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Cu-Catalyzed Hydrodehalogenation of Brominated Aromatic Pollutants in Aqueous Solution

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Abstract: The catalytic effect of copper in Devarda's Al-Cu-Zn alloy (Dev. alloy) and sole metallic copper, copper salts and copper oxides in the coaction of $NaBH_4$ within the hydrodehalogenation (HDH) of polybrominated phenols, such as the herbicide Bromoxynil in alkaline aqueous solution has been investigated. Namely, the hydrodebromination (HDB) activity of Dev. alloy/NaOH system has been compared to heterogeneous Cu-based catalysts using $NaBH_4$ as a reductant. Differences in the solid-state structures of used Cu-based heterogeneous catalysts after the mentioned HDB process have been studied using the powder XRD and SEM techniques. It was found that some of the used copper-based catalysts are reusable and reasonably effective even at room temperature. Efficiency of the most promising copper-based reduction systems (Dev. alloy/NaOH and Cu-based catalysts/$NaBH_4$) have been successfully tested within the HDB of industrially important brominated flame retardant tetrabromobisphenol A (TBBPA). Dev. alloy/NaOH and Cu-based catalyst generated in-situ within the $CuSO_4$/$NaBH_4$ produced were recognized as the most active HDB agents for complete debromination of both BRX and TBBPA.

Keywords: Hydrodebromination; bromophenol; copper; Devarda's Al-Cu-Zn alloy; cuprous oxide; cupric oxide; $NaBH_4$; dehalogenation; Bromoxynil; TBBPA

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1. Introduction

Copper and its salts exhibit broad catalytic activity mainly due to the easily accessible and reasonable stability of Cu(0), Cu(I) and Cu(II) oxidation states [1–5]. They are therefore effective catalysts for both C_{arom}–H bonds transformations [1,2] and C_{arom}–halogen cleavage reactions [3,4].

Hydrodebromination (HDB) involves hydrogenolysis of C-Br bonds, requires an external supply of reductant (usually a source of hydrogen) and is typically promoted using a metal catalyst [4,5].

Brominated aromatic compounds have been broadly used mainly as effective flame retardants [6] and as pesticides [7]. The widespread application of such species has raised concerns about their persistence in the environment and their potential toxic effects on non-target organisms, including humans [8,9].

Bromoxynil (BRX) is a brominated hydroxybenzonitrile-based selective contact foliage herbicide used to control a variety of broadleaf weeds. In the past several years, bromoxynil has been applied in increasing quantities as a possible replacement for atrazine, which has been banned in many countries [10]. BRX has been classified as a Group C possible human carcinogen, and has been shown to be an endocrine disrupter in birds, fish and aquatic invertebrates. BRX can be present in soil, as well as surface water and contaminated ground waters by runoff and leaching [11,12]. In water, it is likely to pose health hazards to non-target aquatic organisms. Even the acute pesticide poisoning by bromoxynil was reported [13].

Tetrabromobisphenol A (TBBPA) has been widely used as brominated flame retardant (BFRs) in printed circuit boards, insulated wires and various polycarbonate plastics owing to its fire-resistant properties [13]. Due to the structural similarity of TBBPA with thyroid hormones, its release into the surroundings threatens the safety and health of the ecosystem, terrestrial and aquatic animals, and human health. The worldwide application releases TBBPA from the manufacturing, consumer product uses, recycling, and disposal process into the surrounding environment. So far, TBBPA and other BFRs pollutants have been detected in various environmental matrices including water [14].

Following toxicity of the mentioned brominated phenols and its increasing application, studying its effective degradation to the readily biodegradable products is desired. In most cases, oxidation processes are used for chemical treatment of recalcitrant contaminants [15–20].

