

See discussions, stats, and author profiles for this publication at:
<https://www.researchgate.net/publication/232392588>

Recovery of Sb(V) using a functional-ligand-containing porous hollow-fiber membrane prepared by radiation-induced graft polymerization

ARTICLE *in* HYDROMETALLURGY · MARCH 2006

Impact Factor: 1.93 · DOI: 10.1016/j.hydromet.2005.12.010

CITATIONS

16

READS

27

6 AUTHORS, INCLUDING:



Hidetaka Kawakita

Saga University

185 PUBLICATIONS 1,562 CITATIONS

SEE PROFILE



Satoshi Tsuneda

Waseda University

242 PUBLICATIONS 5,100 CITATIONS

SEE PROFILE



Kyoichi Saito

Chiba University

190 PUBLICATIONS 3,302 CITATIONS

SEE PROFILE

Recovery of Sb(V) using a functional-ligand-containing porous hollow-fiber membrane prepared by radiation-induced graft polymerization

Hidetaka Kawakita ^a, Kazuya Uezu ^{b,*}, Satoshi Tsuneda ^c, Kyoichi Saito ^d,
Masao Tamada ^e, Takanobu Sugo ^e

^a Advanced Research Institute for Science and Engineering, Waseda University, 2-2 Hibikino, Kitakyushu 808-0135, Japan

^b Department of Chemical Processes and Environments, The University of Kitakyushu, 1-1 Hibikino, Kitakyushu 808-0135, Japan

^c Department of Chemical Engineering, Waseda University, 3-4-1 Ohkubo, Shinjuku, Tokyo 169-8555, Japan

^d Department of Materials Technology, Chiba University, 1-33 Yayoi, Inage, Chiba 263-8522, Japan

^e Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, 1233 Watanuki, Takasaki, Gunma 370-1292, Japan

Received 23 January 2004; received in revised form 5 October 2005; accepted 13 December 2005

Abstract

A ligand-containing porous membrane was prepared by radiation-induced graft polymerization of an epoxy-group-containing monomer of glycidyl methacrylate onto a polyethylene porous hollow-fiber membrane and by subsequent conversion of the epoxy group to an *N*-methylglucamino (NMG) group at a density of 0.78 mmol/g of the membrane. Sb(V) solution was permeated through the NMG-ligand-containing porous hollow-fiber membrane. Optimum pH for Sb(V) recovery was 3.0. Breakthrough curves of Sb (V) overlapped irrespective of residence times of Sb (V) in the membrane, due to negligible diffusional mass-transfer resistance. Maximum amount of Sb (V) adsorbed was 130 mg/g-membrane, which was equivalent to 1.3 binding molar ratio. Repeated usage of the membrane for adsorption and elution was possible.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Antimony; Porous hollow-fiber membrane; Polyol ligand; Radiation-induced graft polymerization; Membrane separation

1. Introduction

Antimony (Sb) is among the most toxic elements and exists in several industrial and mining wastes, such as chemicals and allied products, electrical and electronic equipments, bearings and power transmission equip-

ments (Chwastowska et al., 1995; Meltzer et al., 1990; Ubaldini et al., 2000). Presence of Sb elements and their compounds in the environment is a major concern due to their toxicity to many forms of life. LD₅₀ value as a measure of Sb toxicity was reported to be 100 and 150 mg/kg intraperitoneally in rats and guinea pigs, respectively (Gangolli, 1999). Treatments of water containing Sb and its compounds are necessary.

Various kinds of adsorption treatments of Sb have been investigated. Deorkar and Tavalarides (1997) synthesized pyrogallol-attached silica-gel ceramics with

* Corresponding author. Tel.: +81 93 695 3288; fax: +81 93 695 3368.

E-mail address: uezu@env.kitakyu-u.ac.jp (K. Uezu).

a functional group density of 0.26 mmol/g, to separate Sb(III), copper and lead from aqueous solutions using a column mode, and obtained adsorption of 5.0 mg-Sb(III)/g of ceramics. Petkova and Vassilev (1982) prepared β -stannic acid from the oxidation of pure tin with hot concentrated nitric acid and obtained adsorption of 10 mg-Sb(III)/g.

