Recycling of Spent Hydrodehalogenation Catalysts – Problems Dealing with Separation of Aluminium

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Abstract

Our study is focused on utilization and recycling of copper and nickel applicable for reductive degradation of tetrabromobisphenol A (TBBPA), the high use brominated flame retardant for printed circuit boards. Deactivated and/or poisoned hydrodebromination catalysts are produced by reductive destruction of brominated phenol (TBBPA) dissolved in alkaline aqueous solution using Raney Al-Ni and/or Devarda´s Al-Cu-Zn alloys. Spent metallic slurry is treated with aqueous sulfuric acid to dissolve residual aluminium and/or zinc and decanted residual metal is subsequently treated under oxidation conditions and dissolved in excess of mineral acid by co-action of oxidant. The corresponding metal salt is separated from corresponding leachates containing excess of acid by evaporation and recycling of volatile components. Obtained copper or nickel salts were used as sources of Raney type hydrodebromination catalysts produced for in-situ by action of $NaBH_4$.

Keywords: Raney nickel; copper; tetrabromobisphenol A; hydrometallurgy; borohydride; reduction

Introduction

In sustainable system for use of materials, not only the production of goods needs to be sustainable, but also the management of residues and wastes (Gutknecht et al., 2017).

Copper is with high recovery priority, followed by nickel, aluminum, tin, lead, zinc and other (Wu et al., 2017).

Owing to the current rapid development of electronic technology, electrical and electronic equipment, for example printed circuit boards (PCBs), have a shorter life span compared to products produced in the past. The resultant short life spans of electrical and electronic equipments have generated large amounts of waste, known as e-waste. Useful components can be recovered from e-waste to save resources. This is because e-waste from PCBs has a high metal content. Waste PCBs contain approximately 70% nonmetals, 10% of copper and 20% of another metals (Xiu et al., 2014).

However, the PCBs exhibit complex multilayered metal-woven glass fiber structure which is reinforced by brominated epoxy resin containing 15–20 wt% of flame retardants (Ghosh et al., 2015).

The main structural part of brominated epoxy resins is tetrabromobisphenol A (TBBPA), which is the highest production volume brominated flame retardant. The primary use of TBBPA is as a reactive flame retardant in resins for PCBs (Malkoske et al., 2016).The occurrence of TBBPA can behave as precursor in the formation of highly stable and toxic poly- brominated dibenzo-p-dioxins and benzofurans (PBDD/Fs) (Tang et al., 2014).

Given that brominated flame retardant materials in e-waste plastics have been the major impediment for recycling treatment, chemical recycling has been proposed as an environmentally friendly method of recycling e-waste plastics for clean fuels production or chemical feedstocks (Ma Ch. et al., 2016).

Catalytic hydrodehalogenation is usually used to dispose waste halogenated compounds. The experiments of Shen and Sun (2009) proved that metal salts, FeCl3, NiCl2, CoCl2, CuBr and some iron complexes with benzimidazole ligand are efficient catalysts for hydrodebromination of bromoarenes under mild reaction conditions of room temperature and N2 atmosphere with two equivalents of Grignard reagents (Shen and Sun, 2009).

Moreover, Raney Al-Ni and Devarda´s Al-Cu-Zn alloys also displayed high dehalogenating aktivity in alkaline aqueous solution under room temperature and ambient pressure. (Weidlich T. et al., 2013).

However, the described Al-Ni or Al-Cu-Zn based hydrodebromination method produces copper or nickel slurry (spent Cu or Ni) as solid product with substantially reduced activity for further hydrodebromination. These slurries are simply separated by sedimentation of obtained reaction mixture. These slurries contain around 20 wt. % of unreacted aluminium and 80 wt. % of copper or nickel which are economically valuable metals. In addition, these metals are common components of PCBs. The potential recovery of Cu and Ni from spent hydrodebromination catalysts by simple and cost effective technique helps to solve the economy of the above mentioned remediation process. In addition, at least part of copper and nickel from waste PCBs could be utilized in hydrodebromination of brominated aromatic flame retardants.

Due to these reasons, attempts to recover copper and nickel applicable for hydrodebromination from separated metallic slurries were studied.

