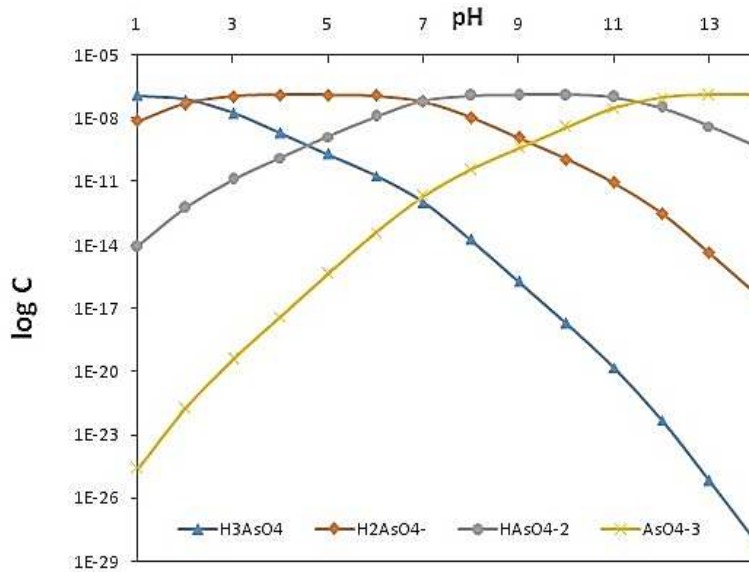
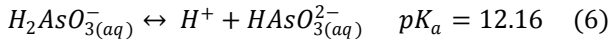


Fig 3. The $\log C - pH$ diagram for As(V) at 25°C and 101.3 kPa for TOT As(III) as 10 µg/L

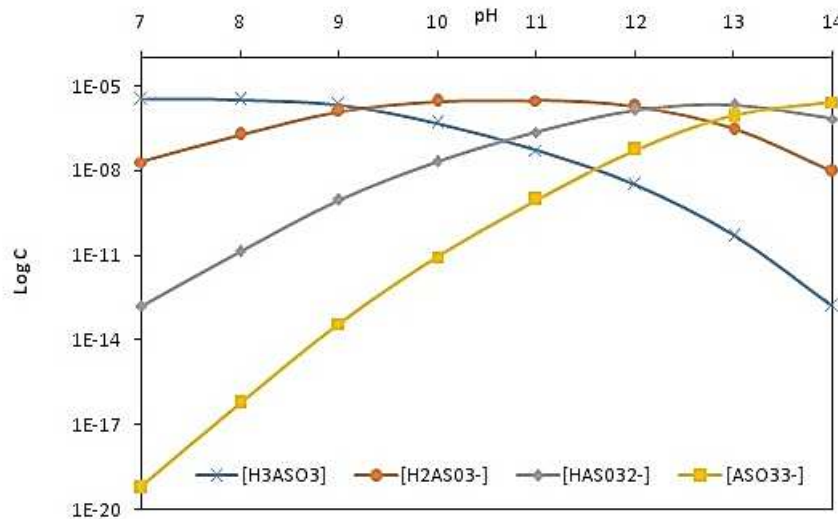
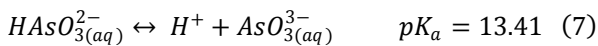


Fig. 4 The $pH - \log C$ diagram for As(III) at 25°C and 101.3 kPa for TOT As(III) as 250 µg/L

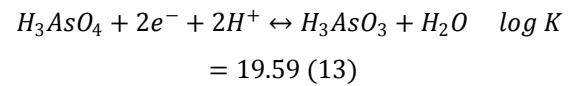
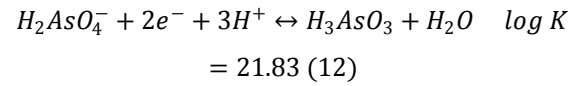
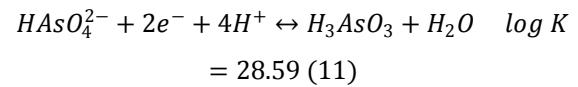
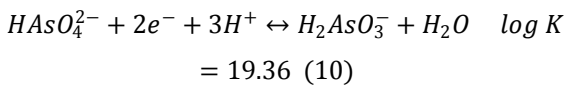
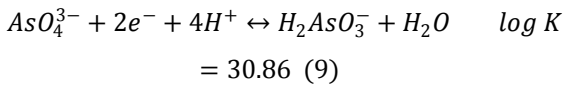
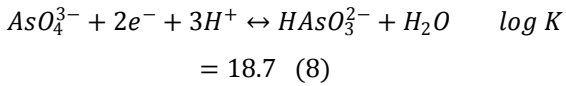


are: H_3AsO_4 (pH 0–2), $H_2AsO_4^-$ (pH 3–6), $HAsO_4^{2-}$ (pH 7–11), and AsO_4^{3-} (pH 12–14).

