



# Antimony Removal from the Polyethylene Terephthalate Manufacture Wastewater

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In this study, antimony removal by coagulation from polyethylene terephthalate resin production wastewater of "Orion Global PET" factory in Klaipėda city was investigated with regard to its dependence on a coagulant type and dosage, pH and presence of organics.  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{TiCl}_4$  salts were used as coagulants. Ti(IV) and Fe(III) appeared to be the most effective coagulants. Antimony removal effectiveness is moderate and low using  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  coagulants, respectively. The addition of  $10 \text{ mg dm}^{-3}$  Ti(IV) and  $30 \text{ mg dm}^{-3}$  Fe(III) reduces Sb by ~98%, when the initial amount of Sb in wastewater is about  $1200 \text{ mkg/l}$ . The action of Fe(III) is practically independent in the pH range 4-9, and that of Ti(IV) slightly decreases in the same pH interval. The Sb amount in wastewater can be reduced to  $13\text{-}20 \text{ mkg dm}^{-3}$ , while the initial Sb concentration is  $1200 \text{ mkg dm}^{-3}$ . The presence of organic compounds in wastewater determines the reduction of Sb removal by coagulation.

Keywords: *Antimony, removal, wastewater, coagulation.*

## 1. Introduction

Antimony is a toxic metal whose toxicity is comparable with that of arsenic. As antimony compounds find application in many manufacturing processes, the removal and/or recovery of dissolved or precipitated antimony from an industrial stream is a relevant ecological problem. Antimony oxide  $\text{Sb}_2\text{O}_3$  is employed as catalyst in production of polyethylene terephthalate (PET) resin, which is used as material for food and other liquid containers. Some dissolved antimony is present in PET production wastewater. This water also contains several organic contaminants, such as ethylene glycol, dioxan, acetic aldehyde, ethanol and some others and generally undergoes biological treatment. The antimony amount in wastewater spilled into municipal sewerage is recommended not to exceed  $0.2 \text{ mg dm}^{-3}$  (Grushko, 1979). Antimony could empoison biological sludge of wastewater treatment plants, although its amount in the sludge is not defined.

Currently there are several technological processes for removal of heavy metals from wastewater: precipitation (sedimentation), ion

exchange, adsorption, electrochemical processes, and recently emerging biological methods. Various methods are specifically applied to Sb removal from water solutions, e.g. by coagulation (Kang et al. 2003, Gannon et al. 1986, Guo et al. 2009, Inoue & Munemori 1980), adsorption onto granular ferric hydroxide (Cumming et al. 2007), using ion-exchange (U.S Patent 1977), adsorption onto activated carbon (Navarro & Alguacil 2002), by reverse osmosis membranes (Kang et al. 2000), and by electroreduction from the copper electrorefining solution (Koparal et al. 2004). In comparison with the other methods, coagulation is the most important treatment process, as it is relatively low-cost, especially when large amounts of wastewater are to be treated. Incidentally, the research into this field related to antimony removal is not very extensive.

The aim of the present work was to investigate the possibility of reducing the antimony amount by coagulation in polyethylene terephthalate resin production wastewater.

**2. Materials and methods**

Wastewater from the “Orion Global PET” factory in Klaipeda city has been studied in this work and named PET solution. Apart from antimony, wastewater contained also some organic compounds ( $\text{mg dm}^{-3}$ )—acetic aldehyde (130-160), 1,4 dioxan (800-820), ethylene glycol (3700-3900), ethanol (200-220), and negligible amounts of inorganic salts ( $<0.05 \text{ mg dm}^{-3}$ ). Sb concentration was measured using ICP-OES OPTIMA 7000 DV (PerkinElmer), analytical spectral line Sb I at 206.833 nm axial viewing. Calibration standards were prepared from the extra pure potassium antimony (III) oxide tartrate salt (Merc) solution. Instrumental parameters: RF power 1300W, argon plasma gas flow rate - 15  $\text{l min}^{-1}$ , auxiliary gas flow rate - 0.2  $\text{l min}^{-1}$ , aerosol carrier gas flow rate - 0.6  $\text{l min}^{-1}$ , cross-flow nebuliser, Scott spray chamber. Sb detection limit 2-3 ppb. Relative Sb measurement error reached ~10%.