Materials and methods

The removal efficiency of reductive debromination of TBBPA was quantified by analysis of AOX content according to the Environmental Protection Agency (EPA Method 1650).

Aqueous alkaline 2.5 mM TBBPA solution was prepared by dissolution of 1.36 TBBPA (Sigma-Aldrich Co.) in 1 liter of 0.1M aq. NaOH solution. The measured AOX content is 425 mg L^{-1}.

Tab. 1. Content of sulfuric acid and metals before and after leaching

Tab. 1. Zawartość kwasu siarkowego i metali przed i po ługowaniu

Description of aq. solution	Concentration (wt %)	Metal concentration (mg L^{-1})	
	H_2SO_4	Ni	Al
Leachate Ni1 (13wt% H_2SO_4)	13	2666	1416
Leachate Ni2 (hot 13wt% H_2SO_4)	13	2655	1307
Leachate Ni3 ($K_2S_2O_8$/H_2SO_4)	32	1455	384
Leachate Ni4 (recycled aq.$NiSO_4$)	-	7362	3764

Tab. 2. Content of sulfuric acid and metals before and after leaching

Tab. 2. Zawartość kwasu siarkowego i metali przed i po ługowaniu

Description of aq. solution	Concentration (wt%)	Metal concentration (mg L^{-1})		
	of acid	Cu	Al	Zn
Leachate Cu1 (13wt% H_2SO_4)	13	1.0	345.4	187.9
Leachate Cu2 (hot 13wt% H_2SO_4)	13	0.2	2570.0	220.0
Leachate Cu3(H_2O_2/35 wt %HCl)	17	3928	7	30
Leachate Cu4 (recycled aq.$CuCl_2$)	-	10715	1.2	0.1

Application and recycling of Ni-based debromination catalyst

Debromination of TBBPA using Raney Al-Ni alloy

Raney Al-Ni alloy (410 mg, Sigma-Aldrich) was added into the 100 mL of alkaline aqueous 2.5 mM TBBPA solution, 150 mL of 0.1 M aqueous NaOH was added and the obtained suspension was stirred at room temperature overnight. After filtration, the content of AOX in filtrate was measured (AOX=2.38 mg L^{-1}) which indicates 98.6% removal efficiency of adsorbable organically bound halogen. The filter cake containing spent Ni catalyst was collected and stored under water.

1. Leaching of Al from spent Raney nickel catalyst in 13 wt% H_2SO_4

The slurry of spent nickel catalyst collected from five debromination experiments described above was filtered by suction and dried on air. 3.0 grams of wet Ni cake was mixed with 200 mL (217.2 g) of 13 wt. % H_2SO_4 (density 1.086 kg L^{-1}) under stirring and the obtained slurry was agitated about 15 hours, insoluble part was separated by sedimentation and 50 mL of liquid phase was filtered (Leachate Ni1). Obtained leachate Ni1 was analysed by inductively coupled plasma optical emission spectrometry (ICP-OES). The compositions of leachates are described in Table 1.

The remaining reaction mixture (150 mL) was heated 60 minutes at 100°C, filtered and filtrate was diluted to exact 200 mL using deionized water (Leachate Ni2) and analysed by ICP-OES.

2. Leaching of Ni from spent Raney nickel catalyst in 32 wt% H_2SO_4 by co-action of $K_2S_2O_8$

To the insoluble part, 540 mg of $K_2S_2O_8$ (2 mmol) was added, dissolved by addition of 40 mL of deionized water and mixed with 10 mL (19.4 g) of concentrated sulfuric acid. The obtained suspension was heated for 16 hours at 100°C. The obtained solution was cooled, the volume was adjusted to 100 mL using distilled water (leachate Ni3). Obtained solution was analysed by inductively coupled plasma optical emission spectrometry (ICP-OES). The composition of leachate 3 is described in Table 1.

3. Separation $NiSO_4$

Crystalline $NiSO_4$ was isolated from leachates 1–3 (300 mL) by evaporation of excess water at 140°C using oil bath (248.3 g of distillate was obtained) and subsequent separation crystals obtained by cooling of distillation residue at room temperature by suction. The green crystalline product was dissolved in deionized water, adjusted to 100 mL using deionized water and analysed by ICP-OES (leachate Ni4).