From the fig 3 & 4. trivalent arsenic is stable at pH 0–9 as neutral H_3AsO_3 , while $H_2AsO_3^-$, $HAsO_3^{2-}$, and AsO_3^{3-} exist as stable species in the pH interval 10–12, 13, and 14, Respectively. For pentavalent arsenic the corresponding stability of species pH Values

So we can see H_3AsO_3 is stable at pH 0-9 and which is in neutral form. That is why As(III) is found mostly in drinking water and this form of arsenic is creating all the problem

The redox equilibrium reactions between As (V) and As (III) are given below



The log C – pH plots for As (V) and As (III) is shown in the figures 3 and 4 respectively. The log C – pH helps to understand the dominant species at a particular pH.

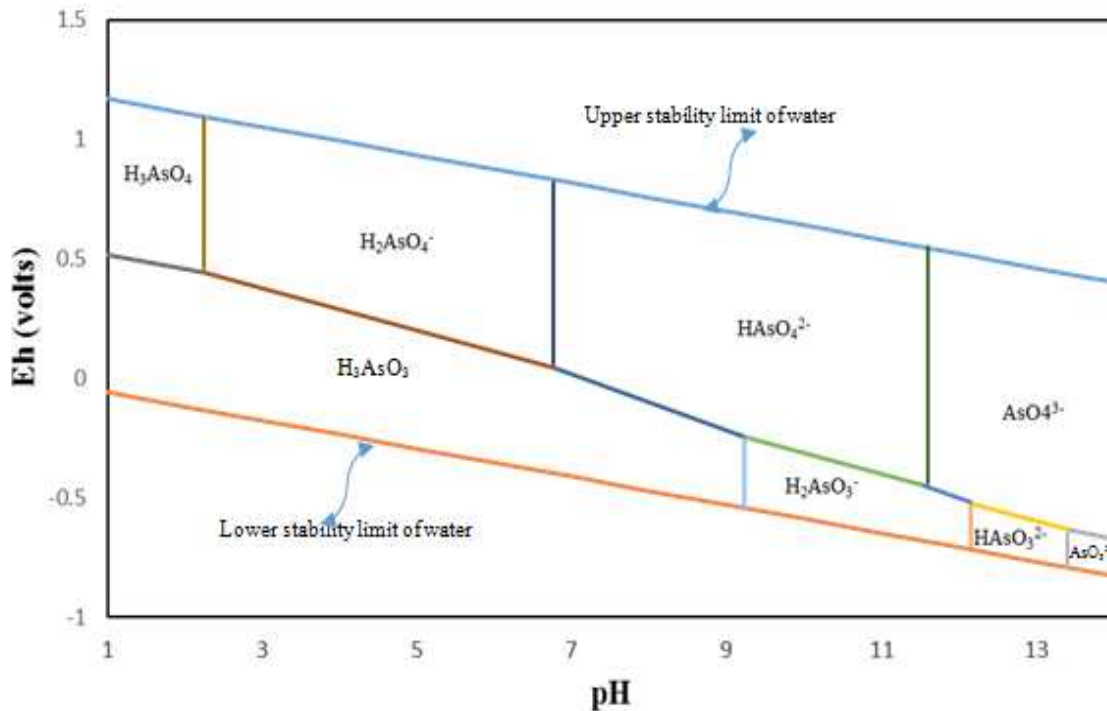
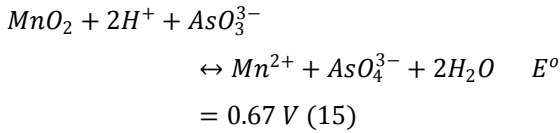
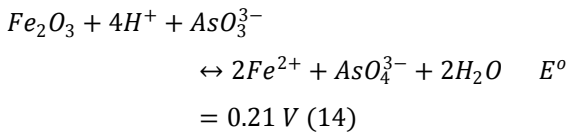


