

STUDY OF ANTIMONY REMOVAL EFFICIENCY USING FERRATE (VI)

Robert PRUCEK, Martin SOLÁR, Aleš PANÁČEK, Jiří TUČEK, Jan FILIP, Radek ZBOŘIL

Palacký University in Olomouc, RCPTM, Olomouc, Czech Republic, EU, robert.prucek@upol.cz

Abstract

Heavy metals are widely used in a range of materials including paints, motor vehicles, guns, and electrical components. After discarding such materials, the metal ions after dissolution can penetrate to the environment and are toxic to plants, organisms, and humans. Among such dangerous heavy metals belongs antimony. The aim of presented work was to study removal efficiency of antimony from waters using ferrate (VI). The experiments were performed for antimony in oxidation state III and V and the influence of ferrate(VI) to antimony ratio on antimony removal efficiency was studied. The experiments were performed under neutral pH value of the reaction mixture. The antimony concentration was determined using AAS method and residual concentration of antimony in reaction mixture was traced within two weeks. With increasing ferrate (VI) to antimony ratio from 10:1 to 60:1, the removal antimony efficiency slightly increased. However, even for ferrate(VI) to antimony equal to 10:1, the removal efficiency was after 30 minutes and after two weeks was even 80 %. This means that the effectiveness of removal increase with prolonged contact time of components and no leaching of antimony back to aqueous solution proceed. The impact of concentration of some inorganic ions (nitrates, phosphates, sulfates, carbonates, and chlorides) usually present in real waters on antimony removal efficiency was also studied.

Keywords: Antimony, removal, ferrate(VI), ions influence

1. INTRODUCTION

Heavy metals are highly resistant to environmental degradation and tend to exhibit accumulative tendencies. In addition, metals are mobile, depending on the surrounding water chemistry. US Environmental Protection Agency (EPA) regulates heavy metals and, therefore, many methods have been studied for their removal. Among the toxic elements belongs the also antimony. Antimony is exploited in semiconductors, infrared detectors and diodes [1]. Among the most famous antimony alloys are the so-called "hard lead", found especially in ammunition. The lead itself without addition of antimony is too soft and unsuitable for this purpose and the antimony itself is too fragile [2]. The antimony is also involved in lead-acid-based automotive batteries electrodes or in corrosion-resistant pipes and alloys used to bearings metals which is also closely related to automotive industry [2], [3]. For another example, Sb_2S_3 is utilized in photoelectric devices or electrophotographic recording media and Sb_2O_3 is exploited in a self-extinguishing additive or as a moisturizing agent in brake pads [3]. Antimony oxides are used to fabrication of dyes, adhesives, plastics, rubber, ceramics, glass enamels, and fireworks [4] or fire protection of materials such as plastics, coatings, electronics or other polybrominated flame retardants [3]. Sb_2O_3 is also used as a catalyst in the production of polyethylene terephthalate (PET) [5]. Sodium antimony is used as a bleaching component, for example, for optical glasses in cameras or telescopes [3]. From all of the above mentioned materials or products, antimony can enter the aqueous and subsequently soil environment. Antimony can be found in four oxidation states: -III, 0, + III and + V. The predominant oxidation states in the environment are + III and + V and these oxidation states can be found in natural waters. Antimony is practically almost completely present as Sb^{+3} ions only in strongly acidic solutions or under anaerobic conditions [6]. In recent years, however, interest in antimony has increased considerably and has been included in the list of priority environmental pollutants. The Council of the European Union has set this limit value under Directive 98/83/EC to a maximum of $5 \mu g \cdot dm^{-3}$. Although in the natural

waters the concentration of antimony ranged usually from 0.01 to 5 $\mu\text{g}\cdot\text{dm}^{-3}$, its concentration may be significantly higher. The toxic properties of antimony are dependent to its form and the oxidation state. The antimony in oxidation state +III is about 10 times more toxic than the oxidation state +V, also the antimony in the oxidation state +III is more mobile in the environment [7]. Inorganic forms of antimony is more toxic than its compounds, organic forms, such as methylated Sb. Trivalent antimony has a high affinity for red blood cells and for thiol groups, but antimony in oxidation state +V is almost impermeable through red blood cells. Heavy metal cations generally tend to bind to the carboxyl or to the amino group, which are characteristic for genetic information related substances. Antimony has also been described to inhibit DNA replication [8]. The mutagenic or carcinogenic properties was reported, in particular antimony oxide Sb_2O_3 was included among potential carcinogens [9]. Long-term inhalation of antimony and its compounds has a dangerous impact on the heart, blood pressure, lung, liver, and kidneys functions [10,11]. Antimony compounds have a very harmful effect on pregnancy and can lead also to loss of fertility [1].