Debromination of TBBPA using recycled Ni:

$NaBH_4$ (0.8 g, 20 mmol) was dissolved in 100 mL of 0.1M aqueous NaOH solution. To this solution was added dropwise 50 mL of obtained leachate 4 (recycled Ni in the form of $NiSO_4$ solution) during 5 minutes and 50 mL of alkaline 2.5 mM aqueous TBBPA solution. The obtained suspension was stirred at room temperature overnight. After filtration, the content of AOX in filtrate was measured (AOX= 18.3 mg L^{-1}) which indicates 83% removal efficiency of adsorbable organically bound halogen. The filter cake containing spent Ni catalyst was collected and stored under water for further recycling. Obtained filtrate was acidified using 13 wt% H_2SO_4 to pH=6.2±0.2 and flocculated $Al(OH)_3$ was removed by filtration.

Application and recycling of Cu-based debromination catalyst

Debromination of TBBPA using Devarda´s Al-Cu-Zn alloy

Devarda´s Al-Cu-Zn alloy (800 mg, Sigma Aldrich Co.) was added into the 100 mL of alkaline aqueous 2.5 mM TBBPA solution, 150 mL of 0.1 M aqueous NaOH was added and the obtained suspension was stirred at room temperature overnight. After filtration, the content of AOX in filtrate was measured (AOX=6.43 mg L-1) which indicates 96.2% removal efficiency of adsorbable organically bound halogen. The filter cake containing spent Cu catalyst was collected and stored under water. Obtained filtrate was acidified with leachate Cu2 (see Table 2) to pH=6.2±0.2 and flocculated $Al(OH)_3$ was removed by filtration.

1. Leaching of Al and Zn from spent Devarda´s alloy in 13 wt% H_2SO_4

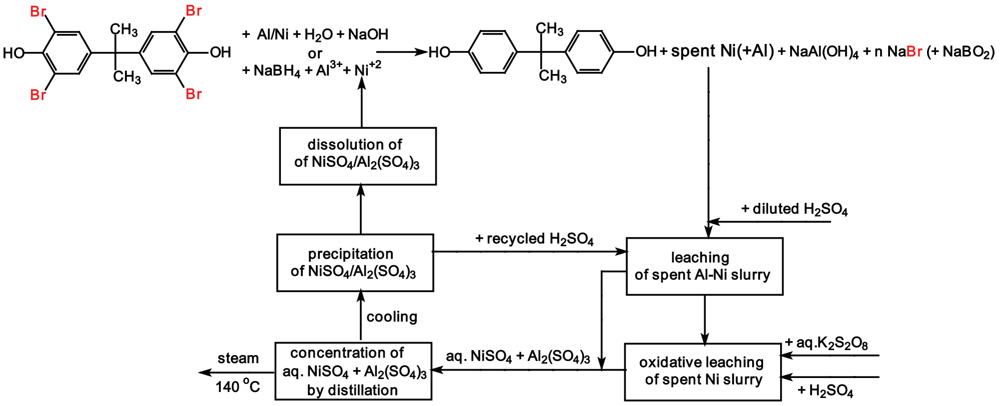

Fig. 1. Scheme of TBBPA hydrodebromination with subsequent recycling of spent Ni catalyst
Rys. 1. Schemat hydrodebrominacji TBBPA z późniejszym recyklingiem zużytego katalizatora Ni