Radiation-induced graft polymerization (RIGP) is a powerful technique which enables modification of various polymeric materials into grafted polymer chains. Using RIGP, sulfonic acid group (Saito et al., 2002), iminodiacetate group (Nishiyama et al., 2003), and 2, 2'-iminodiethanol group (Ozawa et al., 2000) were introduced to polymer chains of poly(glycidyl methacrylate) to recover metal ions such as Cu, Co, and Pd. Permeation of metal ions in solution driven by transmembrane pressure across the porous hollow-fiber membrane minimizes diffusional mass-transfer resistance of metal ions to functional groups on polymer chains, and results in the high-speed capturing of metal ions (Nishiyama et al., 2003).

We have previously prepared a polyol-ligand-containing porous hollow-fiber membrane using RIGP to recover Sb(III) (Saito et al., 2004). *N*-methylglucamine (NMG) was introduced to epoxy-group-containing polymer chains grafted onto pores of a porous membrane made of polyethylene. The resulting polyol-group density was 1.7 mmol/g. Sb(III) solution (10 mg/L) at pH 11 was then permeated through the polyol-ligand-containing porous hollow-fiber membrane to capture 96 mg-Sb(III)/g-membrane.

Antimony is composed of trivalent forms (SbO^+ , HSbO^2 , SbO^{2-} , $\text{Sb}(\text{OH})_4^-$) or pentavalent forms (SbO^{2+} , SbO^{3-} , $\text{Sb}(\text{OH})_6^-$), which are modulated by pH, concentration, and co-dissolved compounds (Pitman et al., 1957).

In this study, Sb(V) solution was permeated through the NMG-group-containing porous hollow-fiber membrane. Effects of the concentration and pH in the feed of Sb(V) on membrane capacity were investigated. Molar binding ratios between Sb(V) and polyol groups were compared with those of Sb(III) to figure out the structure of the polyol-Sb(V) complex.

2. Experimental

2.1. Materials

A commercially available porous hollow-fiber membrane made of polyethylene (Asahi Kasei Corporation, Japan) was used as a trunk polymer for grafting. This hollow-fiber membrane had an inner and outer diameter of 1.9 and 3.1 mm, respectively, with a pore diameter of 360 nm and 71% porosity. Glycidyl methacrylate (GMA) was purchased from Tokyo Kasei, Japan and used without further purification. *N*-methylglucamine (NMG) was purchased from Wako Pure Chemical Industries, Japan. Potassium hexahydroxo antimonite for preparation of Sb(V) solution was obtained from Wako Pure Chemical Industries, Japan. Other chemicals were of analytical grade or higher.

2.2. Preparation of the polyol-ligand-containing porous hollow-fiber membrane

Preparation scheme of the functional porous hollow-fiber membrane consisted of three steps, as shown in Fig. 1: (1) electron-beam: the original porous hollow-fiber membrane was irradiated with an electron beam of 200 kGy in a nitrogen atmosphere at ambient temperature; (2) grafting of GMA: the irradiated hollow-fiber membrane was immersed in a solution

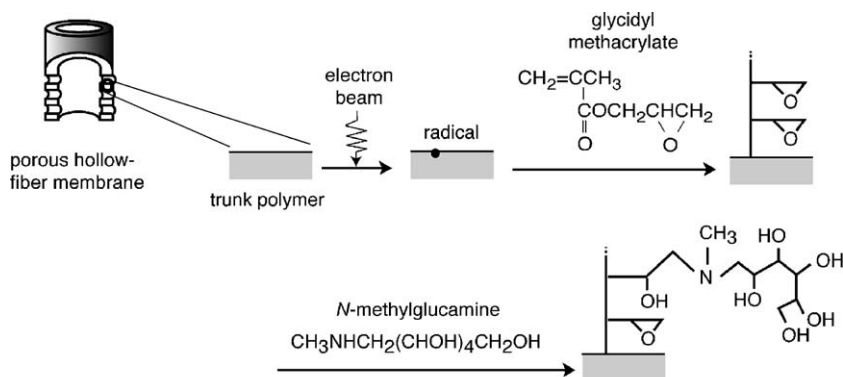


Fig. 1. Introduction of *N*-methylglucamino group to grafted polymer chains on the porous hollow-fiber membrane.

