Chemical Engineering Journal 243 (2014) 364–371

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Photo-oxidation of *p*-arsanilic acid in acidic solutions: Kinetics and the identification of by-products and reaction pathways

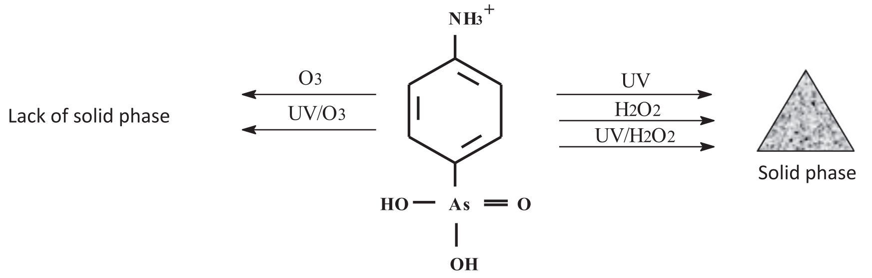
Marianna Czaplicka [a,*], Łukasz Bratek [a], Katarzyna Jaworek [a], Jan Bonarski [b], Sylwia Pawlak [b]

[a] *Institute of Non Ferrous Metals, Sowinskiego 5 Str, Gliwice, Poland*
[b] *Institute of Metallurgy and Materials Sciences, Polish Academy of Sciences, Reymonta 25 Str, Krakow, Poland*

HIGHLIGHTS

- Pseudo-first order rate constants are determined for each processes.
- The degradation pathways are proposed for ozonation and photoozonation.
- The degradation pathways are proposed for oxidation and photooxidation by H_2O_2.
- Formation of solid phases are observed.
- Characterization of solid phases were done.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 September 2013
Received in revised form 19 December 2013
Accepted 8 January 2014
Available online 17 January 2014

Keywords:
Organoarsenic compounds
Photodegradation
Photo-oxidation
Mechanism
Solid phase

ABSTRACT

Arsenic compounds have been used extensively in agriculture for applications ranging from cotton herbicides to animal feed supplements. While studying the kinetics and mechanism of *p*-arsanilic acid degradation via oxidation, the photodegradation and photo-oxidation processes that occurred while using irradiation at 254 nm were assessed. Ozone and hydrogen peroxide were used as oxidants. The relationships among the process efficiency, the process conditions and the type of oxidiser were demonstrated. The rate constants for the decomposition based on pseudo first order kinetics were $0.76 \times 10^{-3}\ min^{-1}$ during photodegradation, $27.85 \times 10^{-3}\ min^{-1}$ during ozonation and $35.1 \times 10^{-3}\ min^{-1}$ during photo-ozonation, $32.3 \times 10^{-3}\ min^{-1}$ during oxidation with H_2O_2 and $36.4 \times 10^{-3}\ min^{-1}$ during photo-oxidation with UV/H_2O_2.

After identifying the major products, degradation mechanisms were proposed. During photodegradation, oxidation and photo-oxidation with H_2O_2, the generation of a solid phase composed primarily of $As_3O_5(OH)$ was observed.

1. Introduction

Arsenic can occur naturally, but it may also be found in products used during various industrial processes, including leather and wood treatment, as well as in pesticides [1–3]. Anthropogenic arsenic contamination mainly arises from the production of metals and alloys, the refining of petroleum and the burning of fossil fuels and wastes. The concentration of arsenic in waters attributed to non-ferrous metallurgy may reach 16 g L^{-1} [4]. Depending on its redox potential (Eh) and pH, arsenic can take three forms in water. A high redox potential facilitates the generation of stable forms, such as H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ at lower Eh values, the stable form is represented by metallic arsenic. Numerous examinations of natural waters have enabled the identification of 25 various arsenic compounds.

In the natural environment, organic compounds containing arsenic are usually due to biological activity or the influence of copper metallurgy on the environment. Also, groundwater and soil contain organoarsenic species: monomethylarsenic acid (MMA), dimethylarsenic acid (DMA), trimethylarsine oxide and trimethyl arsine [5]. The presence of other organic compounds containing

---

[*] Corresponding author. Tel.: +48 23 238 0267.
E-mail address: mariannac@imn.gliwice.pl (M. Czaplicka).

1385-8947/$ - see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cej.2014.01.016

arsenic in the natural environment was also established, including phenylated arsenic compounds (e.g., 4-hydroxy-3-nitrophenylarsenic acid (roxarsone), 4-aminophenylarsenic acid (*para*-arsanilic acid)) [6]. Organoarsenic compounds typically exist in a pentavalent oxidation state and are introduced into the environment due to agricultural applications. *Para*-arsanilic acid (PPA) and roxarsone are used as animal feed additives for both pigs and chickens, while nitarsone and carbarsone are used to control blackhead disease in turkeys [7].

Numerous studies have covered the transformation of inorganic arsenic compounds during natural processes. Numerous oxidative methods have been employed to convert arsenite to arsenate under various conditions, such as with H_2O_2 [8,9], UV/H_2O_2, oxygen and ozone (O_3), MnO_2, Fenton's reagent (Fe(II)/H_2O_2) or UV/Fe(III) [10–12]. However, each method has specific limitations and disadvantages. Photocatalytic processes for arsenic species are widely discussed in the literature, but few processes have been applied to the oxidation of organic arsenic species, such as hydrothermal treatments [13,14], TiO_2 photocatalysis [13–17], and radiolysis [18]. TiO_2 photocatalysis is an effective method for oxidising of organic arsenic species, such as MMA, DMA, and phenylarsonic acid [19–23].

