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Effect of water addition on centrifugal treatment to remove lead compounds from polyvinylchloride in electric wires and cables

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Abstract: Recycling treatment of cable insulation resin generated from electric wires and cables was investigated. Here, PVC is the most common insulation resin and conventional insulation PVC contains a lead component, tribase, as a thermal stabilizer. To recycle this PVC as insulation resin, lead removal is necessary to be able to conform to RoHS. This paper proposes a solvent dissolution and centrifugation method and the effects of flocculants and water addition in the processes involved are described.

Key words: polyvinylchloride, recycling, lead removal, centrifugation

1. INTRODUCTION

Used electric wires and cables recovered from electric power suppliers and building wreckers in Japan are cut to liberate and separate into metal conductors and cable insulation for recycling. Cable insulation is made of several kinds of resin: polyvinylchloride (PVC), polyethylene (PE), and cross-linked polyethylene (XLPE) and the PVC is most common. The amount of collected cable insulation per year is 36,000 tons and the collection ratios of mixed plastics is high (44.1%), followed by PVC at 25.1% in Japan [1]. Material recycling of mixed plastic is difficult and most is discarded in landfills. Thus plastic-plastic separation methods have been investigated [2] and electrostatic separation techniques have been used in cable insulation plastic treatment [3]. The authors [4, 5] have applied jig separation methods to cable insulation plastics, PVC, and non-PVC and reported high separation efficiencies. Single component resin pellets of PVC and PE, crushed used cable insulation, are sold as recyclable pellets, for use in the production of flooring and seat plastics and other usages [6], since these pellets do not meet required performance criteria as cable insulation.

The PVC cable insulation contains lead compounds as a thermal stabilizer [7] and the use of toxic substances such as lead is regulated strictly by RoHS (Restriction of Hazardous Substances in electric and electronic equipment) in the EU. In RoHS, lead concentrations in electric and electronic equipment must be below 1,000 ppm. The vinyloop method [8] can produce recycled resin, which can be reused as flooring material and in other applications, by removing impurities like rubber, glass, and soil from the used PVC. This method has been used in a waste cable recycling plant in Ferrara, Italy and here the PVC products are first dissolved in an organic solvent, and then the PVC solution is filtered to remove large particulate impurities. In the next step, PVC and soluble additives are recovered with a deposition method by steam injection. The used organic solvent is recovered by a salting-out method and reused. In the vinyloop method, removal of the lead compound is difficult because lead is contained in very fine particles (average particle size, 1-2μm) and these lead containing compounds are not caught by the filtration.

To remove the lead compounds some methods have been investigated, including filtration and leaching methods [9] but technical problems such as plugging of filters and treatment of leaching solution are remaining. The authors have investigated lead removal using liquid-liquid interface trapping [10], solid surface adsorption [11], and this paper describes the centrifugation method applied to lead removal. The authors have reported flocculation of lead compounds in methyl ethyl ketone using water addition [12] and the effects of water addition on lead removal using the centrifugation method is reported here.

2. MATERIALS AND METHODS

2.1 Materials

Virgin cable insulation PVC was used in the experiments. This sample contains tribasic lead sulfate (tribase, $3PbO\ PbSO_4\ H_2O$, Pb concentration: 17,600 ppm) and calcium carbonate ($CaCO_3$, Ca concentration: 120,000 ppm). Methyl ethyl ketone (MEK, Daishin Chemical Corporation) was used as the organic solvent. Poly acrylamide (Polyscience Inc.), polyethylene glycol (Wako Pure Chemical Industries, Ltd.), and sodium lauryl sulfate (Tokyo Chemical Industry Co., Ltd.) were used as flocculants.

