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Arsenic removal from water using advanced oxidation processes

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Abstract

Consumption of groundwaters containing natural arsenic at several hundred μg/l (ppb) in countries such as Bangladesh has lead to the increased occurrence of many cancers particularly those of the skin and bladder, while concerns in the USA and Australia regarding the unknown health impact of drinking water containing tens of ppb of arsenic is leading to increasingly stringent maximum contaminant levels. The anaerobic conditions of these groundwaters result in the arsenic being present in its reduced form, hence the use of an oxidant is necessary if the arsenic is to be successfully removed by precipitation or ion exchange methods. Advance oxidation methods which utilise ultraviolet light and a photo absorber have been developed and patented, in which both iron salts and sulphite can be used as the photoabsorber. The former absorber has been developed for arsenic removal in rural areas of Bangladesh and the latter for groundwaters in countries such as the USA. © 2002 Elsevier Science Ireland Ltd. All rights reserved.

Keywords: Arsenic; Removal; Advanced oxidation processes; Acid mine water; Tubewell water

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1. Introduction

Arsenic (As) is a ubiquitous element present in various compounds throughout the earth's crust. Contamination of the environment with arsenic from both natural and anthropogenic sources is widespread, occurs in many parts of the world and may be regarded as a global issue. It is widely distributed and mainly transported in the environment by water. Arsenic can impact human health through the ingestion of surface and ground water used for water supply. Chronic arsenic poisoning occurs in Argentina, Bangladesh, Chile, China, India, Inner Mongolia, Mexico and Taiwan by drinking water, in which the arsenic concentration is up to 2 mg/l. It is estimated that more than 20 million people in Bangladesh are drinking water with arsenic concentrations exceeding the current Bangladesh standard of 0.05 mg/l. In recent years, environmental authorities have taken a more stringent attitude to arsenic in the environment; WHO (1993) and NHMRC (1996) guidelines for arsenic in drinking water are 0.01 and 0.007 mg/l because of the concerns for health/cancer risk (Chen et al., 1988).

With these new regulations, the need to remove arsenic from groundwaters and wastewaters such as acid mine waters, tailings and process liquors

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becomes important. Many of the waste streams contain As(III), which requires oxidation before it can be removed by common methods such as iron co-precipitation or ion exchange. Since the oxidation rate of dissolved As(III) by oxygen is extremely slow, oxidants such as chlorine, ozone or permanganate need to be used. Chlorine has traditionally been the oxidant of choice, but there are growing concerns regarding the generation of organochloride byproducts from the naturally occurring organic matter which may also be present. Recently, it was discovered that, in the presence of near-UV light and dissolved iron (Fe) compounds, the oxidation rate of dissolved As(III) by air can be increased by more than four orders of magnitude without using chemical oxidants (Khoe et al., 1997); the oxidised arsenic can then be removed by an iron co-precipitation. Thus the added iron acts as an oxidant as well as a coagulant. The oxidation of As(III) to As(V) provides an additional benefit by producing more stable solids for safe disposal.

The light-enhanced oxidation and immobilisation process was used to treat acid mine water from an abandoned gold-lead-silver mine during a demonstration project in Montana, USA in 1996. This iron-based sunlight assisted process was also demonstrated in a village in Bangladesh in December 1998. Elevated concentrations of arsenic in groundwater in Bangladesh are generally caused by the dissolution of naturally occurring arsenic-bearing minerals (BGS, 1999).

More recently, a new advanced oxidation process has been developed which is more effective at neutral or alkaline pHs. (Khoe et al., 1998). Dissolved sulphur(IV) (or other oxidisable sulphur forms) is used as a photo-absorber in an UV assisted sulphite-oxygen process.

2. The iron-based UV-oxidation process

2.1. Treatment of acid mine water

The light enhanced iron-based oxidation process (Khoe et al., 1997) was used to treat acid mine waters from an abandoned gold-lead-silver mine located in Rimini, Montana (USA). Australian Nuclear Science and Technology Organisation (ANSTO) collaborated with MSE Technology Applications, Inc. of Butte, Montana to carry out the demonstration in August–September 1996 (MSE Final Report, 1997). In this project, test streams with low (acid mine water draining from Susie Mine, parts per million) arsenic concentrations were treated. Two types of photo-reactors were used for the demonstration: (a) light weight plastic troughs ($\sim$ 85 l each) for the sunlight-based process, and (b) a 570 l commercial UV lamp reactor with 24 low pressure mercury lamps each of 65 W capacity. The dissolved oxygen in all cases was maintained by air sparging.