Due to the use of PAA as an animal feed additive, particularly in the USA [7] and its presence in the process stream that enters the environment [4], determining the conditions of the degradation of PAA is important. The main objective of this study was to determine the kinetics and mechanisms of photodegradation, specifically the oxidation and photo-oxidation of *p*-arsanilic acid in an acidic environment. Ozone and hydrogen peroxide were used as oxidising agents. The efficiency of the processes depend the on process conditions and type of oxidiser. During photodegradation, oxidation and photo-oxidation with hydrogen peroxide, a solid phase mostly composed of $As_3O_5(OH)$ was generated. The results indicated that the AOP processes in an acidic environment can be used to remove arsenic from water as an insoluble precipitate.

2. Materials and methods

The studies were performed using a 8.9 mmol L^{-1} *para*-arsanilic acid (Supelco Analytical, USA) solution, corresponding to 4.4 mmol L^{-1} arsenic. The base solution was prepared with demineralised water, and the pH was corrected to approximately 2 with hydrochloric acid (1:1).

The photodegradation and photo-oxidation studies were conducted with a photoreactor (Kendrolab laboratory UV "System 4" reactor, Heraeus, Germany) and a low-pressure mercury-discharge lamp (14 W) cooled by a water jacket emitting at 254 nm.

The oxidising agents (ozone and hydrogen peroxide) were introduced into the reactor. A predefined dose of H_2O_2, 50 mL (18.5 g) per 1 L of the input solution with 4.4 mmol L^{-1} arsenic was added to the reactor in 10 equal batches at 5 min intervals. A Wofil Ozone Technology (Ozonia, Switzerland) O1 ozone generator with a 5 g O_3 m^{-3} capacity, corresponding to 12 g O_3 h^{-1}, was supplied with oxygen from a cylinder and was used to provide 2.2 g O_3 h^{-1} to the reaction.

During photodegradation, ozonation, oxidation with hydrogen peroxide and the advanced oxidation processes (UV/O_3 and UV/H_2O_2) the pH, redox potential (Eh), conductance and temperature were continuously measured. Studies regarding the photodegradation, oxidation and photo-oxidation were conducted for 360 min.

After each cycle, the reaction solutions were stored in the dark for 72 h. After a solid phase was generated, the solutions were filtered; the residue was dried at 50 °C. The duration used to age the solutions was determined using the kinetics of their sedimentation.

2.1. Analytical procedures

The *para*-arsanilic acid (PPA) was determined using HPLC with a Perkin Elmer Series 200 DAD detector (Perkin Elmer, USA) and an Aquapore OD-300 (7 μm, 250 × 4.6 mm) column (Perkin Elmer, USA) in a reversed phase system. The isocratic elution was performed using 50 mM pH 2.6 phosphate buffer (potassium dihydrogenphosphate and water with the pH adjusted with phosphoric acid to pH 2.6) as a mobile phase. The determination was made at $\lambda = 260$ nm wavelength.

The oxidation and photo-oxidation products of *PPA* were determined using gas chromatography coupled with a mass detector (GC/MS) with Perkin Elmer equipment. Solid phase microextractions were used to separate the analytes from the solutions by applying fibres with varying polarities: 65 μm polydimethylsiloxane divinylbenzene (PDMS/DVB), 75 μm Carboxen (CAR), 85 μm polyacrylate (PA) [24,25]. The process products were identified based on the retention time and mass spectrum of the compounds. A spectrophotometric method was applied to determine the ammonium ions.

The arsenic in solid phase was determined after mineralisation in a mixture of nitric(V) and sulphuric(VI) acids using atomic absorption spectroscopy with atomisation in a graphite furnace (GFAAS) through a direct method.

2.2. X-ray diffraction analysis of solid phase

The X-ray phase analysis of the solids was based on X-ray diffraction patterns recorded with a Bruker *D2 Phaser* (Bruker Cooperation, USA) diffractometer equipped with an *X Flash* detector and energy-filtered radiation. In the experiments Cu Kα-serie radiation was applied. The phases were identified with *EVA* software delivered by *Bruker Comp*. and the *ICDD* crystallographic database (*PDF + 4* package). Based on the experimental patterns, the volume fractions of the identified phases were estimated.

3. Results and discussion

The efficiency of PPA decomposition by photolysis, oxidation, UV/O_3 and UV/H_2O_2 processes in acidic environment depends on the conditions, the type of process and the oxidant. Of the examined processes, photodegradation is the least efficient for PPA decomposition; only 17.7% PPA was removed, and the constant of decomposition rate under pseudo first order kinetics was 0.76×10^{-3} min^{-1} (Table 1). The rate constants for ozonation and photo-ozonation were 27.89×10^{-3} min^{-1} and 32.3×10^{-3} min^{-1}, respectively. In Fig. 1, the linear relations of $\ln(c_t/c_o)$ versus t are presented.

Using hydrogen peroxide as the oxidiser resulted in 100% decomposition of the arsenic compound after 180 min. The process ran at a constant rate of 32.3×10^{-3} min^{-1}. Upon comparison between ozonation and the oxidation with hydrogen peroxide, hydrogen peroxide is a more efficient oxidiser for PPA than ozone under the examined conditions (Table 1). The slower rate of ozonation relative to the oxidation with H_2O_2 was due to the pH dependence of the ozone form. At pH 2, the ozone remains in its molecular state and can participate in the direct oxidation reactions. Hoigné and Bader [26] found out that under acidic conditions, the direct oxidation with molecular ozone is the most important. Direct oxidations with aqueous ozone are relatively slow compared to indirect oxidations with hydroxyl free radicals. Using a UV/H_2O_2 system resulted in 100% decomposition of PPA after 140 min, achieving a rate constant of 36.4×10^{-3} min^{-1}. The rate of PPA photo-oxidation with H_2O_2 exceeded that of photo-ozonation.