2.2 Methods

Fig. 1 shows an outline of the lead removal treatment from PVC and this treatment is composed of two processes, a dissolution process and a centrifugation process. In the dissolution process MEK was used as solvent for the PVC and various amounts of PVC was added into 300 cm^3 of MEK and dissolved at 80 ^oC, for 2 hours, at 1200 rpm by an impeller. In the water addition experiments, a mixture of MEK and water was used in the dissolution process. After the dissolution the dissolved solution was distributed into bottles of 50 cm^3 and centrifuged at a given centrifugal force. After centrifugation 20 cm^3 of supernatant was removed by a pipette and put on a petri dish for drying. Drying was carried out in two stages (first drying: at room temperature for 12 hours in a draft chamber, and second drying: at 70 ^oC for 12 hours in an oven). The dried sample was analyzed for lead concentration by acid dissolution and the elemental concentration measurement was performed by inductively coupled plasma analysis. In the acid dissolution process, 0.2 g of shredded PVC was added to 8 cm^3 of nitric acid (60 wt% conc.) and this was treated by a microwave digestion method.

Flocculant addition experiments were carried out by a two stage centrifugal method. At first, dissolved PVC was centrifuged at 1000 G, gravity force, for 1 minute and the supernatant was placed in another bottle for the second stage. Here, flocculants were added to the supernatant and the bottle was shaken by hand, 180 strokes/min 30 cm of amplitude, then centrifuged at 2000 G for 5 minutes.

3. Results and discussion

According to RoHS the lead concentration in recovered PVC must be less than 1000 ppm to allow use as cable insulation. Lead removal tests were carried out under several conditions.

3.1 Effect of sample concentration on lead removal

The PVC sample contains tribase and calcium carbonate and the average diameter of particles is 1-2 μm for tribase and 4-5 μm for calcium carbonate. The purpose of this centrifugation experiment is the removal of lead as the sink product together with calcium carbonate. The viscosity of the solution affects the centrifugation and the viscosity changes with the PVC content in the dissolved solutions. Fig. 2 shows the effect of PVC sample content in the dissolved solutions on lead removal (centrifugal force: 2300 G, for 30 minutes) and the viscosity of the dissolved solutions. Dissolution of PVC was carried out by mixing 9, 15, 21, or 30 g of PVC and 300 cm^3 (241.4 g) of MEK. This corresponds to a PVC content of 3.59, 5.85, 8.00, 11.05 wt%. The viscosity of the solutions with dissolved PVC was from 1.3 cps (PVC content 3.59 wt%) to 14 cps (11.05 wt%) and the lead concentration in the recovered PVC increased with increasing PVC content. The lead concentration shows as less than 1000 ppm below the

PVC content of 5.85 wt% and the following experiments were carried out at the 5.85% PVC content.

3.2 Effect of centrifugal force on lead removal

The centrifugation treatment was carried out at given centrifugal forces for 30 minutes, and Fig. 3 shows the effect of centrifugal force on the lead removal. The lead concentration in the recovered PVC was less than 1000 ppm over the centrifugal force of 2300 G and the lead concentration decreases with increasing centrifugal force and reached less than 100 ppm over a centrifugal force of 8300 G. Two stage centrifugation experiments are reported in the next section.

3.3 Two stage centrifugal experiments

Considering actual operational conditions, lower treatment times and centrifugal forces are desirable, and two stage centrifugal experiments were conducted, first: 1000 G, for 1 min and second: 2000 G, for 5 min. Fig. 4 shows the effect of this two stage centrifugation on the lead removal. The lead concentration in the recovered PVC did not reach below 1000 ppm by this two stage centrifugation and this indicates that assistance of flocculation is required for the low speed centrifugation treatment.

In the two stage centrifugal experiment calcium concentration in the recovered PVC decreased from 120,000 ppm to 1500 ppm with centrifugation at 1000 G, for 1 min and 91.7% of the calcium was concentrated in the sink product. The process of recovering calcium first as sink and then recovering lead at a higher centrifugal force can obtain a calcium rich product and a lead rich product separately and the calcium rich product can be used as raw material after removal of the small amount of lead impurities. The calcium and lead content in the sink product at a centrifugal force of 1000 G, for 1 min were 93% calcium and 6.6% lead.