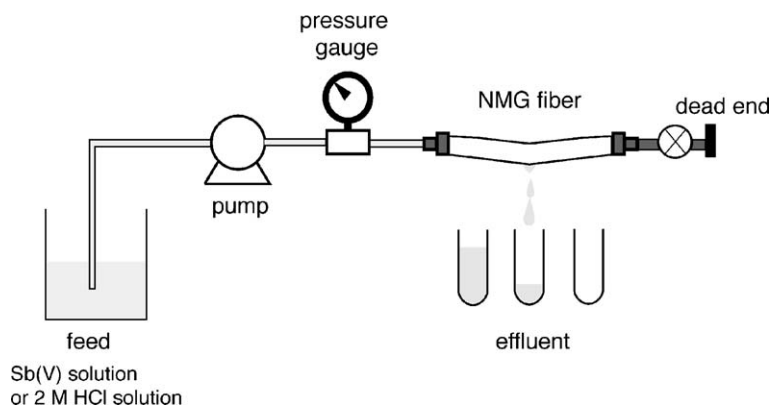


Fig. 2. Experimental apparatus for permeation of Sb(V) solution and 2 M HCl solution.

of 10% (v/v) GMA-methanol at 313 K for 12 min to graft-polymerize GMA. The degree of grafting (dg) was defined as:

$$\text{dg (\%)} = 100(\text{mass of poly-GMA grafted}) / (\text{mass of the trunk polymer}) \quad (1)$$

The resultant porous hollow-fiber membrane was referred to as the GMA fiber; (3) introduction of *N*-methylglucamino group: the GMA fiber was immersed in 0.5 M *N*-methylglucamine (50% (v/v) dioxane) at 353 K for 20 min. Molar conversion of epoxy groups of polymer chains to *N*-methylglucamino groups and the corresponding functional group density were defined as:

$$\begin{aligned} \text{molar conversion (\%)} \\ = 100(\text{moles of } N\text{-methylglucamino group} \\ \text{introduced}) / (\text{moles of epoxy group}) \end{aligned} \quad (2)$$

$$\begin{aligned} \text{functional group density (mmol/g)} \\ = (\text{moles of } N\text{-methylglucamino group}) \\ / (\text{gram of } N\text{-methylglucamino-group-containing} \\ \text{membrane}) \end{aligned} \quad (3)$$

The resultant porous hollow-fiber membrane was referred to as the NMG fiber.

2.3. Permeation of Sb(V) solution through the NMG fiber

NMG fiber (effective length 2.0 cm) was set onto the permeation apparatus as shown in Fig. 2. Sb(V) solution was permeated from the inner to the outer surface of NMG fiber at various permeation pressures using a pump. pHs at 5.2, 7.0, and 8.5 were used for buffers of 50

mM acetic acid, and 50 mM Tris–HCl, respectively. No buffers were used at pHs of 1.0 and 3.0. The effluent penetrating the outside surface of the hollow-fiber membrane was continuously sampled and Sb(V) in the effluent was determined by ICP-AES (Perkin Elmer, OPTIMA 4300 DV CYCLON) at the Instrumental Center, the University of Kitakyushu.

Equilibrium binding capacity and molar binding ratio of the NMG fiber for Sb(V) were evaluated as follows:

$$\begin{aligned} \text{equilibrium binding capacity (mg/g)} \\ = \int_0^{V_e} (C_0 - C) dV / W \end{aligned} \quad (4)$$

$$\begin{aligned} \text{binding molar ratio (-)} \\ = (\text{equilibrium binding capacity}) \\ / (\text{functional group density}) \end{aligned} \quad (5)$$

where C_0 and C are concentrations of Sb(V) in the feed and the effluent, respectively. W is the mass of NMG fiber. V and V_e are the effluent volume and the effluent volume when C reaches C_0 , respectively.