Fig. 5. The Eh-pH diagram for As at 25°C and 101.3 kPa

Eh-pH plot for As is shown in fig 5. The parameters redox potential and pH plays a crucial role in arsenic speciation and its solubility in water. At higher redox potential say in the range from 500 -200mV As (V) predominates in the water. Moreover this can

be substantiated by the point that the As (III) is more thermodynamically stable than As (V) under reducing soil conditions; i.e., where electron activity (pE) + pH < 8, and pH < 6 (Sadiq et al., 1983). Some researchers also contradict this that sometimes under reducing

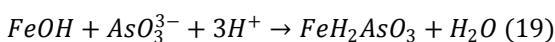
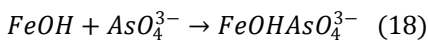
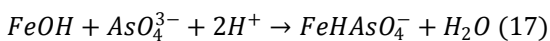
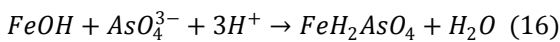
conditions As (V) also predominates according to the following equations



In equation (14) competition of Fe (III) as a terminal electron acceptor in microbial respiration and in equation (15) Mn (IV) oxidants oxidizes As (III).

Removal techniques

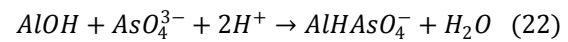
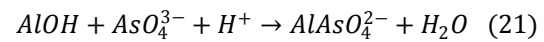
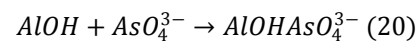
Arsenic from the water can be removed by some of the physic-chemical principles such as adsorption, oxidation, and precipitation. Most of the researchers made extensive research on adsorption using ferric hydroxide, aluminium oxides etc.



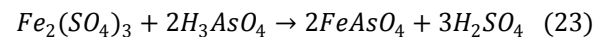
Hydrous ferric oxide (FeOH) is an important sorbent in natural and engineered aquatic systems. Adsorption of AS (III) increases with

decrease of As/Fe ratios. As (V) adsorption is higher at high pH (Wilkie and Hering, 1996).

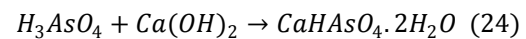
Dousova et al. (2003) explained the natural boehmite (monohydrates of trivalent aluminium oxide) is found to adsorb large amounts of As (V) and thus is suitable for As removal from water and waste waters and the reactions are as follows



Papassiopi et al., (1996) showed the precipitation of As using Fe³⁺. A molar ratios (FeAs) of 4, and an optimum pH of 5 at 33° C achieved less residual As in solution and the reaction as follows



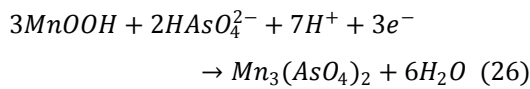
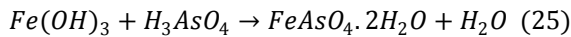
Stefanakis and Kontopoulus (1988) tried precipitation of As as calcium arsenate according to the following equation



Calcium arsenate which is unstable in aqueous environment and becomes insoluble.

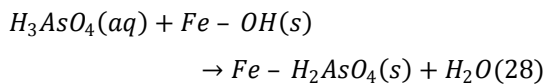
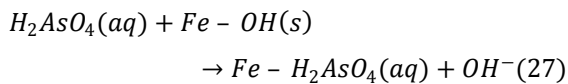
Masscheleyn et al., (1991) tried co-precipitation of As with hydrous Fe-oxide or hydrous Mn oxide, the As (V) can be

immobilized according to the following reaction

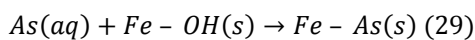


Adsorption of arsenic (kinematic and thermodynamic aspect)

Activated alumina (AA) and granular ferric hydroxide (GFH) are two most common used adsorbents used for arsenic removal. The ligand exchange is the only mechanism present for adsorption of arsenic (V) and arsenic (III) by hydrous iron oxide. The generalized reaction will be



For formulating the Kinetics, above two can be written as



The rate law of this reaction is (in general form)

$$\frac{d[As(aq)]}{dt} = -k_{ads} [As(aq)]^n [Fe - OH(s)]^m \quad (30)$$

n, m are constants representing the orders of reaction & [] represents molar concentration. Kinetics is nth order with respect to arsenic and mth order with respect to Fe - OH & n+m

overall. In the experiment conducted, the initial concentration of Fe - OH $\gg \gg$ [As(aq)]. Therefore this will behave as a pseudo order reaction. Therefore the transformed equation will be

$$d \frac{[As(aq)]}{dt} = -k'_{ads} [As(aq)]^n \quad (31)$$

$$k'_{ads} = k_{ads} [Fe - OH(s)]^m \quad (32)$$

The values from the experiments show that the value of n=1 represents the best curve fit. Thus it will be a pseudo first order reaction. And it can be written as

$$\ln[As(aq)_t / As(aq)_0] = -k't \quad (33)$$

As(aq)₀ is the initial concentration and As(aq)_t is the concentration at any time t.