Adsorption, chemical precipitation, ion flotation, membrane filtration, and reverse osmosis have been used to remove metals from water. Among several methods, sorption/adsorption, based on iron containing compounds, has received greater attention because of the environmentally friendly nature and magnetically separable attributes of iron-containing compounds. In recent years, potassium salt of tetraoxy iron(VI) (K_2FeO_4 , Fe(VI)) has emerged as an effective agent for the oxidation, disinfection, and coagulation/coprecipitation to remove a wide range of contaminants. Ferrate(VI) represents an environmentally friendly oxidant; its redox potential ranges from 2.20 V in acidic environment to 0.72 V in basic environment [12]. It has been reported to be effective for the treatment of various contaminants, for example, ibuprofen, sulfamethoxazole, phenol and cyanides, and a variety of inorganic compounds. [13,14] The rate of ferrate(VI) reaction with various compounds mostly varies from several milliseconds to several minutes. [15] The additional benefit of using ferrate(VI) lies in the fact that resulting secondary iron oxide nanoparticles can further serve as an efficient adsorbent for oxidized pollutants. [16]

The aim of this work is to study of antimony (III, V) removal using ferrate(VI) treatment, investigate the influence of ferrate(VI) to antimony ratio and impact of the presence of inorganic ions usually present in real water on efficiency of antimony removal.

2. EXPERIMENTAL

Stock solutions of antimony at a concentration of 1000 mg L^{-1} were prepared using SbCl_3 or SbCl_5 (Sigma-Aldrich). Inorganic Salts (NaCl , NaNO_3 , NaHCO_3 , and Na_2SO_4) were purchased from Sigma-Aldrich. Standard solutions of Sb and Fe for atomic absorption spectroscopy (AAS) measurements were prepared using commercial standards TraceCERT (concentration 1000 mg/L of element in nitric acid), which were purchased from Fluka Inc. All chemicals were used as received without any further purification. Potassium ferrate (K_2FeO_4) (>90 %, Sigma-Aldrich) was used throughout the experiments. Solutions of ferrate(VI) were prepared with deionized water ($18 \text{ M}\Omega \text{ cm}^{-1}$, Millipore system).

The influence of concentration of ferrate(VI) on the removal of antimony was tested at neutral pH value. In the experiments, the initial concentration of antimony (III, V) was 10 mg L^{-1} (as elemental Sb). The concentrations of ferrate(VI) as Fe were varied from 100 to 600 mg L^{-1} . In all these experiments, solutions of ferrate(VI) were added to the solutions of antimony (III, V) water in the Erlenmeyer flasks (the final volume was 100 mL). Mixed solutions were shaken on a conventional end-over-end shaker for 30 min, 1 week, and 2 weeks and thereafter filtered through 0.2 μm syringe filters. The residual concentration of antimony in the filtrate were immediately determined using an AAS-flame ionization technique.

In the investigation of the effect of ions on antimony (III, V) removal efficiency using ferrate(VI), chlorides, nitrates, carbonates, sulfates, and phosphates were employed. After adding ferrate(VI), the pH of the solutions was adjusted and solution was shaken for 2 weeks. Samples for AAS analyses were taken 30 min, 1 week,

and 2 weeks after the mixing of the components. The concentrations of ions were in the range from 25 to 200 mg L⁻¹ of element in ion (i.e., chlorides ion as Cl, nitrates as N, carbonates as C, sulfate as S, and phosphates as P). The experiments were carried out in triplicates.