3.4 Effect of flocculants on lead removal

Flocculants addition experiments were carried out with two stage centrifugation, after the first centrifugation (1000 G, 1 min.) flocculants were added to the supernatant of first stage and then the solution was centrifuged a second time at 2000 G for 5 minutes. Poly acrylamide (PAA) and polyethylene glycol (PEG) were used as polymer flocculants to bridge particles and sodium lauryl sulfate (SLS) was used as surfactant to decrease the dispersibility of the lead particles by surface modification. The concentrations of PAA, PEG, and SLS were 0.02, 0.75 and 0.72 wt%, respectively. Fig. 5 shows the effect of the flocculants on the lead removal. The value of the lead concentration with the PAA, PEG, and SLS was lower than the value without flocculant addition but did not reach below the lead concentration of 1000 ppm.

3.5 Effect of H_2O addition on lead removal

In a previous study, the authors have reported that the presence of small amounts of H_2O in MEK solutions leads to flocculation of lead particles [12]. Fig. 6 shows the particle size distribution of the lead particles in the MEK solutions containing various concentration of H_2O. With increasing H_2O addition, the particle size of the lead component became larger. Fig. 7 shows the effect of H_2O addition on the lead removal. At 5 vol% of H_20 addition, the lead concentration with two stage centrifugation becomes lower than 1000 ppm. This suggests that flocculation of lead particles occurred by the H_2O addition.

The PVC recovery at a H_2O addition of 5 vol% showed a lower value, 53% of that with no H_2O addition, 85%, and gel formation was observed in the sink product. This may have occurred by deposition of PVC since the power to dissolve PVC of MEK decreases with increasing H_2O content. The lead concentration in this gel showed a higher value, 28,750 ppm, than that of the feed, 17,600 ppm, showing that this gel formation also may improve lead removal.

4. Conclusions

A solvent dissolution and centrifugation method to remove the lead component from PVC containing tribase as thermal stabilizer of cable insulation resin is proposed. High acceleration at centrifugation improved lead removal and the lead content in the recovered PVC was below 1000 ppm at the centrifugal force of 2300 G.

A two stage centrifugal method can obtain a calcium carbonate rich product as sink from the first low speed centrifugation and a tribase rich product as the sink of the second centrifugation. The second centrifugation was carried out with higher speed and for a longer time than the first stage since the particle size of the tribase is smaller than that of calcium carbonate. Flocculants and water addition improved lead removal and water addition of 5 wt% could achieve the regulation value required by RoHS, 1000 ppm.

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Figures

Fig. 1 Outline of the lead removal treatment for PVC proposed here.

Fig.2 Effect of the PVC content on the lead concentration in the recovered PVC and the viscosity of the PVC dissolved solutions.

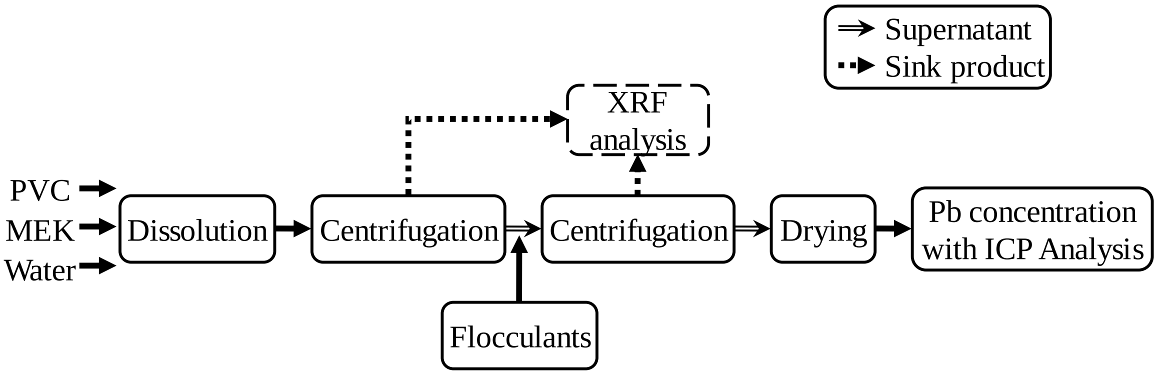
Fig.3 Effect of the centrifugal force on the lead concentration of the recovered PVC.