2.4. Elution of Sb(V) captured to the NMG fiber

HCl solution (2.0 M) was permeated to elute bound Sb(V) through the Sb(V)-adsorbed-NMG fiber using the permeation apparatus. Elution percentage was calculated as follows:

$$\begin{aligned} \text{elution percentage (\%)} \\ = 100(\text{amount of Sb(V) eluted}) \\ / (\text{equilibrium binding capacity}) \end{aligned} \quad (6)$$

3. Results and discussion

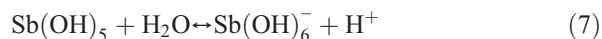
3.1. Properties of the *N*-methylglucamino-group-containing porous hollow-fiber membrane

Properties of the NMG fiber are summarized in Table 1. Degree of grafting and molar conversion of epoxy groups of polymer chains were 160% and 21%, respectively. Membrane thickness increased by 25% compared with the trunk polymer. Pure water flux, defined by dividing the permeation rate of water at 0.1 MPa by the inside surface area, was 20% of the trunk polymer. Polymer chains formed both in the matrix of the trunk polymer membrane and on the pore surface; the former allowed the matrix to swell and the latter reduced pore size. Molar conversions of epoxy group in grafted poly-GMA chains to *N*-methylglucamino groups were controlled in the range of 5–80% by reaction time of the GMA fiber with the reagent solution (Saito et al., 2004).

3.2. Performance of NMG fiber for Sb(V)

The pH dependence of equilibrium binding capacity of Sb(V) at a feed concentration of 25 mg/L to the NMG fiber is shown in Fig. 3. Optimum pH of the NMG fiber for Sb(V) recovery was 3.0 and amount of Sb(V) decreased by the rapidly increasing pH and became insignificant at above pH 7.0. This behavior could be explained by the following.

The following equilibrium between the two species of antimonous acid $\text{Sb}(\text{OH})_5$ and $\text{Sb}(\text{OH})_6^-$ exists in an aqueous solution (Baes and Mesmer, 1976),



At high pH, dominant species of Sb(V) is $\text{Sb}(\text{OH})_6^-$; whereas at low pH, Sb(V) forms a cluster of $(\text{HSb}_2\text{O}_6)^-$, $(\text{HSb}_6\text{O}_{17})_3$, $(\text{H}_4\text{Sb}_6\text{O}_{17})_n$ (Gate and Richardson, 1961). Equilibrium is governed by proton concentration, i.e. pH. In acid conditions, with increasing pH, amounts of

Table 1
Properties of NMG-ligand-containing porous hollow-fiber membrane

Degree of grafting (%)	160
Molar conversion (%)	21
Functional group density (mmol/g)	0.78
Inner diameter (mm)	2.3
Outer diameter (mm)	3.8
Pure water flux (m/h) ^a	0.5

^a Transmembrane pressure 0.1 MPa at 298 K.

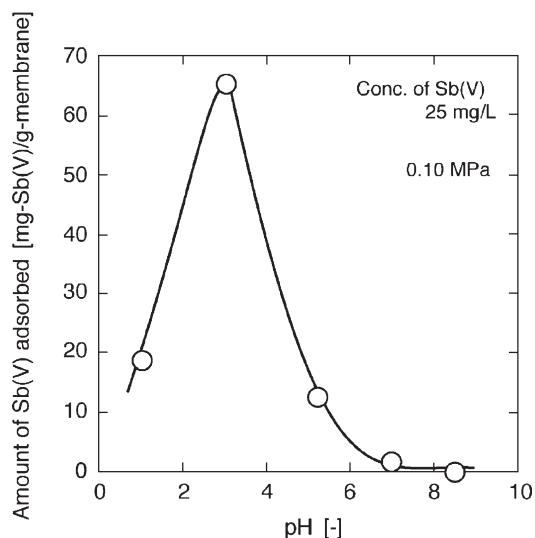
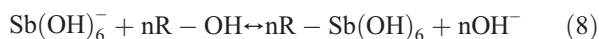


Fig. 3. pH dependence on the adsorption of Sb(V).