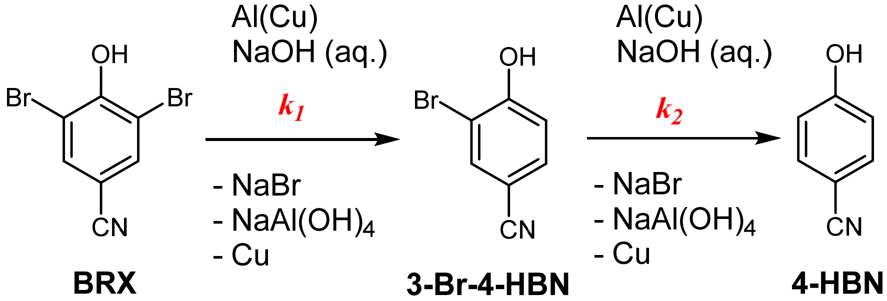
However, especially ortho-halogenated phenols tend to be transformed to the significantly more toxic dibenzo-p-dioxines using some oxidation processes [5,21]. It was published that photochemical H-atom abstraction from the OH group of BRX results in the formation of unstable phenoxy radical, which can undergo self-reaction resulting in the formation of brominated dibenzo-p-dioxins [21].

These brominated compounds are considered as the most dangerous persistent organic pollutants (POP) [22]. Due to the aforementioned reasons, the reductive treatment to non-halogenated and readily biodegradable products has recently gained attention [14,23–25]. Cu-catalyzed or Cu-mediated reductive treatment via the HDB plays important role in detoxification of polybrominated aromatic contaminants, as was previously published [26–30].

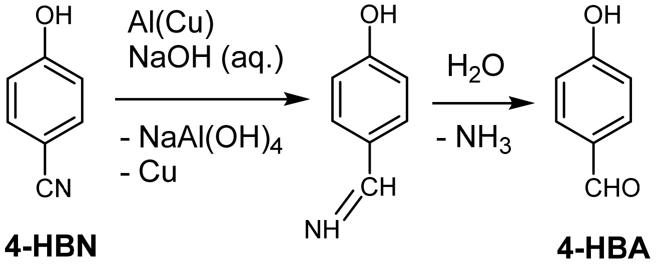
In this study, our primary objectives were to; (1) test the reaction conditions (minimal excess of reagents) necessary for the complete Cu-mediated HDB of BRX in alkaline aqueous solution, including the possibility of used/spent Cu-catalyst recycling, (2) compare effect of metallic copper, different copper alloys and copper compounds on the HDB efficiency of BRX, and finally (3) apply and compare studied reaction conditions for the possible HDB of TBBPA.

2. Results and Discussion

A set of experiments, involving chemically diverse reductants within the HDB of 3,5-dibromo-4-hydroxybenzonitrile (BRX), and dissolved in alkaline aqueous solution, were performed. Electropositive metals, various copper alloys containing electropositive metals and $NaBH_4$ were employed as potential HDB agents in these experiments. The results summarized in Table 1 show that only the Dev. alloy exhibits high HDB activity at room temperature over one hundred minutes of vigorous stirring of the respective reaction mixture (Table 1, Entries 1–8, Schemes 1 and 2, Figures 1 and 2). Other employed copper alloys are not effective within the HDB of BRX even at elevated temperature under such basic conditions (Table 1, Entries 9–11). Powdered aluminium, Fe_3Al alloy or zinc without coaction of copper exhibited no HDB efficiency towards BRX (Entries 12–15). Similarly, BRX is inert toward action of powdered elemental copper and other tested copper compounds without added reductant (Supplementary Materials Table S1). As expected, sole sodium borohydride causes mostly only partial HDB of BRX without addition of copper, even at elevated temperatures (Table 1, Entries 16 and 17). Upon the addition of metallic copper to $NaBH_4$, complete conversion of BRX is accomplished under comparable conditions (Table S2, Entries 5–7). The quantitative HDB of BRX is observed at elevated temperature (Table S2, Entry 5). These findings are in the agreement with our previous results regarding the HDB of 2,4,6-tribromophenol [26].