Fig.4 Effect of the second stage centrifugation on the lead concentration in the recovered PVC.

Fig.5 Effect of flocculants addition on the lead concentration in the recovered PVC (PAA: poly acrylamide, PEG: polyethylene glycol, SLS: sodium lauryl sulfate).

Fig.6 Particle size distribution of lead particles in MEK solutions containing various concentrations of H2O.

Fig. 7 Effect of H2O addition on the lead concentration in the recovered PVC.



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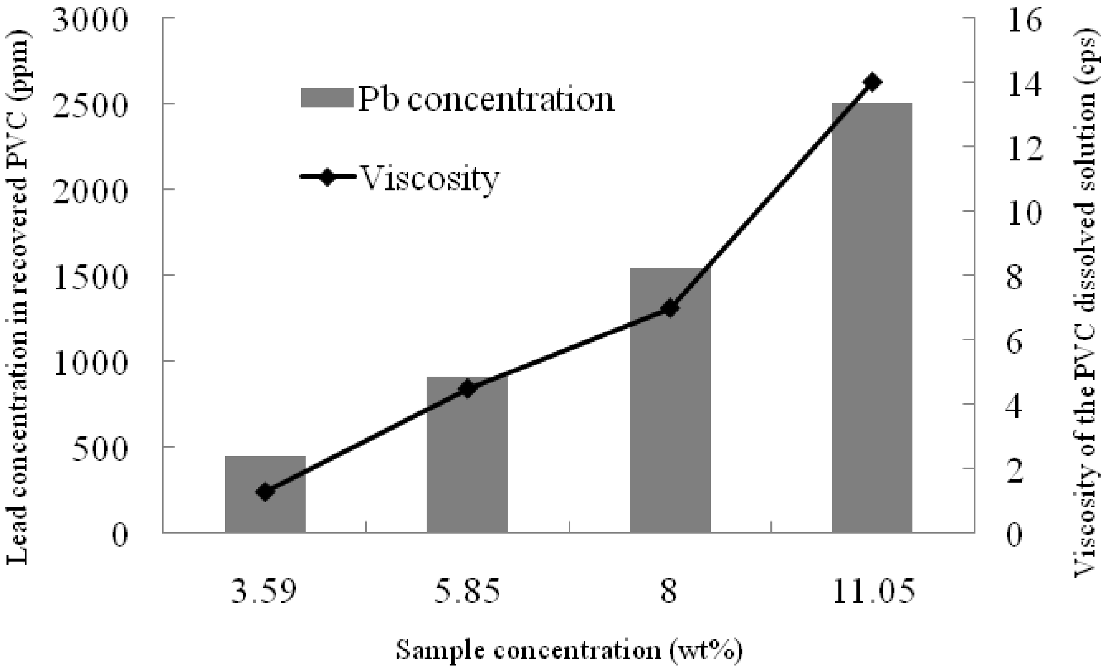

Fig.2 Effect of the PVC content on the lead concentration in the recovered PVC and the viscosity of the PVC dissolved solutions.