$\text{Sb}(\text{OH})_6^-$ increase to form a complex with NMG. In strong acidic solution, adsorption will decrease by increasing of $\text{Sb}(\text{OH})_5$.

At neutral pH, $\text{Sb}(\text{OH})_6^-$ is the main species. Sb(V) could be related with NMG by the following equilibrium;



The equilibrium shifts to the left with increasing pH, so that the complex between Sb(V) and NMG does not form. The pH dependence of Sb(V) adsorption on

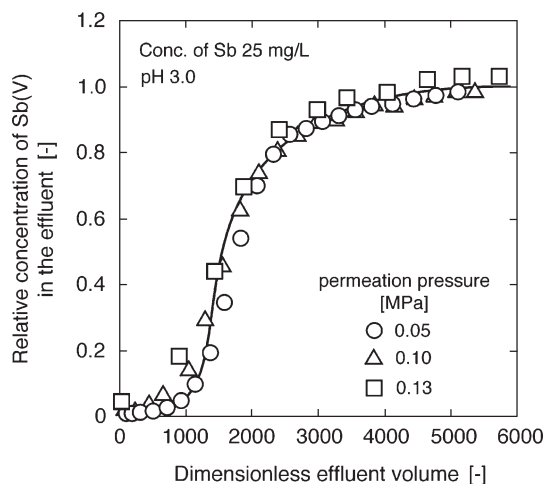
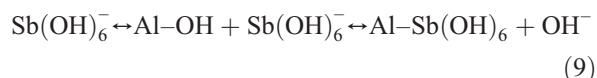


Fig. 4. Breakthrough curves of Sb(V) for various permeation pressures of Sb(V) solution through NMG-ligand-containing porous hollow-fiber membrane.

activated alumina gave the same pH optimum at 3–5 as in our study (Xu et al., 2001). Equilibrium such as the one described in Eq. (8) can be described as follows;



The following experiments were performed at pH 3.0. Sb(V) (25 mg/L) in solution at pH 3.0 was permeated through an NMG fiber using various permeation pressures. Breakthrough curves are shown in Fig. 4. Dimensionless effluent volume was defined as the ratio of effluent volume to membrane volume excluding the lumen part. Breakthrough curves overlapped irrespective of permeation pressures. Residence times of antimony solution using the permeation pressure of 0.13 and 0.05 MPa were 1.5 and 7.3 s, respectively. These data indicated that there was negligible diffusional mass-transfer resistance of the ionic species of Sb(V) to the NMG group. Therefore, the higher the permeation rate of the antimony solution, the higher the overall capturing rate of antimony.

Equilibrium binding capacity of Sb(V) and its binding molar ratio were evaluated from breakthrough curves at various feed concentrations (Fig. 5). By increasing feed concentration of Sb(V), equilibrium binding capacity increased. At a feed concentration of 200 mg/L, 130 mg Sb(V) adsorbed on 1 g NMG fiber. GMA fiber never captured Sb(V) at various feed concentrations.

Binding molar ratio increased with increasing feed Sb(V) concentration, and reached a plateau at 1.3. Roberts et al. (1998) demonstrated that Sb(V) and NMG were composed of various complexes such as, Sb-NMG, Sb₂-NMG, Sb-NMG₂, Sb₂-NMG₂, Sb₂-NMG₃, Sb₃-NMG₄, and Sb₄-NMG₅, in aqueous solution using fast atom bombardment (FAB) and electrospray ionization (ESI) mass spectrometry. Complex structures of Sb(V) and NMG-ligand-containing polymer chains could be modulated according to feed concentration; Sb-NMG₂ with a binding molar ratio of 0.5, Sb₂-NMG₃ at 0.67, and Sb₃-NMG₄ at 0.75, Sb-NMG, Sb₂-NMG₂, Sb₃-NMG₃, and Sb₄-NMG₄ at 1.0, and Sb₅-NMG₄ at 1.25 (Table 2). A binding molar ratio of 1.25 corresponded to that of a