Coagulation tests were performed in chemical beakers adding to 100 ml wastewater volume a desirable amount of coagulants – analytical grade salts:  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  or  $\text{TiCl}_4$ . Liquids with the coagulant were shaken for 10 min. and let settle for 2h., then filtered through a dense paper filter and the antimony amount was determined. As seen from Table 1, 2 hours are sufficient to set the Sb coagulation equilibrium.

Table 1. Dependence of residual Sb concentration ( $\text{mkg dm}^{-3}$ ) on coagulation time in wastewater solution. Coagulant - Fe(III) ( $30 \text{ mg dm}^{-3}$ ). Initial Sb concentration -  $1190 \text{ mkg dm}^{-3}$ . pH - 5,6

Time, hours	2	4	7	24	48	96
Residual Sb, $\text{mkg dm}^{-3}$	61	63	63	77	80	70

The artificial solution was made dissolving  $\text{SbCl}_3$  salt in distilled water with or without addition of organic compounds and filtering it through a paper filter to separate insoluble  $\text{SbOCl}$  precipitate formed. The amount of the remnant of Sb(III) was analyzed by ICP-OES. In several cases the samples were filtered through 0.22  $\mu\text{m}$  micro porous membrane filter and the Sb analysis results were compared with those established in paper filtered solutions. The test showed a small difference ( $<3\%$ ) of Sb amount in both filtrates, therefore in further work the patterns were filtered through the paper filter.

**3. Results**

The application of routine coagulants shows the most effective reaction of Fe (III) to Sb removal (Fig.1).

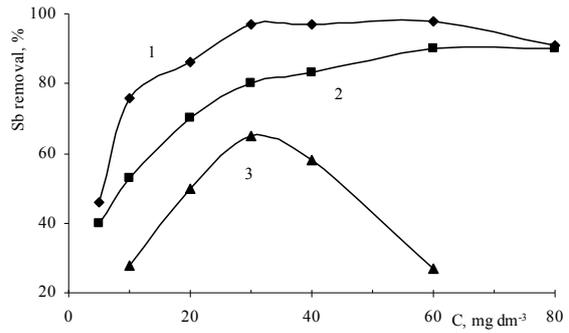


Fig.1. Sb removal versus coagulant (C) concentration. 1- Fe(III), 2-Fe(II), 3-Al(III), pH=7. Initial Sb concentration -  $1200 \text{ mkg dm}^{-3}$

To achieve 97-98% of Sb removal, a  $30 \text{ mg dm}^{-3}$  Fe(III) portion was needed. Fe(II), and especially Al(III) coagulants showed worse results. Figure 2 shows that Fe(III) effect is practically pH-independent in the pH interval 4-9.

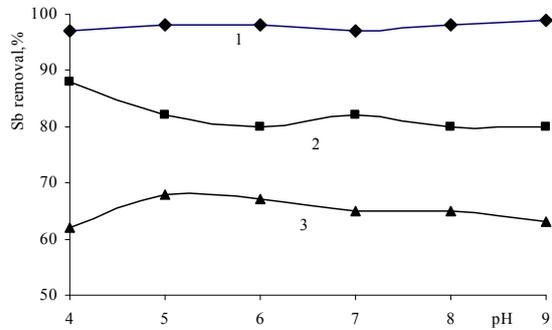


Fig.2. Dependence of Sb removal on pH. Coagulants ( $30 \text{ mg dm}^{-3}$ ): 1- Fe(III), 2-Fe(II), 3-Al(III), pH=7. Initial Sb concentration -  $1200 \text{ mkg dm}^{-3}$

These results conform to the antimony coagulation data of Kang et al. and Guo et al. assuming the presence of antimony in the Sb(III) form. According to the data of Guo et al. (2009) removal of Sb(V) by  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  proceeds at a lower rate than that of Sb(III), and is considerably pH-dependent.

Using a rarely operational coagulant –Ti(IV), better results were achieved (Fig.3).