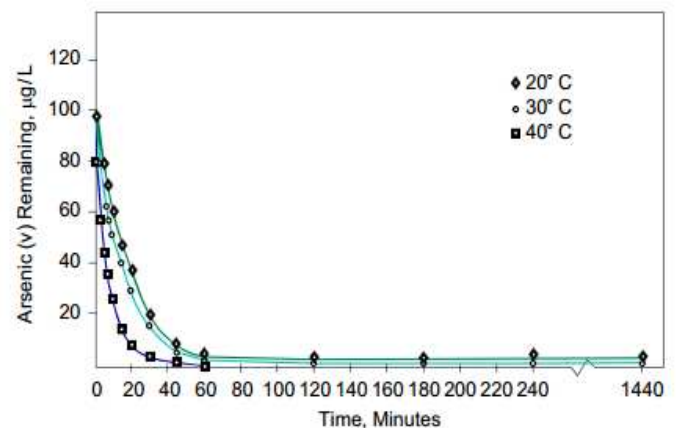


Fig 6. Rate of adsorption of As(V) at pH 6.5

Now we will consider the Thermodynamic aspect

$$\Delta G^0 = -RT \ln K \quad (31)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (32)$$

ΔG^0 is change in free energy kcal/mol; ΔH^0 is enthalpy change. Kcal/mol; ΔS^0 is the entropy

change; R be the gas constant; K is equilibrium constant. K can also be written as

$$K = \frac{[Fe - As(s)]}{[As(aq)]} \quad (33)$$

Considering $\{\} = []$, infinite dilution. The ΔH^0 can be estimated from the slope of $\ln K$ versus $1/T$ which follows the following equation.

$$\ln K = -\frac{\Delta H^0}{RT} + \text{constant} \quad (34)$$

Case Study of Arsenic in Bangladesh

About 90 percent of the districts (59 out of 64) in Bangladesh were suffering because of contamination of groundwater by arsenic. Concentration of arsenic in water had reached in mg/l while the prescribed limit is in $\mu\text{g/l}$

(**10 $\mu\text{g/l}$** suggested by WHO and $50\mu\text{g/l}$ by the government). It had been addressed as a '***national disaster***' by the government.

In 1998, British Geological Survey (BGS) collected 2022 water samples from 41 arsenic-affected districts. Laboratory tests revealed that 35% of these water samples were found to have arsenic concentrations above 0.05 mg/l and the highest concentration of arsenic of **14mg/l** was observed in Pabna district. About 1.2 million people were expected to be exposed by the arsenic in Bangladesh. The source of arsenic was not only the groundwater but also the food chain such as rice, fish and vegetables and because of this the problem is getting worse day by day.