Table 2
Possible structure of Sb(V)-NMG complex for each binding molar ratio

Binding molar ratio	Possible structure
0.50	$\begin{array}{c} \text{N M G} \\ \diagdown \quad \diagup \\ \text{Sb} \\ \diagup \quad \diagdown \end{array}$
0.67	$\begin{array}{c} \text{N M G} \\ \diagdown \quad \diagup \\ \text{Sb} \quad \text{Sb} \\ \diagup \quad \diagdown \quad \diagup \quad \diagdown \\ \text{N M G} \end{array}$
0.75	$\begin{array}{c} \text{N M G} \\ \diagdown \quad \diagup \\ \text{Sb} \\ \diagup \quad \diagdown \end{array} \quad \text{N M G} = \text{Sb} = \text{N M G}$
1.0	$\begin{array}{c} \text{N M G} \\ \diagdown \quad \diagup \\ \text{Sb} \\ \diagup \quad \diagdown \end{array} \quad \text{N M G} = \text{Sb} = \text{N M G}$
1.25	$\begin{array}{c} \text{N M G} \\ \diagdown \quad \diagup \\ \text{Sb} \\ \diagup \quad \diagdown \end{array} \quad \text{N M G} = \text{Sb} = \text{N M G}$

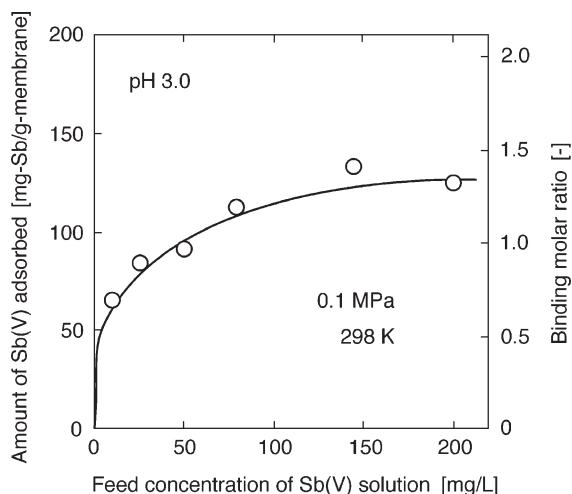


Fig. 5. Equilibrium binding capacity of Sb(V) as a function of feed concentration along with binding molar ratio.

feed concentration of more than 150 mg/L, as shown in Fig. 5.

NMG-ligand-containing porous hollow-fiber membrane adsorbed Sb(III) at binding molar ratio of 0.5 (Saito et al., 2004), while adsorbing Sb(V) at a ratio greater than 1. NMG-ligand-introduced polymer chains and Sb(III) formed a coordination complex with two adjacent hydroxyl groups of two NMG moieties (Saito et al., 2004). Different Sb(V) bindings to NMG-ligand-containing polymer chains could come from the very strong Lewis acidity of Sb(V).

3.3. Repeated use and elution of the NMG fiber

Four times of adsorption and elution cycles were performed. Constant equilibrium binding capacities and elution percentage (100%) irrespective of cycle numbers were obtained. The NMG-containing porous hollow-fiber membrane possessed a high durability for Sb(V) recovery.

Because NMG fibers adsorb less Sb(V) at pH 8.5, 50 mM Tris–HCl (pH 8.0) was permeated through Sb(V)-adsorbed NMG fibers resulting in an elution percentage of 52%, which corresponds to a possibility of eluting with pure water.

4. Conclusions

For recovery of Sb(V), *N*-methylglucamino group were introduced to a porous hollow-fiber membrane made of polyethylene by radiation-induced graft polymerization and by subsequent modifications. High-speed recovery of Sb(V) at an optimum pH of 3.0 was

achieved because convective flow of Sb(V) minimized the diffusional path of Sb(V) to NMG groups of the polymer chains. Higher molar binding ratio of antimony with pentavalent forms rather than trivalent forms allowed plural Sb(V)s to adsorb to polyol-ligand polymer chains compared with Sb(III). Four repeated use of the functional membrane and 100% elution percentage could be obtained. Industrial application of polyol-ligand-containing porous hollow-fiber membrane would be attractive for Sb(V)-containing-solution treatments.