Antimony concentrations were determined by the AAS-flame technique using a ContraAA 300 (Analytik Jena AG, Germany) equipped with a high-resolution Echelle double monochromator (spectral band width of 2 pm at 200 nm) and with a continuum radiation source (xenon lamp). The absorption line used for Sb analyses was 206.8300 nm. TEM images of formed nanoparticles were performed by transmission electron microscopy (TEM) on a JEOL JEM-2010 transmission electron microscope equipped with a LaB₆ cathode (accelerating voltage of 160 kV; point-to-point resolution of 0.194 nm). A drop of high-purity distilled water was placed onto a holey carbon film supported by a copper-mesh TEM grid (SPI Supplies, USA) and air-dried at room temperature.

3. RESULTS AND DISCUSSION

The K₂FeO₄ material was tested for the removal of antimony(III) and antimony(V) ions. The ferrate(VI) anions react with water which leads to in-situ formation of ferric oxides. The capacity of antimony species, as well as arsenic species sorption by iron oxides is generally influenced by pH value of the solution. Based on our previous studies with arsenic removal using ferrate(VI), we focused on experiments performed at neutral pH value (approx. 7). These experiments were aimed to the examination of the influence of K₂FeO₄ concentration on the efficiency of antimony removal. The initial concentration of antimony (III, V) was 10 mg L⁻¹ (as Sb) and the concentrations of ferrate(VI) (referred as Fe) were varied from 100 to 600 mg L⁻¹, i.e. that ratio of Fe:Sb was ranged from 10:1 to 60:1. The limit of antimony in drinking waters is 5 mg L⁻¹. However, in some case, for example in mining area in China, concentrations up to 30 mg L⁻¹ were reported.[17] The kinetics of antimony (III, V) removal was monitored by time-dependent changes of arsenic concentration in the solution. From the **Figure 1** it is clear that with increasing ferrate (VI) to antimony(III) ratio from 10:1 to 60:1, the removal antimony efficiency slightly increased. For ferrate(VI) to antimony(III) equal to 10:1, the removal efficiency of antimony(III) was approximately 65 % after 30 minutes and for higher ferrate (VI) to antimony ratio, the removal effectiveness reached up to almost 90 %. In the case of Sb(V), the efficiency was very similar just in the case of Sb(III) (**Figure 2**). The more important is the fact, that after 1 week and 2 weeks after mixing of ferrate(VI) and the antimony(III, V) the antimony concentration gradually decreased and no leaching of antimony back to the aqueous environment was observed (**Figures 1 and 2**). So, the using the ferrate(VI) can be an effective tool for antimony treatment in waters. The TEM image of iron nanoparticles formed after the reaction of ferrate(VI) in the presence of antimony(V). Concentration of ferrate(VI) was 200 mg·dm⁻³ (as Fe) and the concentration of antimony was 10 mg·dm⁻³ (as Sb) is shown at **Figure 3**. Just in the case arsenic (III), also in the case of antimony(III) the fast oxidation to antimony(V) and possible incorporation of antimony to the structure of the formed iron oxide can be assumed.[18,19] This hypothesis needs to be confirmed by in-field ⁵⁷Fe Mössbauer spectroscopy and XPS measurement. The ionic radius of antimony is 0.076 nm, so this ion can be embedded into the structure of formed iron oxide just in the case of arsenic because the limit of ionic radii for possible incorporation is 0.092 nm.[18] In the subsequent experiment, the influence of selected ions (chlorides, nitrates, sulfates, carbonates, phosphates) concentrations were examined. In this type of experiments, the ratio of ferrate(VI) and antimony(III, V) was set up to 20:1. The concentrations of the above mentioned ions were ranged between 25 to 200 mg L⁻¹ of element in ions. In case of the presence of sulfates, nitrates, and chlorides, the efficiency of antimony (III, V) remained unchanged. Residual concentrations of antimony was very similar, just in the case when only antimony (III, V) was present in the solution together ferrate(VI). Also of antimony concentrations decreasing with time show the same trend. The situations were very different in the case of presence of phosphates and carbonates. The presence of phosphates even in the lowest tested concentration (25 mg/L) eliminates completely removal of antimony from aqueous environment. The carbonates influence the removal of antimony at the higher concentrations (100 and 200 mg/L).