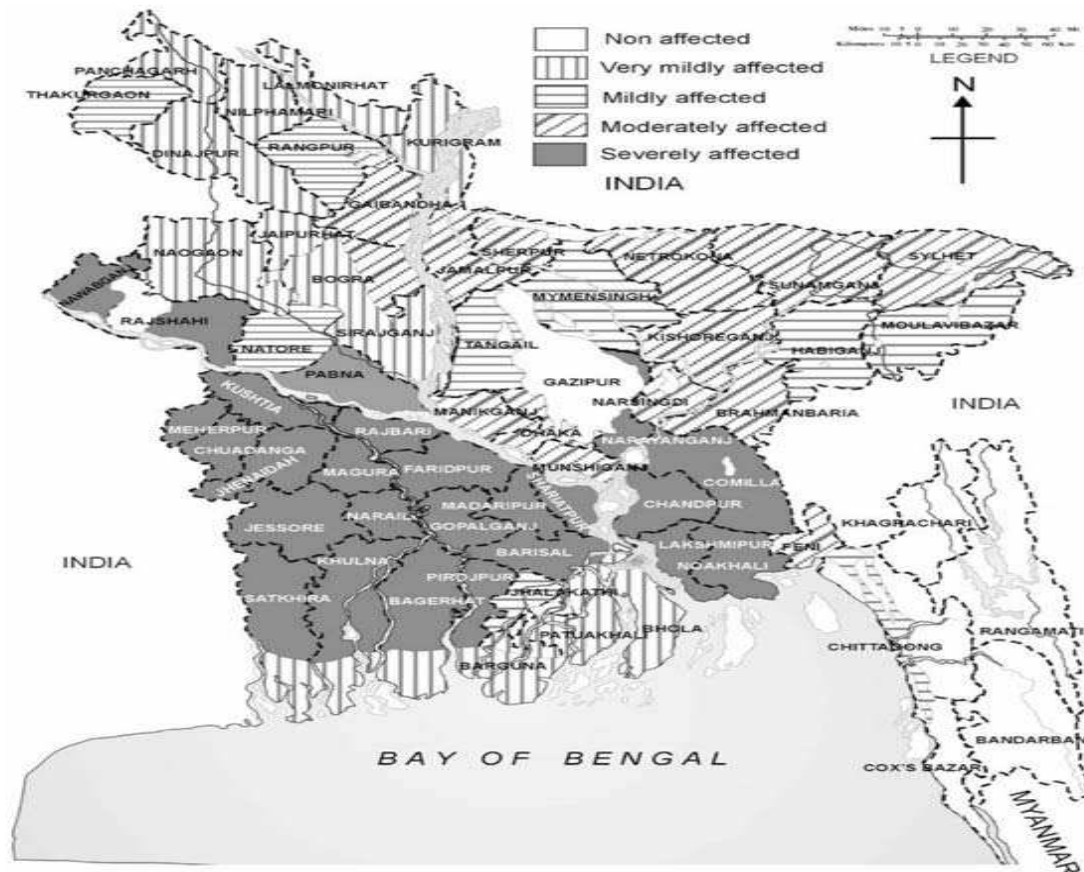


Fig. 6 (reproduced) Arsenic affected areas in Bangladesh (Chakraboorthy et al., 2002)

Conclusions

The excessive extraction of underground water is one of the many reasons of the arsenic contamination in Bangladesh which leads to the creation of aeration zones. At $\text{pH} \cong 7$, Arsenic (V) will mostly be present in the form of HAsO_4^{2-} and Arsenic (III) will be mostly be present in the form of H_3AsO_3 . And at this $\text{pH}=7$, if $\text{Eh} \cong 0.5$ the arsenic in water will be in the form of HAsO_4^{2-} . While doing adsorption of arsenic with granular ferric hydroxide most of removal is achieved in first one hour of adsorption at normal pH near 7. However the above results cannot be considered directly into the field conditions as here the concentration of Fe – OH is very large with respect to arsenic which may not be the case in real conditions. It was also observed that the adsorbed arsenic increases with increase in the temperature. Although adsorption processes have been well studied, further work is needed in understanding desorption processes and the factors that influence the kinetics of these

processes. Scope also exists for studies on both plant and microbial uptake of As and the possible use of plants as low-cost, long-term means of remediation of As-contaminated sites.

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Notes:

1. A **metalloid** is a chemical element that has properties in between, or is a mixture of, those of metals and nonmetals. There is no standard definition of a **metalloid**, nor is there complete agreement as to which elements are appropriately classified as such. The six commonly recognised metalloids are [boron](#), [silicon](#), [germanium](#), [arsenic](#), [antimony](#), and [tellurium](#). Elements less commonly recognised as metalloids include [carbon](#), [aluminium](#), [selenium](#), [polonium](#), and [astatine](#). On a standard periodic table all of these elements may be found in a diagonal region of the [p-block](#), extending from boron at one end, to astatine at the other

Metalloids					V·T·E
	13	14	15	16	17
2	B Boron	C Carbon	N Nitrogen	O Oxygen	F Fluorine
3	Al Aluminium	Si Silicon	P Phosphorus	S Sulfur	Cl Chlorine
4	Ga Gallium	Ge Germanium	As Arsenic	Se Selenium	Br Bromine
5	In Indium	Sn Tin	Sb Antimony	Te Tellurium	I Iodine
6	Tl Thallium	Pb Lead	Bi Bismuth	Po Polonium	At Astatine