Scheme 1. Total HDB of BRX using the Dev. alloy in aqueous NaOH proceeding via the 3-bromo-4-hydroxybenzonitrile (3-Br-4-HBN).



Scheme 2. Reduction of the cyano group in 4-HBN using the Dev. alloy in aqueous NaOH.

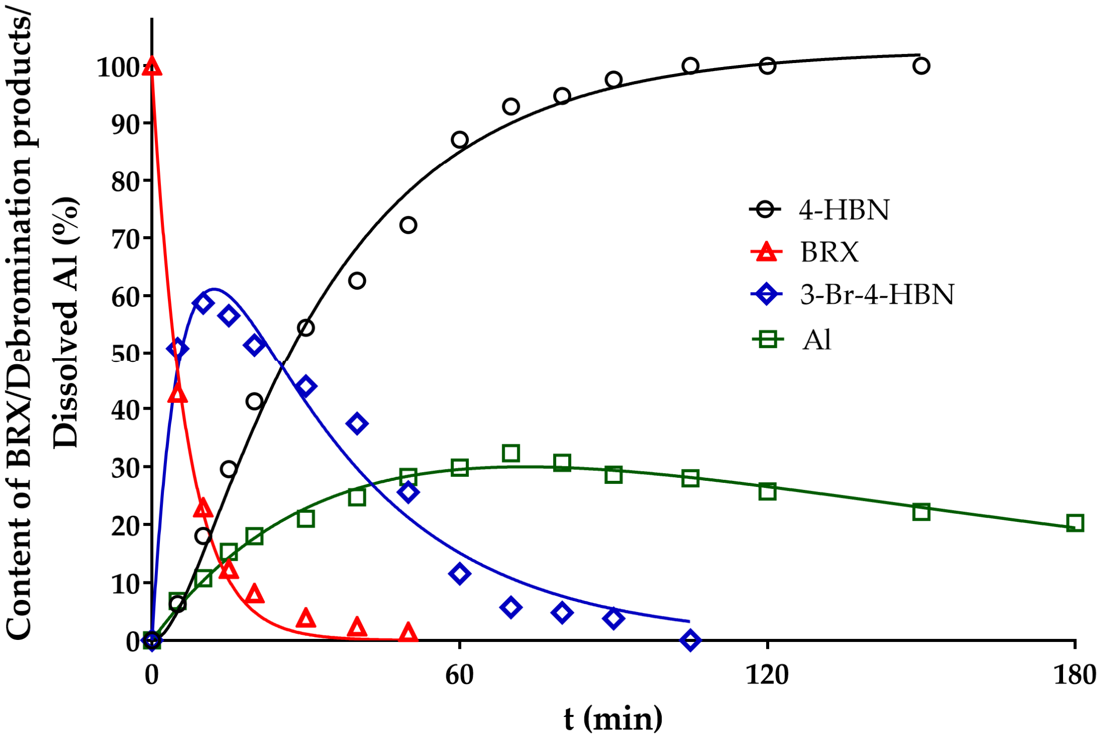


Figure 1. Kinetics of the HDB of BRX (5 mM) in 100 mM aq. NaOH using Dev. alloy (3 g/L). In addition, the percentage of soluble part of Al from original Dev. alloy is supplemented.

Table 1. Efficiencies of different electropositive metals, their alloys and $NaBH_4$ on the HDB of BRX.