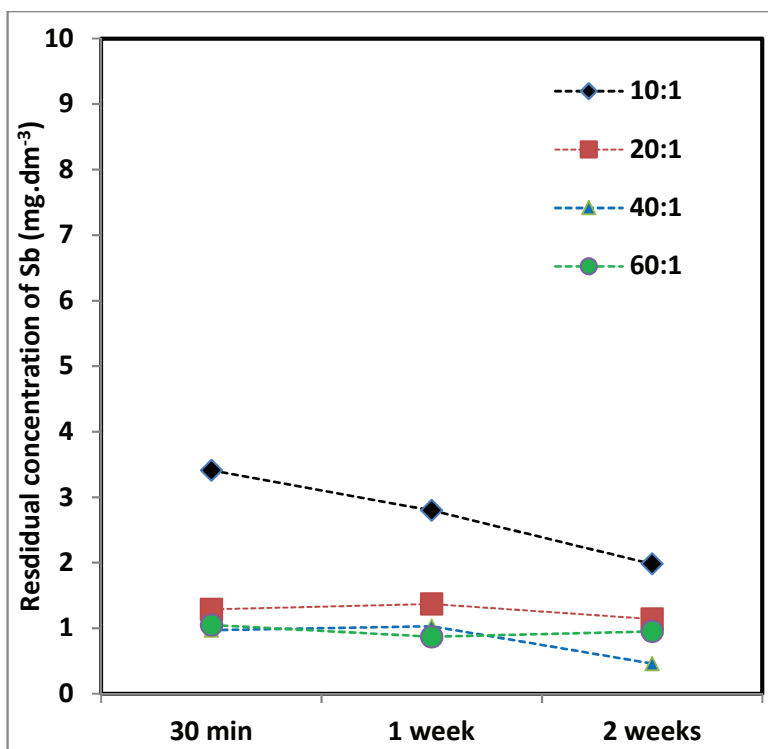


Figure 1 Residual concentrations of Sb for different antimony(III) to ferrate(VI) weight ratios. The initial concentrations of antimony(III) was 10 mg·dm⁻³.

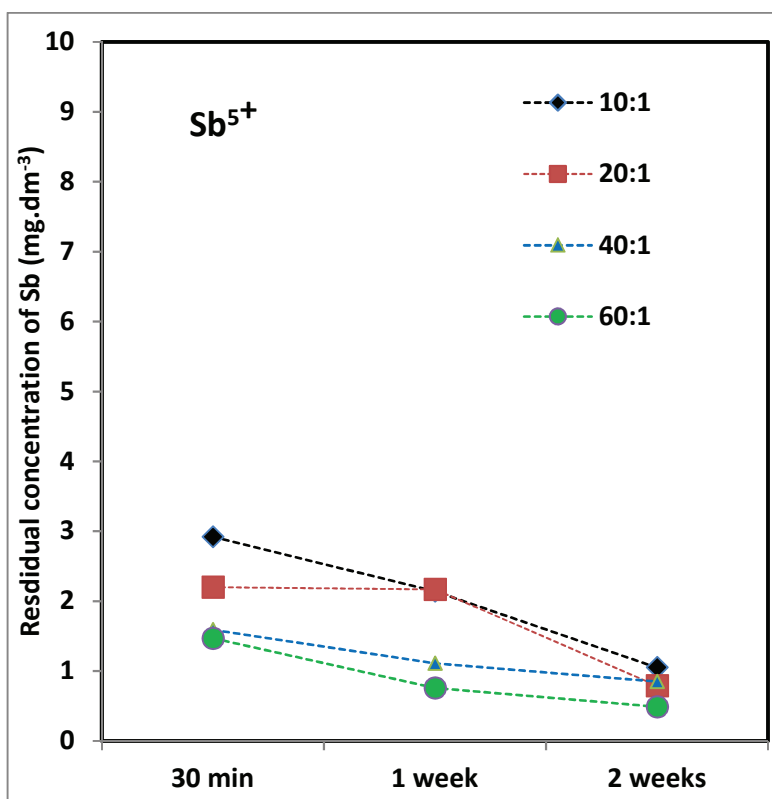


Figure 2 Residual concentrations of Sb for different antimony(V) to ferrate(VI) weight ratios. The initial concentrations of antimony(V) was 10 mg·dm⁻³.

