Organic matter decomposition before arsenic speciation analysis of water sample — "Soft decomposition" using nano-photocatalysts
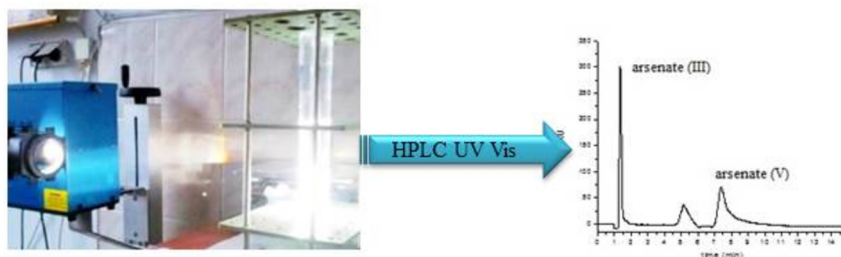
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HIGHLIGHTS

- Organic matter in water limits applicability of speciation analysis.
- Nano-semiconductors supports decomposition of surfactants.
- Argon saturation limits the formation of active oxygen species.
- Decomposition assisted with nano-photocatalysts do not disrupts arsenic speciation analysis.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

The applicability of photolysis in the speciation analysis of arsenic is investigated. The use of nano scale semiconductors ($Fe_2O_3/WO_3/Fe_2O_3$ at pH 6) as an active film during solar light irradiation of a water sample, containing some surfactants (SDS), results in the simplification of the organic matter and gives no speciation change in the arsenic. The reproducibility of active layer is shown to be high and the surface roughness of each photoactive sample and photocurrent do not differ by more than 6 and less than 8%, respectively. The procedure of sample pretreatment caused a minimum (8—10%) amount of speciation change, whilst the irradiation is no longer that 2 h. The study indicates that "soft decomposition" can be performed for as long as 4 h, and still give photostable arsenates (III) and methylarsenate species. However, the saturation of the water sample with Ar is required (to reduce the oxygen content) for the longer the decomposition time being applied.

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1. Introduction

The environmental water is responsible for the spread of mobile and bioavailable forms of elements. Moreover, there are specific elements which have varying toxicity and mobility depending on their chemical form. Arsenic belongs to a group of potentially very toxic elements, listed as priority hazardous substances and considered within the top 20 contaminants by the US Environmental Protection Agency (US EPA, 2015). It is a well-documented human carcinogen, which affects numerous organs. Extensive toxicity studies of As show that inorganic arsenic species are about 100 times more toxic than organic arsenic compounds. Trivalent arsenic is about 60 times more toxic than the oxidized pentavalent state (Rajaković et al., 2013). Methylation of inorganic arsenic, in

the environment and in the tissues of living organisms, is a detoxification process. Such organic derivatives like arsenobetaine (AsB), arsenocholine (AsC), and arsenosugers are considered non-toxic. In natural water, arsenic appears most often in inorganic forms and to a lesser extent as monomethylo- (MMA) and dimethyloarsenic acids (DMA). As(V), MMA, and DMA are stable in oxidized systems, while As(III) is unstable (Kumar and Riyazuddin, 2010). The increase of oxidizing potential in water, the activity of microorganisms, and the redox reaction with Mn(IV) or Fe(III) cause As(V) ions to be the dominant form of As (Kumar and Riyazuddin, 2010). Nevertheless, it must be stressed, that arsenic compounds may be converted from one form to another and equilibria may be shifted between different chemical forms of this element in the environment (Bednar et al., 2002; Fayiga and Ma, 2005; Francesconi et al., 2002; Zhang et al., 2002). Distinction between chemical forms of As is a key factor in monitoring the contamination of aquatic environment.

Numerous analytical techniques and methods may be used to complete speciation analysis of arsenic in water samples. The most popular methods utilize high performance liquid chromatography (HPLC), used for separation of particular compounds, and this is coupled with a spectroscopic detector: to perform UV/VIS spectrometry (Ali and Aboul-Enein, 2002; Jedynak et al., 2008) or ICP MS (mass spectrometry after plasma ionization) (Bednar et al., 2002; Komorowicz and Barałkiewicz, 2011; Wuilloud et al., 2006; Zheng et al., 2003). Most of the analytical methods considerably suffer from the presence of organic matter in the test samples (Korolczuk et al., 2014; Krasnodebska-Ostrega et al., 2011). Even during ICP MS measurements the interferences are noted. Carbon resulting from high temperature oxidation of organic compounds, can settle on the cones and sulfur can create isobaric interferences. In addition, these compounds cause a decrease in the surface tension of the solution during nebulization of the sample, which results in undercounting and decreases the limit of detection (LOD) (Ospina-Alvarez et al., 2015).