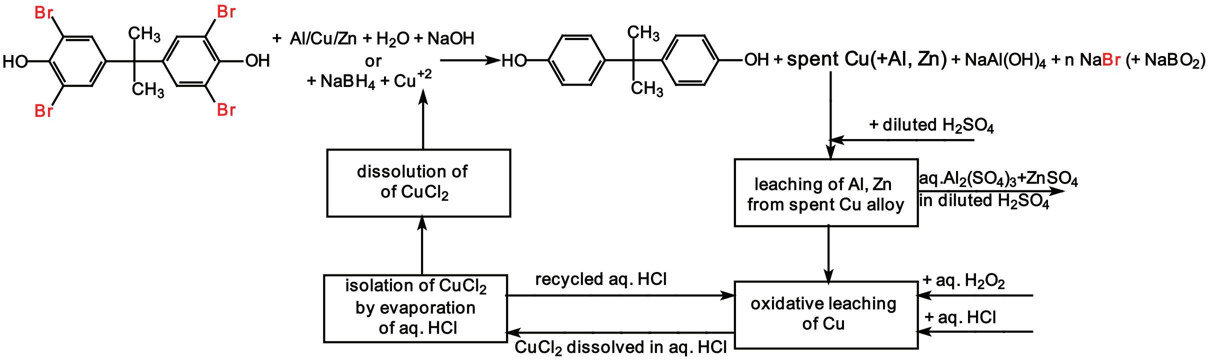

Fig. 2. Scheme of TBBPA hydrodebromination with subsequent recycling of spent Cu catalyst
Rys. 2. Schemat hydrodebrominacji TBBPA z późniejszym recyklingiem zużytego katalizatora Cu

The slurry of spent copper catalyst collected from three debromination experiments described above was filtered by suction and dried on air. 3.0 grams of wet Cu cake was mixed with 200 mL (218.3 g) of 13 wt. % H_2SO_4 (density 1.086 kg L^{-1}) under stirring and the obtained slurry was agitated about 15 hours, insoluble part was separated by sedimentation and 50 mL of liquid phase was filtered (Leachate Cu1). Obtained leachate 1 was analysed by inductively coupled plasma optical emission spectrometry (ICP-OES). The compositions of leachates are described in Table 2.

The remaining reaction mixture was heated 60 minutes at 100°C under stirring, filtered and filtrate was diluted to exact 200 mL using deionized water (Leachate Cu2) and analysed by ICP-OES.

2. Leaching of Cu from spent Devarda´s Al-Cu-Zn catalyst in 17 wt% HCl by co-action of H_2O_2

To the insoluble part, 25 mL (30 g) of 35 wt% aq.HCl was added and 11 mL (12 g) of 33 wt% H_2O_2 diluted with 18 mL of deionized water was added dropwise and subsequently stirred 60 minutes at 70°C. The obtained green solution was cooled, the volume was adjusted to 200 mL using distilled water (Leachate Cu3). Obtained solution was analysed by inductively coupled plasma optical emission spectrometry (ICP-OES). The composition of leachate 3 is described in Table 1.

3. Separation of $CuCl_2$

Crystalline $CuCl_2$ was isolated from leachate 3 (195 mL) by evaporation of excess water at 120°C using oil bath (178.7 g of distillate was obtained) and subsequent suction of precipitated crystals obtained by cooling of distillation residue at room temperature. The green crystalline product was dissolved in 100 mL of deionized water and analysed by ICP-OES (Leachate Cu4).

Debromination of TBBPA using recycled Cu:

NaBH4 (0.8 g, 20 mmol) was dissolved in 100 mL of 0.1M aqueous NaOH solution. To this solution was added dropwise 50 mL of obtained leachate Cu4 (recycled Cu in the form of CuCl2 solution) during 5 minutes and 50 mL of alkaline 2.5 mM aqueous TBBPA solution. The obtained suspension was stirred at room temperature overnight. After filtration, the content of AOX in filtrate was measured (AOX= 0.703 mg L^{-1}) which indicates 99.3% removal efficiency of adsorbable organically bound halogen. The filter cake containing spent Cu catalyst was collected and stored under water for further recycling. Alkaline filtrate was acidified with leachate Cu2 (see Table 2) to pH=6.2±0.2 and flocculated Al(OH)3 was removed by filtration.

Results and discussion

Both spent nickel and copper catalysts were produced by reductive destruction of harmfull tetrabromobisphenol A

(TBBPA, commonly used as flame retardant for PCBs) in model waste water using Raney Al-Ni or Devarda´s Al-Cu-Zn alloy as reductant at room temperature, ambient pressure in diluted NaOH solution (Figure 1 and 2). Slurry of used Ni (or Cu) catalyst was separated by filtration and treated using hydrometallurgical technique. Obtained aqueous phase from hydrodebromination steps were neutralized and treated with flocculation using dissolved aluminium salts.

The recycling procedure for spent Ni catalyst consists of three steps. At first, most of residual aluminium content and part of Ni in separated nickel slurry (spent Raney Ni) was dissolved in excess of diluted sulfuric acid and remaining insoluble part (metallic Ni) was subsequently dissolved in $K_2S_2O_8/H_2SO_4$ mixture. Both leachate were collected and crystalline $NiSO_4$ was isolated by concentration of leachates (evaporation of excess of water). The isolated green product was dissolved in 50 mL of deionized water, analysed by ICP-OES, and used in debromination step.