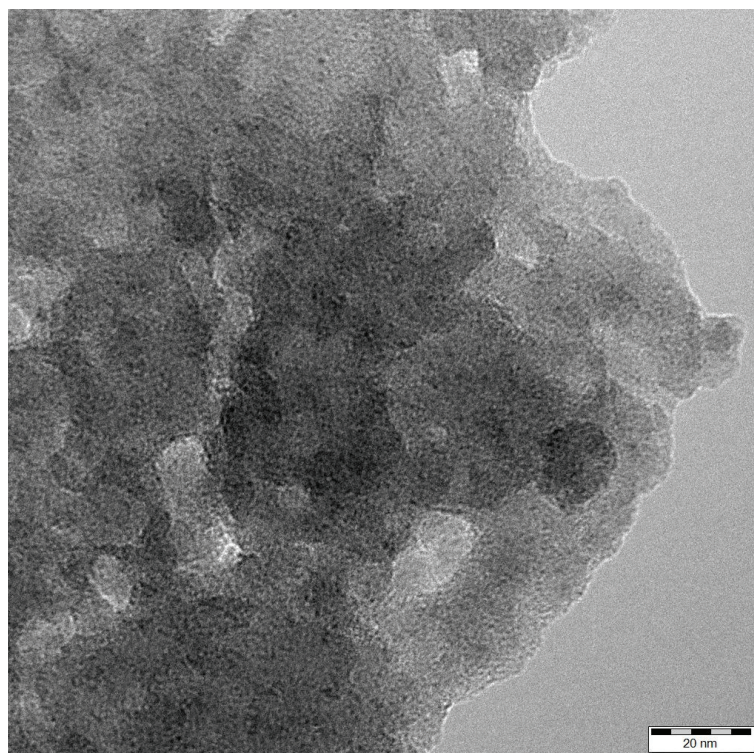


Figure 3 TEM images of iron based particles after the reaction of ferrate(VI) in the presence of antimony(V). Concentration of ferrate(VI) was $200 \text{ mg} \cdot \text{dm}^{-3}$ (as Fe) and the concentration of antimony was $10 \text{ mg} \cdot \text{dm}^{-3}$ (as Sb) .

4. CONCLUSION

The reported study reported possibilities of antimony treatment using ferrate(VI). The achieved results have demonstrated that selected inorganic ions, typically present in natural waters, have different impact on removal of antimony(III, V) by ferrate(VI) from aqueous environment. Interestingly, ions such as chlorides, nitrates, and sulfates had marginal on removal efficiency of antimony by ferrate(VI). On the contrary, presence of phosphates and carbonates had negative influence on efficiency of antimony removal by ferrate(VI). With the increased concentration of phosphates, the efficiency of antimony removal was decreased.

ACKNOWLEDGEMENTS

The authors are grateful for the support by the projects LO1305 of the Ministry of Education, Youth and Sports of the Czech Republic.

REFERENCES

- [1] CHOMISTEKOVÁ, Z., CULKOVÁ, E., BELLOVÁ, R., MELICHERČÍKOVÁ, D., DURDIK, J., BEINROHR, E., RIEVAJ, M., TOMČÍK, P.: Metódy a postupy stanovenia antimónu ako environmentálne významného analytu. Chem. Listy, 2016, vol. 110, no.10, pp. 671-677.
- [2] ANDERSON, C. G.: The Metallurgy of Antimony. Chemie der Erde - Geochemistry. 2012, vol. 72, no. 4, pp. 3-8,.
- [3] DUPONT, D., ARNOUT, S., JONES, P. T., BINNEMANS, K.: Antimony Recovery from End-of-Life Products and Industrial Process Residues: A Critical Review. J. Sustain. Metall., 2016, 2 (1), s. 79-103, ISSN 2199-3831.
- [4] HOUSECROFT, C. E., SHARPE, A. G.: Anorganická chemie. Prekl.: Ondřej BENEŠ. Praha: Vysoká škola chemicko-technologická. 2014, pp. 389, 472, 474-476, 481-482, 500-501, 527, 694, 730-732.