An increasing content of organic compounds and surfactants in the water samples is a result of development throughout various industrial fields. As their presence very often precludes obtaining the reliable results from analysis, a digestion procedure of the matrix is usually required. Unfortunately, application of any commonly used digestion strategy with the concentrated inorganic acids cannot be applied during speciation analysis, as all information about initial speciation would be obscured. Undoubtedly ultraviolet light (with a wavelength between 100 and 400 nm) can degrade chemical bonds to a large extent, but it may also cause oxidation or reduction of the analytes (Golimowski and Golimowska, 1996). For example arsenate (III) in the presence of UV irradiation can be oxidized by approximately 30–40%. When the process is carried out with the addition of hydrogen peroxide, the oxidation efficiency significantly increased (Lescano et al., 2011; Sorlini et al., 2014). Very efficient phytochemical oxidation of As(III) (>90%) is also observed in the presence of iron ions (Emett and Khoe, 2001; Hug et al., 2001; Molinari and Argurio, 2017). The speciation of arsenic could also be disturbed by nitrate reduction assisted by UV radiation in natural water (Bednar et al., 2002). Bissen has reported a very efficient process of oxidation of As(III) in water, 54% of As(III) was oxidized to As(V) within 45 min, in the presence of TiO_2 (Bissen et al., 2001). Moreover, the presence of O_2 and CO_2 in the sample can change the equilibrium between the particular species of studied elements (US EPA, 2015). There is reported work showing that the oxidation of arsenic can take place with dissolved oxygen in water, and its influence on hydrogen peroxide as a direct oxidative agent. It was estimated that by using air or pure oxygen, approximately 54–57% of As(III) can be oxidized to As(V), in contaminated groundwater (Kim and Nriagu, 2000).

Changes in the pH value as well as the content of chloride or iodide ions should be also taken into consideration. It is postulated that As(III) is stable in water at neutral pH. No changes in inorganic arsenic speciation are documented in sea water within the pH range of 6–8. While acidification of the water sample to pH 1 showed that As(III) is gradually oxidized to As(V) within 30 min (Salaün et al., 2007).

The literature, indicates that high energy photolysis assisted with TiO_2 and UV light is a very efficient process for the oxidation of As(III). The phyotocatalytic oxidation of As(III) to As(V), followed by adsorption of As on TiO_2 is proposed by Dutta et al. (Dutta et al., 2005, 2004; Miller et al., 2011). The application of nanocrystalline Al_2O_3 and TiO_2 impregnated chitosan is described by Yamanti (Yamani et al., 2012). It is postulated that As(III) is photooxidised to As(V) by TiO_2 and then adsorbed by Al_2O_3, but complete oxidation requires a sufficient amount of TiO_2. Complete photocatalytic conversion of As(III) to As(V) was observed in the presence of a MoO_x/TiO_2 catalyst supported on quartz flasks under 120 min of UV irradiation (Vaiano et al., 2016).

In speciation analysis, a simplification of the sample matrix, without species transformation, is crucial, especially in the case of water polluted with surfactants. Therefore, in the presented work the application of phytocatalysis using a solar lamp (380–800 nm) is proposed as a pretreatment method for the samples. The method utilizes safe phytocatalysts, such as metal oxides: TiO_2, WO_3, ZnO, SnO_2, ZrO_2 and metal sulfides: CdS, ZnS, WS_2, that are activated by absorbing a photon of electromagnetic radiation with an energy equal or higher than the band gap energy (Chupakova et al., 2018; Golimowski and Golimowska, 1996; Krasnodebska-Ostrega et al., 2016; Lejbt et al., 2016). This is an alternative to "wet" mineralization with inorganic acids or mixtures of acids. It is environmentally friendly (limiting the added reagents to the sample), does not require additional preparation of the sample before analysis, and provides sufficient removal of organic compounds (Chupakova et al., 2018; Vilhunen et al., 2010).

If photocatalysis is to be used as a method of matrix simplification, before speciation analysis of arsenic, all the abovementioned aspects must be taken into consideration. In the work presented here, a photocatalyst active layer composed of a nanoscale semiconductors ($Fe_2O_3/WO_3/Fe_2O_3$) was used (previously obtained experimental data). The pH condition, light energy, influence of the presence of oxygen, and the time of solar light exposition on the stability of inorganic as well organic arsenic form was investigated. Moreover, the efficiency of the surfactant degradation was controlled, as well as the stability of photoactive layer using surface analysis being examined.

2. Material and methods

2.1. Chemicals, reagents and standards

In this work the following reagents were used: arsenic trioxide (Sigma Aldrich), arsenate (V) standard solution, monomethylo- and dimethyloarsenic acids (Merck), sodium dodecyl sulfate SDS $M = 288.38 \, g \, mol^{-1}$ (Sigma Aldrich), sodium diethylenetriaminepentaacetate (DTPA, Merck), sodium dihydrogen phosphate (V) (99%, Fluka, Sigma Aldrich, HPLC grade), disodium hydrogen phosphate (V) (99%, Fluka, Sigma Aldrich, HPLC grade), sodium tungstate (Fluka), Dowex 50WX2 cation exchange resin (Fluka Analytical), iron (III) oxide (hematite, 98%, 325 μm, Alfa Aesar), borododecatungstic acid ($H_5BW_{12}O_{40} \, xH_2O$ −BW_{12}, 99%, City Chemical LLC), ethanol (99.8%, Aldrich), and polyethylene glycol (Aldrich). Arsenic (III) standard solution was prepared by dissolving arsenic (III) oxide in 1.5 mL of 30% NaOH (Suprapur, Merck) and then adjusting pH to a neutral value using HCl (Ultranal,