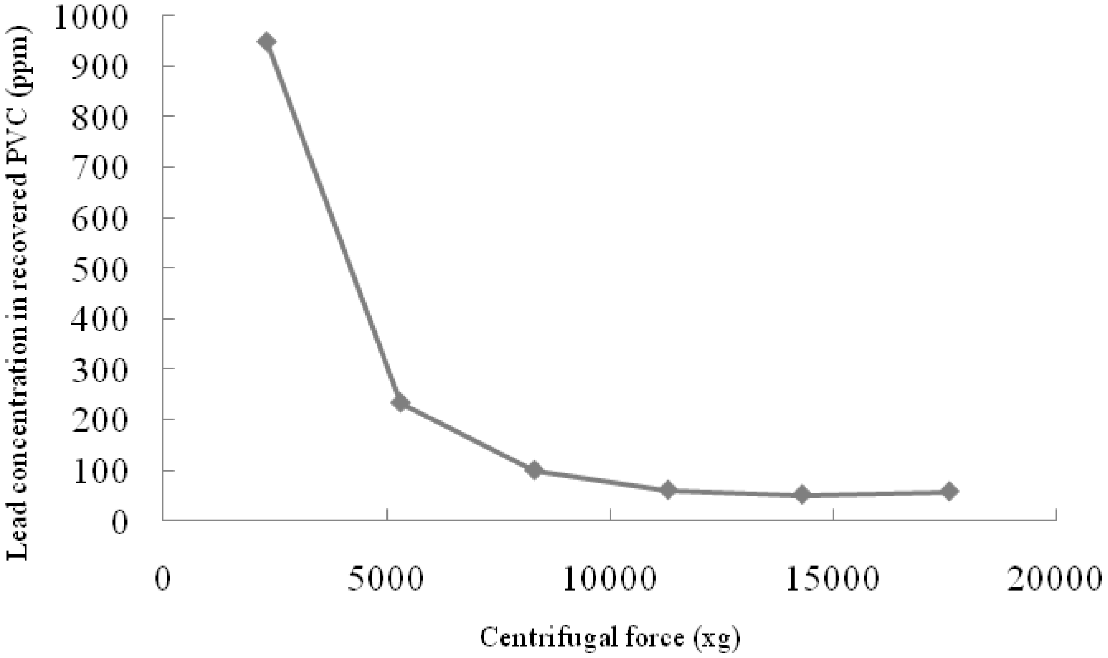

Fig.3 Effect of the centrifugal force on the lead concentration of the recovered PVC.

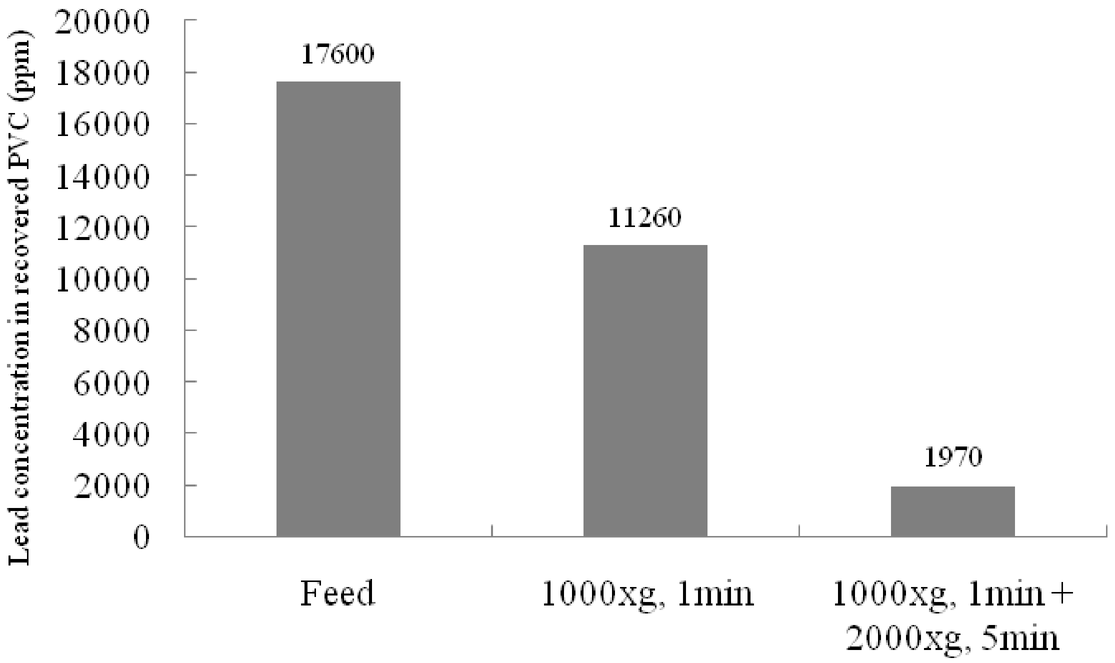

Fig.4 Effect of the second stage centrifugation on the lead concentration in the recovered PVC.