Many of these waters contain dissolved arsenic in the trivalent and pentavalent states, while iron is usually present in significant concentrations in acid mine waters. Depending on the oxidation-reduction potentials of the waters, a high proportion of the iron can be present as Fe(II); for example the mole ratio of Fe(II)/As(III) present in five acid mine waters surveyed in Montana in 1994–1996 varied from 12 to 506 (MSE Final Report, 1997). In conventional treatment plants, the presence of a large excess of Fe(II) in the feed water would result in an extra requirement for chemical oxidant because all the dissolved Fe(II) would need to be oxidised first in order to ensure the completion of arsenic oxidation.

In this project, dissolved Fe(III) in the presence of UV light was used to initiate and sustain the oxidation of As(III) in acid water. The arsenic oxidation process in the abandoned mine water was complete in about 1–6 h in the presence of sunlight during an autumn afternoon (Fig. 1a). The 10 mg/l As(III) initially present was oxidised in the presence of a large excess of Fe(II) [180 mg/l and Fe(II) to As(III) mole ratio of 24]. Hydrochloric acid was added to adjust the typical pH range in acid mine waters to between 1.5 and 3 (Kelly, 1988) because of the unusually high pH (4.8) of the mine water. No extra Fe(III) addition was necessary for acid mine waters containing sufficient dissolved Fe(III). Fig. 1b shows that the arsenic oxidation kinetics are much faster than those produced by sunlight alone. This is due to the higher intensity and shorter wavelength of the light. The rate of As(III) oxidation is proportional to the concentration of hydrochloric acid addition. The photolysis reactions of Fe(III) in water involve the transfer of one electron from the complexed ligand, such as organic, hydroxide or chloride species, to a Fe(III)-centred orbital forming Fe(II) and a free radical (Zafiriou et al., 1984). The generated hydroxyl radicals then oxidise As(III).

$$Fe^{3+}(OH)^{-} \xrightarrow{hv} Fe^{2+} + {}^{\bullet}OH$$

2.1.1. Solidification of the iron sludge

The oxidised arsenic in the Susie Mine water was removed from the solution by iron co-precipitation at pH 7. Oxidation of ferrous ions to ferric and precipitation of the hydroxide was achieved by aeration and pH adjustment with lime. The obtained precipitated hydroxide with co-adsorbed arsenic containing excess iron (Fe/As mole ratio of at least 22/1) was dried at room temperature. For the preparation of the cement-solidified samples, the dried filter cakes were weighed and then mixed with ordinary Portland cement, lime and a measured quantity of water. The mixture was packed into a 125 ml PVC mould and cured for 28 days before being subjected to standard Toxicity Characteristic Leaching Procedure (TCLP) test (US EPA, 1990) and aerated water leach tests (Zaw et al., 1999). Both tests were performed on the precipitates with and without cement solidification.

2.1.2. Leachability test of arsenic-bearing solids

All the treatment residues (with and without cement solidification from both Solar and Ultrox tests) met the requirements of the US-EPA standard TCLP test for landfill disposal. Arsenic concentrations in the TCLP leachates were < 10 μg/l for dried filter cakes and < 32 μg/l for cement solidified samples. In addition to the standard TCLP test, the long-term aerated water leach test (up to 3 months) was also performed to verify whether arsenic was present in the residues as iron-arsenate material. Calcium arsenate compounds, which are subject to attack by dissolved atmospheric carbon dioxide (Robins and Tozawa, 1982), may form during the lime neutralisation operation usually practised in conjunction with the iron co-precipitation process. Arsenic concentrations in the aerated leachates were < 12 μg/l for dried filter cakes and < 85 μg/l for cement solidified samples after 3 months.