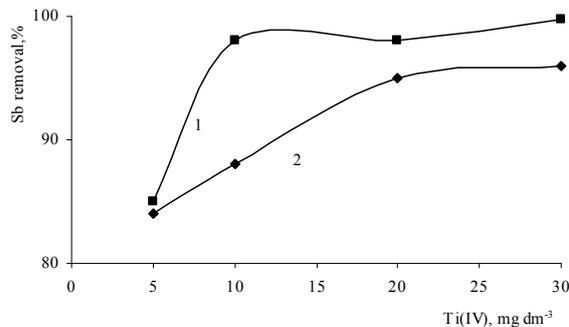


Fig.3. Dependence of Sb removal on Ti(IV) concentration. pH: 1-4, 2-6. Initial Sb concentration  $1200 \text{ mkg dm}^{-3}$

10 mg dm<sup>-3</sup> Ti(IV) was sufficient to obtain 98% of Sb removal and nearly full elimination (>99%) with 30 mg dm<sup>-3</sup> Ti(IV) at pH 4. The Ti(IV) effect slightly decreases with pH increase (Fig.4).

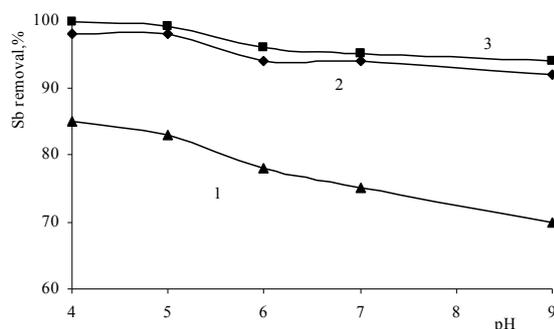


Fig.4. Dependence of Sb removal on pH. Coagulant Ti(IV) mg dm<sup>-3</sup>: 1-5, 2-20, 3-30. Initial Sb concentration 1250 mkg dm<sup>-3</sup>

Thus, Fe(III) and Ti(IV) coagulants make it possible to reduce the Sb amount in wastewater to 13-18 mkg dm<sup>-3</sup>, when the initial Sb concentration is about 1200 mkg dm<sup>-3</sup>.

Kang et al. (2003) have established the influence of organics on antimony coagulation, namely, that presence of organics (dissolved organic carbon) determines the reduction of Sb removal by coagulation. Sb removal from the artificial solution, SbCl<sub>3</sub> dissolved in water (Fig.5), is more complete than from the PET solution (Fig.1) with minor amounts of Fe(III) coagulant.

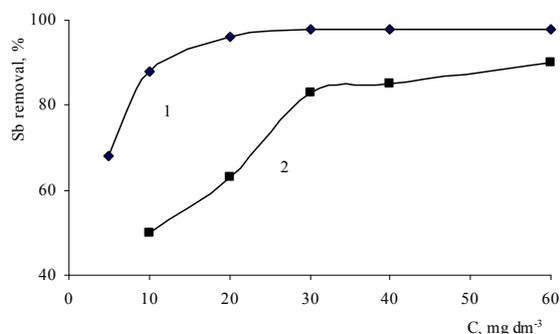


Fig.5. Dependence of Sb removal on coagulant (C) concentration in the artificial solution. Coagulants: 1- Fe(III), 2-Fe(II). pH=7. Initial Sb concentration 1370 mkg dm<sup>-3</sup>

This difference might be determined by the presence of organics in the PET solution. Actually, when the artificial solution possesses organic compounds inherent to the PET solution, Sb removal proceeds to a lesser extent (Fig.6).

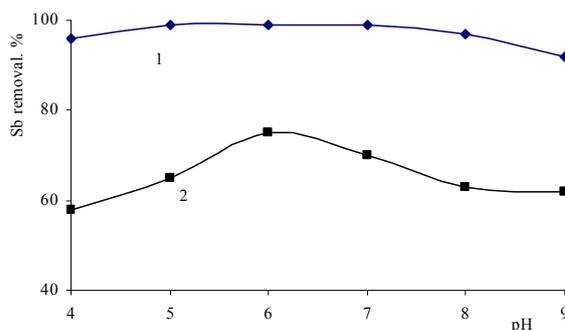


Fig.6. Dependence of Sb removal in artificial solution on pH. 1- without organics, 2- with addition (mg dm<sup>-3</sup>): acetic aldehyde 150, 1,4 dioxan 810, ethylene glycol 3830, ethanol. Coagulant - Fe(III) 30 mg dm<sup>-3</sup>. Initial Sb concentration 1370 mkg dm<sup>-3</sup>