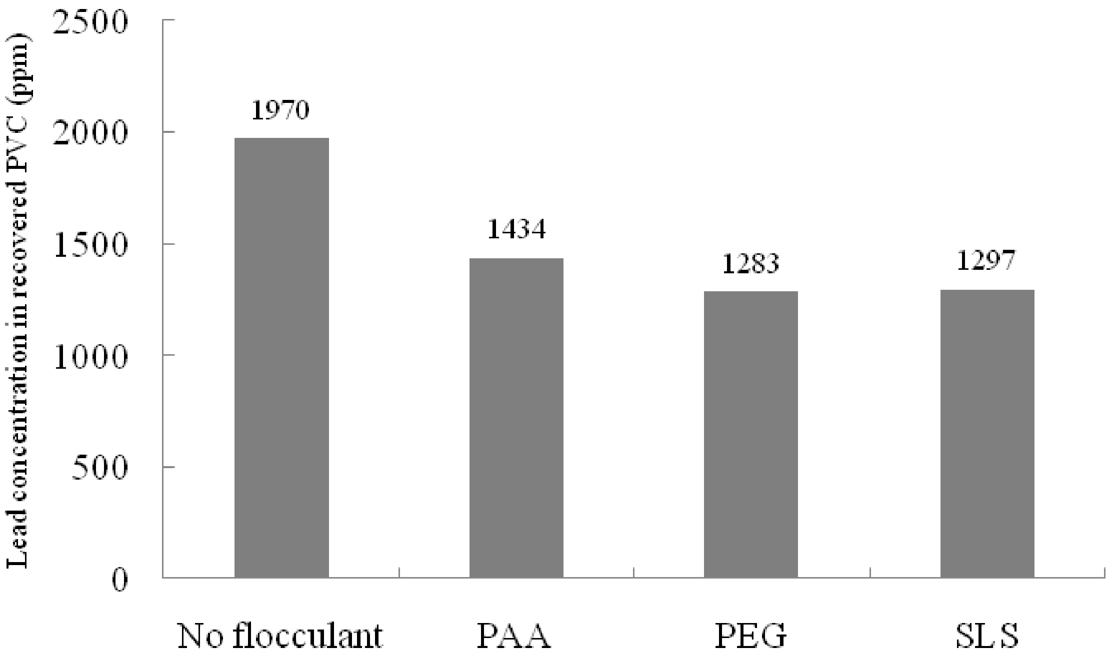

Fig.5 Effect of flocculants addition on the lead concentration in the recovered PVC (PAA: poly acrylamide, PEG: polyethylene glycol, SLS: sodium lauryl sulfate).