2.2. Treatment of tubewell water in Bangladesh

In December 1998, a field demonstration of the ANSTO-CRCWMPC process (Khoe et al., 1997) was performed in Sonargaon village about 30 km from Dhaka. Arsenic was successfully oxidised and removed from water taken from four tube-

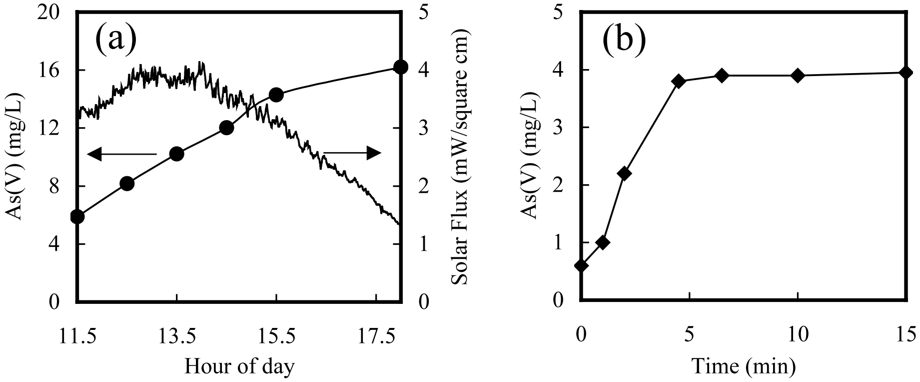

Fig. 1. The oxidation of As(III) in acid mine water and ground water from Susie Mine in Montana in the presence of (a) sunlight (added Fe(III) 190 mg/l and total As 16 mg/l in acid mine water) and (b) UV light (254 nm) with power input 3 W/l (added Fe(III) 25 mg/l and total As 4 mg/l in ground water) at pH 2.

wells. Analyses of the tubewell waters show that the initial total arsenic concentration was between 0.25 and 1 mg/l with 60–90% of the arsenic present as As(III) (phosphate concentration was between 0.9 and 1.8 mg/l). The bicarbonate concentration in the water was in the range of 360–500 mg/l and the water pH from 7 to 7.5.

Bench-scale testings using tubewell water in Sonargaon indicated the following information.

1. The naturally occurring iron concentration of 5 mg/l only removed a quarter of the arsenic and only a small amount of arsenic was oxidised on exposure to sunlight for 3 h.
2. For a given Fe(III) dose, an exposure to sunlight for 3 h reduced the residual arsenic concentration. This effect is most marked once sufficient Fe(III) is added (20 mg/l); further addition of iron does not increase the amount of arsenic oxidation. It should be noted that the intensity of the sunlight during this test was lower than usually experienced in Bangladesh, as the test was performed near the winter solstice, and that there was a high haze (the solar flux was measured using a non-tracking Solar Light Co UV meter).
3. The high alkalinity in the groundwater (360–500 mg/l bicarbonate) precludes the need for pH adjustment even when a significant quantity of iron(III) salt is added. This makes the process simple to use for the villagers.

A shallow plastic tray was used for the photo-oxidation and complete settling of the precipitated iron hydroxide sludge was achieved overnight using a plastic urn. The arsenic concentrations in the tubewell water obtained from one test site before and after treatment, with/without light are shown in Fig. 2. The initial total arsenic concentration was 1 mg/l with 90% as As(III).

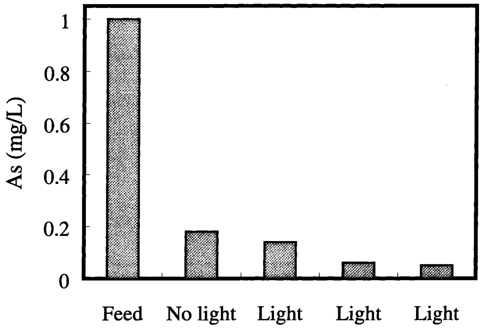

Fig. 2. Arsenic content of water from a tubewell before and after treatment. The three sunlight-assisted tests were performed on three occasions.

3. The sulphite-based UV-oxidation process

Recently, a new advanced oxidation process using dissolved sulphur(IV) (sulphite) as the photo-absorber has been developed and patented. It has been known for more than 70 years that when a mixture of sulphur dioxide and oxygen is bubbled in a solution, the mixture behaves as an oxidant, e.g. the oxidation of dissolved ferrous in acid solution (Ralston, 1927). The novelty introduced in the ANSTO-CRCWMPC process (Khoe et al., 1998) is the use of UV light to accelerate the oxidation reaction, which in some cases hardly proceeds without illumination, e.g. the oxidation of arsenic in the presence of dissolved carbonate, which is common in groundwater.