Acknowledgments

We thank Noboru Kubota and Kohei Watanabe of the Specialty Products and Systems Company of Asahi Kasei Corporation for providing the starting porous hollow-fiber membrane.

References

- Baes Jr., C.F., Mesmer, R.E., 1976. The Hydrolysis of Cations. Wiley, New York, pp. 370–375.
- Chwastowska, J., Zmijewska, W., Sterlinska, E., 1995. Determination of antimony(III, V) in natural waters by separation and preconcentration on a thionalide loaded resin followed by neutron activation analysis. *J. Radioanal. Nucl. Chem.* 196, 3–9.
- Deorkar, N.V., Tavalariades, L.L., 1997. A chemically bonded adsorbent for separation of antimony, copper, and lead. *Hydrometallurgy* 46, 121–135.
- Gangolli, S., 1999. Antimony, The Dictionary of Substances and their Effects, 2nd ed. The Royal Society of Chemistry, Cambridge U. K., pp. 332–335.
- Gate, S.H., Richardson, E., 1961. Some studies on antimonic acid-I, some properties, effect of H₂O₂, and reaction with polyhydroxy compounds. *J. Inorg. Nucl. Chem.* 23, 257–263.
- Meltzer, M., Callahan, M., Jensen, T., 1990. Metal-Bearing Waste Stream: Minimizing Recycling and Treatment. Noyes Data Corporation, Park Ridge, N. J.
- Nishiyama, S., Saito, K., Saito, K., Sugita, K., Sato, K., Akiba, M., Saito, T., Tsuneda, S., Hirata, A., Tamada, M., Sugo, T., 2003. High-speed recovery of antimony using chelating porous hollow-fiber membrane. *J. Membr. Sci.* 214, 275–281.
- Ozawa, I., Saito, K., Sugita, K., Sato, K., Akiba, M., Sugo, T., 2000. High-speed recovery of germanium in a convection-aided mode using functional porous hollow-fiber membranes. *J. Chromatogr. A* 888, 43–49.
- Petkova, E.N., Vassilev, H., 1982. The kinetics of antimony(III) sorption on inorganic ion exchangers for its removal from copper refining electrolysis. *Hydrometallurgy* 8, 185–191.
- Pitman, A.L., Pourbaix, M., Zoubov, N., 1957. Potential-pH diagram of the antimony–water system. *J. Electrochem. Soc.* 104, 594–600.
- Roberts, W.L., McMurray, W.J., Rainey, P.M., 1998. Characterization of the antimonial antileishmanial agent meglucamine antimonite (glucatime). *Antimicrob. Agents Chemother.* 42, 1076–1082.
- Saito, K., Saito, K., Sugita, K., Tamada, M., Sugo, T., 2002. Cation-exchange porous hollow-fiber membranes prepared by radiation-induced cografting of GMA and EDMA which improved pure

- water permeability and sodium ion adsorptivity. *Ind. Eng. Chem. Res.* 41, 5686–5691.
- Saito, T., Kawakita, H., Uezu, K., Tsuneda, S., Hirata, A., Saito, K., Tamada, M., Sugo, T., 2004. Structure of polyol-ligand-containing polymer brush on the porous membrane for antimony(III) binding. *J. Membr. Sci.* 236, 65–71.
- Ubaladini, S., Veglio, F., Fornari, P., Abbruzzese, C., 2000. Process flow-sheet for gold and antimony recovery from stibnite. *Hydrometallurgy* 57, 187–199.
- Xu, Y.-H., Ohki, A., Maeda, S., 2001. Adsorption and removal of antimony from aqueous solution by an activated alumina. *Toxicol. Environ. Chem.* 80, 133–144.