- [5] UNGUREANU, G., SANTOS, S., BOAVENTURA, R., BOTELHO, C. Arsenic and antimony in water and wastewater: Overview of removal techniques with special reference to latest advances in adsorption. *Journal of Environmental Management*. 2015. vol. 151, pp. 326-342.
- [6] MUBARAK, H., CHAI, L.-Y., MIRZA, N., YANG, Z.-H., PERVEZ, A., TARIQ, M., SHAHEEN, S., MAHMOOD, Q.: Antimony (Sb)-Pollution and Removal Techniques-Critical Assessment of Technologies. *Toxicological & Environmental Chemistry*. 2015. vol. 97, no. 10, pp. 1296-1318.
- [7] SHARMA, M., PATEL, K. S.: Determination and Speciation of Antimony in Waters. *International Journal of Environmental Analytical Chemistry*. 1993. vol. 50, no. 1, pp. 63-71.
- [8] OBIAKOR, M. O., TIGHE, M., PEREG, L., WILSON, S. C.: Bioaccumulation, trophodynamics and ecotoxicity of antimony in environmental freshwater food webs. *Critical Reviews in Environmental Science and Technology*, 2017, 47 (22), s. 2208-2258, ISSN: 1064-3389.
- [9] FOWLER, B. A., YAMAUCHI, H., CONNER, E. A., AKKERMAN, M.: Cancer risks for humans from exposure to the semiconductor metals. *Scand J Work Environ Health*. 1993. Vol. 19, no. 1, pp. 101-103.
- [10] JOHNSON, M., LORENZ, B.: Antimony Remediation Using Ferrate(VI). *Separation Science and Technology*. 2015. vol. 50, no. 11, pp. 1611-1615.
- [11] BRUNE, D., NORDBERG, G., WESTER, P. O.: Distribution of 23 Elements in the Kidney, Liver and Lungs of Workers from a Smeltery and Refinery in North Sweden Exposed to a Number of Elements and of a Control Group. *The Science of the Total Environment*. 1980. vol. 16, no. 1, pp. 13-35.
- [12] WOOD, R. H. The heat, free energy and entropy of ferrate(VI) ion. *J. Am. Chem. Soc.* 1958. vol. 80, 2038-2041.
- [13] SHARMA, V. K.; MISHRA, S. K. Ferrate(VI) oxidation of ibuprofen: A kinetic study. *Environ. Chem. Lett.* 2006, vol. 3, 182-185.
- [14] SHARMA, V. K.; MISHRA, S. K.: Oxidation of inorganic contaminants by ferrates (VI, V, and IV)-kinetics and mechanisms: A review. *J. Environ. Manage.* 2011, vol. 92, 1051-1073.
- [15] SHARMA, V. K.; MISHRA, S. K.; NESNAS: Oxidation of sulfonamide antimicrobials by ferrate(VI) [Fe^{VI}O₄²⁻]. *Environ. Sci. Technol.* 2006, vol. 40, 7222-7227.
- [16] MURMANN, R. K.; ROBINSHON, P. R. Experiments utilizing FeO₄²⁻ for purifying water. *Water Res.* 1974, vol. 8, pp. 543-547.
- [17] HE, M.C., WANG, X.Q., WU, F. C., Fu Z. Y. Antimony pollution in China. *Sci. Total. Environ.* 2012, vol. 421, pp. 41-50.
- [18] PRUCEK, R., TUČEK, J., KOLAŘÍK, J., FILIP, J., MARUŠÁK, Z., SHARMA, V. K., ZBOŘIL, R. Ferrate(VI)-Induced Arsenite and Arsenate Removal by In Situ Structural Incorporation into Magnetic Iron(III) Oxide Nanoparticles. *Environ. Sci. Technol.* 2013. vol. 47, no. 7, pp. 3283-3292.
- [19] PRUCEK, R., TUČEK, J., KOLAŘÍK, J., HUŠKOVÁ, I., FILIP, J., VARMA, R. S., SHARMA, V. K., ZBOŘIL, R. Ferrate(VI)-Prompted Removal of Metals in Aqueous Media: Mechanistic Delineation of Enhanced Efficiency via Metal Entrenchment in Magnetic Oxides. *Environ. Sci. Technol.* 2015, vol. 49, no. 4, pp. 2319-2327.