Nonselective leaching of collected spent nickel catalyst obtained from hydrodebromination of TBBPA described above was carried out using excess of 13 wt. % aqueous sulfuric acid and subsequent action of 32 wt. % sulfuric acid by co-action potassium peroxosulphate under reflux overnight (see Figure 1). The composition of leachates are depicted in Table 1.

It is desirable to recycle excess of used sulfuric acid from leach liquors due to the environmental and economic reasons. This is possible by use of diffusion dialysis (Bendova and Weidlich, 2018) or by evaporation of excess water and recycling of H_2SO_4 separated from precipitated salts. The separated H_2SO_4 (filtrate) could be recycled in Ni leaching step.

The separated mixture of $NiSO_4/Al_2(SO_4)_3$ salts was used as a source of Ni catalyst for hydrodebromination of TBBPA using excess of $NaBH_4$. However, as we tested, mixture of NiSO4 contaminated with $Al_2(SO_4)_3$ is not suitable source of Ni catalyst applicable for complete hydrodebromination of TBBPA.

Spent Cu catalyst recycling procedure consists of three steps. Separation of Cu and electropositive Al and Zn from spent catalyst slurry is quite selective using 13 wt. % sulfuric acid (see Table 2). High selectivity enables separation of $Al_2(SO_4)_3$ and $ZnSO_4$ in diluted H_2SO_4 and this leachate is suitable as neutralization/flocculation agent for alkaline filtrate obtained in hydrodebromination step. Subsequent leaching of remaining Cu slurry using aqueous HCl and H_2O_2 enables very effective dissolution of Cu. Produced CuCl2 was isolated simply by distillation of aqueous HCl. In addition, distilled aqueous HCl is simply recyclable in another Cu leaching step.

Prepared aqueous solution of recycled $CuCl_2$ in co-action of excess $NaBH_4$ was discovered as very effective hydrodebromination agent.

Conclusions

In conclusion, waste TBBPA is simply debrominated using Al-Ni or Al-Cu-Zn alloys. However, application of Cu-based catalyst is much more favourable due to its simple recycling by hydrometallurgical re-working and due its possible simple availability from recycled waste PCBs. Potentially, hydrometallurgical separation of Cu from spent PCBs with subsequent utilization of obtained $CuCl_2$ in hydrodebromination of waste flame retardant TBBPA produced by hydrolytic treatment of PCBs based epoxy resins enables safe, cheap and simple destruction of harmful TBBPA and production of metallic Cu.

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Recykling zużytych katalizatorów hydrodehalogenacji – problemy z separacją aluminium

Nasze badania koncentrują się na wykorzystaniu i recyklingu miedzi i niklu stosowanym do redukcyjnej degradacji tetrabromobisfenolu A (TBBPA), wysokowydajnego bromowanego środka zmniejszającego palność płytek obwodów drukowanych. Dezaktywowane i/lub zuzyte katalizatory hydrodebromowania wytwarza się przez redukcyjne zniszczenie bromowanego fenolu (TBBPA) rozpuszczonego w alkalicznym roztworze wodnym przy użyciu stopów Al-Cu-Zn Raneya Al-Ni i/lub Devarda. Zużyta metaliczna zawiesina jest traktowana wodnym roztworem kwasu siarkowego w celu rozpuszczenia resztkowego aluminium i/lub cynku, a zdekantowany pozostały metal jest następnie obrabiany w warunkach utleniania i rozpuszczany w nadmiarze kwasu mineralnego przez współdziałanie utleniacza. Odpowiednia sól metalu jest oddzielana od odpowiednich odcieków zawierających nadmiar kwasu przez odparowanie i zawracanie lotnych składników. Otrzymane sole miedzi lub niklu zastosowano jako źródła katalizatorów hydrodebromowania typu Raneya wytworzonych in situ przez działanie $NaBH_4$.

Słowa kluczowe: nikiel Raneya, miedź, tetrabromobisfenol A, hydrometalurgia, borowodorek, zmniejszenie