Possibly, Sb forms links with the organic compounds, and therefore the Sb coprecipitation is limited. Undoubtedly, Sb removal proceeds through coprecipitation of Sb species present in the solution with metal hydroxides added, or formed by hydrolysis of metal salts. Coprecipitation is due to the adsorption, which can occur in different ways - through electrostatic interaction, van der Waals forces, dipole-dipole interactions (physisorption) or coordination between the participant species (chemisorption). On the ground of the published data it is difficult to state which mechanism of adsorption prevails. Enders and Jekel (1996) propose that Sb(III) is specially bound to iron oxyhydroxide and the adsorption behavior can be described using the triple layer model assuming the formation of mono and binuclear complexes. Guo et. al. (2009) have shown that Sb(III) and Sb(V) removal by ferric coagulation fits the diffuse-layer model. It has been reported (Stumm & O'Melia 1968) that the cationic Fe hydroxide species transform to the anionic ones by pH increase from 5 to higher values. Meanwhile, Sb(III) removal by the Fe(III) coagulant is slightly dependent on pH in 5-9 pH range both in PET and artificial solutions (Fig.2 and Fig.6). Likely, coprecipitation in this case is determined not by electrostatic interaction, but, presumably, by chemical coordination. Generally, physisorption is an exothermic process and runs by heating in the reverse direction. Our tests have shown that the temperature practically has no effect on the antimony removal using Fe(III) and Ti(IV) coagulants (Table 2) and support the point about the chemical nature of coprecipitation reason.

Table 2. Sb removal efficiency (%) by coagulation in the PET solution with Fe(III) (30 mg dm<sup>-3</sup>) and Ti(IV) (20 mg dm<sup>-3</sup>) coagulants. Initial Sb concentration 1200 mkg dm<sup>-3</sup>. Efficiency data is an average of 4 parallel tests

Coagulant, mg dm <sup>-3</sup>	20°C	30°C	40°C	60°C
Fe(III)	94	95	94	95
Ti(IV)	96	93	94	96

#### 4. Conclusion

The amount of antimony in the wastewater of polyethylene terephthalate (PET) resin production can be reduced by coagulation using  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{TiCl}_4$  salts. The most effective coagulants are Ti(IV) and Fe(III). The addition of  $10 \text{ mg dm}^{-3}$  Ti(IV) and  $30 \text{ mg dm}^{-3}$  Fe(III) reduces by ~98% of Sb amount, when the initial amount of Sb in wastewater is about  $1200 \text{ mkg dm}^{-3}$ . The action of Fe(III) is practically independent in the pH range 4-9, and that of Ti(IV) slightly decreases in the same pH interval. The presence of organic compounds in wastewater determines the reduction of Sb removal by coagulation. Using Fe(III) and Ti(IV) coagulants the Sb amount in wastewater can be reduced to 13-20  $\text{mkg dm}^{-3}$ , when the initial Sb concentration is  $1200 \text{ mkg dm}^{-3}$ .

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## **Stibio šalinimas iš polietileno tereftalato gamybos nutekamųjų vandenų**

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Klaipėdos įmonėje „Orion Global Pet“ polietileno tereftalato granulių gamybai katalizatoriumi naudojamas stibio oksidas. Nedidelis kiekis stibio patenka į nuotėkas. Stibio nuodingumas lygintinas su arsenu, todėl jo patekimas į gamtinę aplinką ribojamas. Šiame darbe siekta sumažinti stibio kiekį nutekamuosiuose vandenyse koaguliacijos būdu. Koaguliantais naudotos  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  ir  $\text{TiCl}_4$  druskos. Efektyviausi koaguliantai buvo  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  ir  $\text{TiCl}_4$  druskos, ne taip efektyviai veikė  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  ir  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ . Į nuotėkas, turinčias apie  $1200 \text{ mkg dm}^{-3}$  stibio pridėjus  $10 \text{ mg dm}^{-3}$  Ti(IV) ir  $30 \text{ mg dm}^{-3}$  Fe(III) koagulantų, stibio kiekį galima sumažinti iki  $13 - 20 \text{ mkg dm}^{-3}$ , t. y. apie 98 %. Fe(III) koaguliacinio poveikio efektyvumas pH intervale beveik vienodas, o Ti(IV) koagulianto efektyvumas, didėjant pH, mažėja. Organiniai junginiai, esantys nuotėkose, mažina stibio pašalinimo naudotais koaguliantais efektyvumą.