Entry No.	Reduction Agent Used in aq. Sol of BRX[1]	NaOH Conc. (mmol)	Temperature	Reaction Time	Content of Phenolic Compounds (%)				Content of Dissolved Al (g/L)	Insoluble Matter (g)
					BRX	4-HBN	4-HBA	3-Br-4-HBN		
1	0.6 g Dev. alloy	10	R.T.	overnight	-	57.9	42.1	-	1.565	0.3
2	0.6 g Dev. alloy	10	R.T.	66 h	-	64.5	35.5	-	1.103	0.36
3	0.4 g Dev. alloy	10	R.T.	66 h	-	80	20	-	1.525	0.14
4	0.4 g Dev. alloy	20	R.T.	overnight	-	87.7	12.3	-	1.561	0.21
5	0.5 g Dev. alloy	10	R.T.	overnight	-	100	-	-	0.671	0.41
6	0.3 g Dev. alloy	10	R.T.	150 min.	-	100	-	-	0.794	0.22
7	0.25 g Dev. alloy	10	R.T.	overnight	-	100	-	-	n.d.	n.d.
8	0.3 g Dev. alloy	2	R.T.	180 min.	5.3	34.9	-	59.8	n.d.	n.d.
9	1 g Cu-Zn alloy	10	1 h at 70 °C + 92 h at R.T.	93 h	100	-	-	-	-	n.d.
10	0.91 g silver brazing alloy Ag:Cu:Zn	10	1 h at 70 °C + 92 h at R.T.	93 h	100	-	-	-	-	n.d.
11	0.7 g Cu-Sn alloy	10	1 h at 70 °C + 92 h at R.T.	93 h	100	-	-	-	-	n.d.
12	1 g Fe_3Al alloy	10	R.T.	overnight	100	-	-	-	n.d.	n.d.
13	0.3 g Al	10	R.T.	overnight	100	-	-	-	n.d.	0
14	0.36 g Al foil	10	R.T.	overnight	100	-	-	-	n.d.	0
15	0.5 g Zn	10	R.T.	overnight	100	-	-	-	-	n.d.
16	0.8 g $NaBH_4$	10	R.T.	96 h	100	-	-	-	-	0
17	0.4 g $NaBH_4$	10	1 h at 70 °C + 92 h at R.T.	93 h	-	6.4	-	93.6	-	0

[1] 0.5 mmol of BRX dissolved in 100 mL of aqueous NaOH with specified concentration. R.T. = room temperature. n.d.= not determined.