Commonly recognised as a metalloid (93%): B, Si, Ge, As, Sb, Te

Irregularly (44%): Po, At

Less commonly (24%): Se

Rarely (9%): C, Al

Metal–nonmetal dividing line (arbitrary): between Be and B, Al and Si, Ge and As, Sb and Te, Po and At

Allotropes are different structural modifications of an element; the atoms of the element are bonded together in a different manner

Arsenic	<ul style="list-style-type: none"> • Yellow arsenic – molecular non-metallic As₄, with the same structure as white phosphorus • Gray arsenic, polymeric As (metalloid) • Black arsenic – molecular and non-metallic, with the same structure as red phosphorus
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Gray (alpha) Arsenic [As_4 up to 800°C, As_2 above 1700°C]

The most stable allotrope of arsenic, with a rhombohedral structure. It has a layered microstructure, metallic glow, steel grey colour, it is soft and very brittle. It conducts electricity.

At atmospheric pressure it sublimates at 613°C, and at a pressure of 36.4 kPa it melts at 817°C.

Up to 800°C arsenic vapours are as As_4 , and above 1700°C it is As_2 . With humid air it reacts at room temperature, and if heated in air it burns a blue flame, creating thick fumes of As_2O_3 with a garlicky smell. At room temperature it directly bonds with [fluorine](#) and [chlorine](#), and when heated it bonds with [bromine](#), [iodine](#) and [sulphur](#).

It does not bond with [nitrogen](#), [boron](#), [silicon](#) and [carbon](#). Strong oxidative acids, as concentrated [nitrogen](#) acid, oxidize it to arsenic acid, dissolved [nitrogen](#) acid doesn't oxidize to arsenate acid. It forms alloys with most metals.

Yellow (beta) Arsenic [As_6]

An allotrope of arsenic with a hexagonal structure which forms by abrupt cooling of arsine gases (AsH_3). It is soft as wax and doesn't conduct electricity. It is unstable at room temperature, when affected by light it quickly and easily turns to grey arsenic.

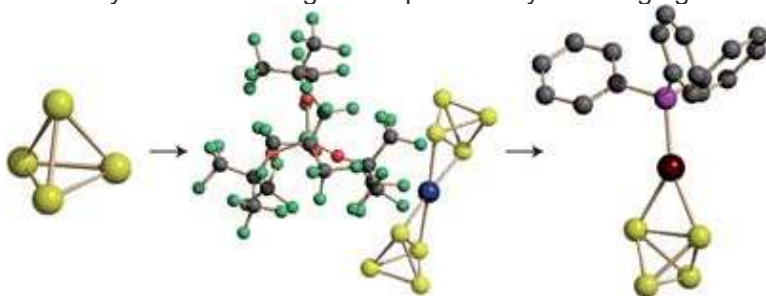
Amorphous Black Arsenic []

Amorphous black arsenic is produced by sublimation of arsenic without the presence of air. It also forms from the break up of arsenic-hydrogen with heat where it is excreted as vapour by creating a mirror layer (so called "arsenic mirror"). This reaction is used to prove small amounts of arsenic in case of suspicion of poisoning (Marsh test).

When heated at 360°C it turns to stable grey arsenic

Yellow arsenic is the most toxic and the most unstable; it decomposes quite readily, especially when exposed to light. It resembles the white allotrope of the lighter pnictide phosphorus — also a toxic and unstable tetrahedral species

It is still possible to use As_4 in chemistry by freshly preparing it from the grey allotrope — but its light-sensitivity makes working with it particularly challenging.



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For these reasons, there has been limited research on the reactivity, properties, and potential uses of yellow arsenic. Now, a team of scientists in Germany led by Manfred Scheer at the University of Regensburg have prepared a relatively stable silver complex featuring two As_4

ligands. The complex can be stored at $-30\text{ }^{\circ}\text{C}$ without decomposing and can be used as an As_4 transfer agent (pictured)

Extremely light sensitive yellow arsenic (As_4) reacts with a weakly coordinated silver cation to afford $[\text{Ag}(\eta^2\text{-As}_4)_2]^+[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]^-$ as the first known homoleptic arsenic complex. DFT calculations and Raman spectroscopy clearly indicate the coordination of two intact As_4 tetrahedra. This unprecedented complex is used as an As_4 transfer agent, which is demonstrated by the synthesis of $[(\text{PPh}_3)\text{Au}(\eta^2\text{-As}_4)]^+[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]^-$.