The acceleration in the rate of oxidation of arsenic in the presence of UV light and dissolved sulphite is depicted in Fig. 3. It shows the increase in As(V) concentration and the concomitant decrease in sulphite concentration when 1.7 l of solution containing 0.47 mg/l of As(III) and 10 mg/l of sulphite was illuminated with 11 mW/cm^2 of UV light from a low-pressure mercury lamp (non-ozone producing). The corresponding

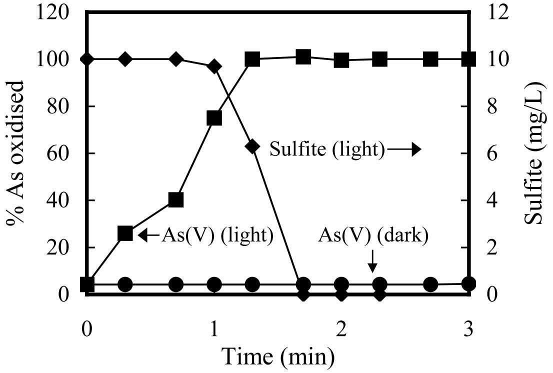

Fig. 3. As(V) and sulphite concentration as a function of elapsed time in the presence and absence of UV light.

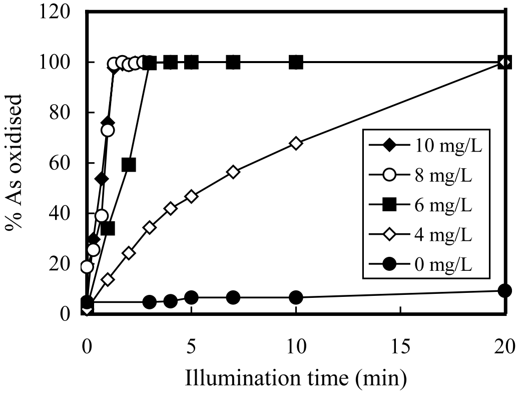

Fig. 4. Arsenic oxidation rate as a function of the initial sulfite concentration in the reaction mixture (varied from 0 to 10 mg/l of sulphite (as SO_3^{2-}) and initial arsenic concentration 0.47 mg/l).

change in As(V) concentration in the absence of UV light is also shown. Air was bubbled at a rate of 2.5 l/min and the solution was adjusted to pH 9 using sodium carbonate. The corresponding changes in As(V) concentrations in the present and absence of UV light were measured by the molybdenum blue spectrophotometric method (Johnson and Pilson, 1972). Sulphite concentrations were also determined spectrophotometrically (Humphrey et al., 1970).

The rate of As(III) oxidation as a function of the initial sulphite concentration is shown in Fig. 4. In the absence of sulphite no arsenic oxidation was observed as the 254 nm photons were not absorbed. In contrast, complete oxidation occurred when 4 mg/l of sulphite was added and the time required for completion was decreased by the use of higher concentrations up to 8 mg/l. Although not shown, the sulphite was also completely oxidised so that the oxidised water contained sulphate at less than one tenth of its maximum contaminant level.

4. Conclusions

The iron-based photo-oxidation process was successfully used to oxidise and remove arsenic from mine water draining from an abandoned hard rock gold, silver and lead mine in Montana. The water treatment residues with and without cement solidification passed the standard US EPA leach test for landfill disposal. In addition, the solids were shown to be stable when subjected to leach testing using aerated water for 3 months. The ability of the sunlight-assisted process to oxidise and remove arsenic from tubewell water was also demonstrated in a village in Bangladesh. The high carbonate alkalinity usually present in the groundwater precludes the need for pH adjustment even when a significant quantity of iron(III) salt is used for photo-oxidation; the subsequent arsenic removal is achieved by coagulation/settling. This makes the process simple to use for villagers in rural areas without electricity.

The new advanced oxidation process using sulphite as the photo-absorber is being applied to drinking water treatment. The UV/sulphite process is preferred for use with commercial UV disinfection hardware as no solids are generated which may foul the lamps. The effluent from the UV/Sulphite process is also amenable to all techniques for As(V) removal.

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