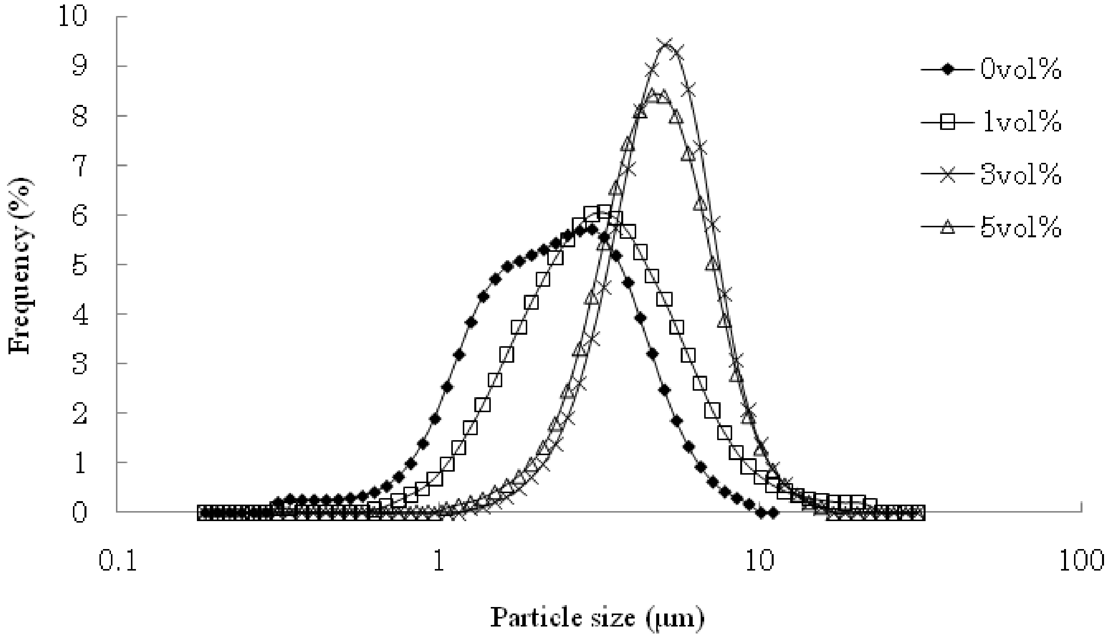

Fig.6 Particle size distribution of lead particles in MEK solutions containing various concentrations of H_2O.

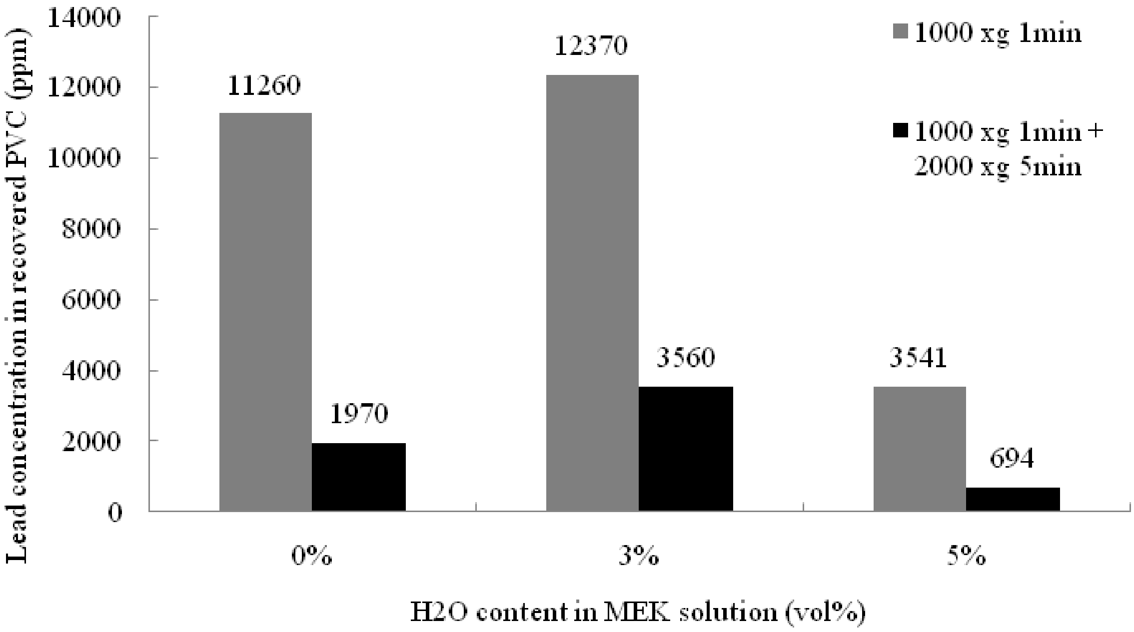

Fig. 7 Effect of H_2O addition on the lead concentration in the recovered PVC.