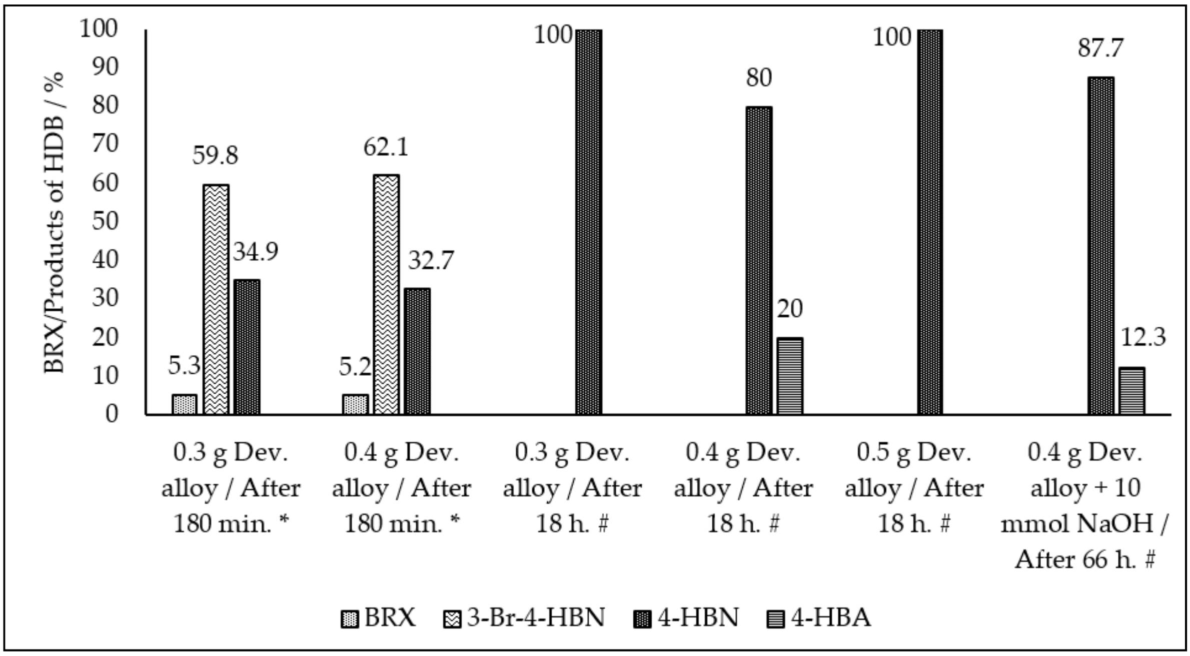


Figure 2. HDB of BRX using appropriate amount of Dev. alloy and NaOH. Dev. alloy was added to the solution containing 0.5 mmol BRX + 2 mmol NaOH in 100 mL H_2O (*); or 0.5 mmol BRX + 10 mmol NaOH in 100 mL H_2O (#).

Except the above mentioned superior HDB activity of the Dev. alloy towards BRX, formation of 4-hydroxybenzaldehyde (4-HBA) generated by a reduction of the cyano group (Scheme 2) was observed in the case of prolonged reaction times and/or use of a higher excess of the Dev. alloy (Table 1, Entries 1–4). Such C≡N moiety reduction using a nickel-based catalyst [31] or aluminium hydrides under strictly anhydrous conditions has been already reported [32]. To the best of our knowledge, no Cu-catalyzed cyano-group reductions in aqueous solutions at ambient temperatures have been published in the literature.

The reaction rate of the Dev. alloy-mediated HDB of BRX has been studied using 3 g of the Dev. alloy per liter of 5 mM of BRX in 100 mM NaOH aqueous solution (Figure 1). The quantity (wt. %) of dissolved Al from the original Dev. Alloy is depicted in Figure 1, too. The complete HDB of BRX along with the presence of brominated by-product 3-Br-4-HBN was observed after ca. 120 min at room temperature under vigorous stirring. Unfortunately, however, the minimal quantity of the Dev. alloy for exhaustive HDB of 1 mol of BRX dissolved in 20-fold molar excess of 0.4 wt.% NaOH was 0.5 kg/mol (or 250 g Dev. alloy per 1 mol of reduced C-Br bonds, calculated from exp. Table 1, Entry 7).

Although the overall amount of the Dev. alloy required for complete HDB of BRX could be probably further optimized, the question of circular economy of the studied Dev. alloy based HDB process arises. Spent aluminium and zinc metals are almost completely removed in the form of its appropriate metal hydroxides from the subsequently neutralized reaction mixtures after the HDB process, which has been proven in the past [5,26,33]. These by-product hydroxides could be utilized as important components for cement production, eventually. Nevertheless, the amount of undissolved part of the spent Dev. alloy remained high and the used copper (which is mostly converted to Cu_2O) requires recycling for sustainability of this potential decontamination process.

The attempts to test recyclability of the used Dev. alloy (with already lower content of non-consumed aluminium) have been carried out. The starting Dev. alloy and its reaction products were identified by the X-ray powder diffraction (see Figures 3–5) and ^{1}H NMR spectroscopy (Figure 6). The present crystalline phases were identified by comparison with standards in the PDF-4+ database [34,35]. For multiphase samples, the mass content of the individual components was calculated.

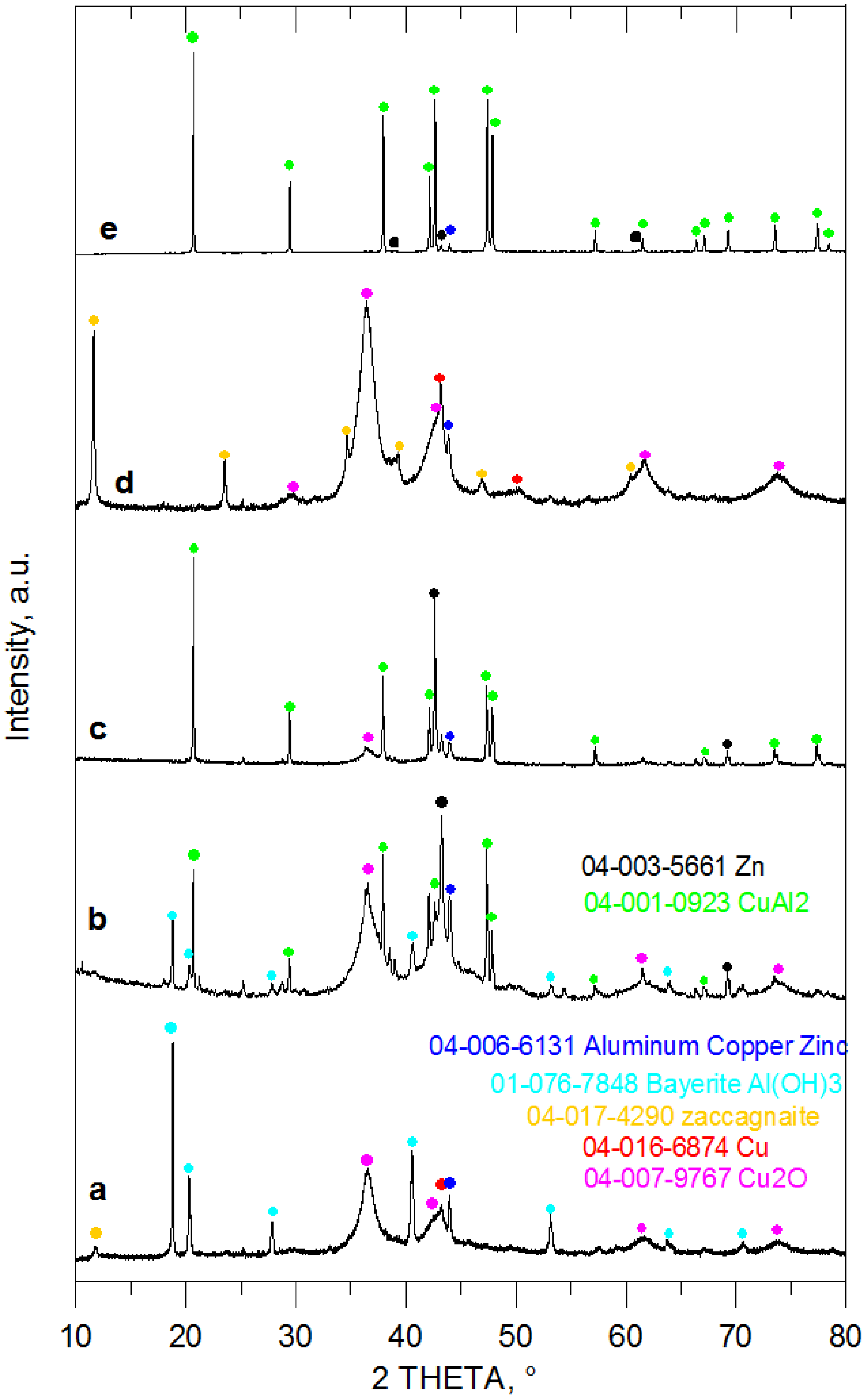


Figure 3. Powder X-ray diffractograms of undissolved residues obtained from different amounts of Dev. alloy used for the HDB of 5 mM BRX dissolved in 100 mM aqueous NaOH after 16 h of action (100% conversion to 4-HBN in all cases): (**a**) 0.5 g/100 mL; (**b**) 0.6 g/100 mL; (**c**) 0.3 g/100 mL (+0.8 g of $NaBH_4$); (**d**) 2.7 g of Dev. alloy after 180 min. action 5 mM BRX in 100 mM aqueous. NaOH (900 mL) and after subsequent 16 h of action of 5 mM BRX in 100 mM aqueous NaOH (100 mL). (**e**) starting Dev. alloy (predominantly contains $CuAl_2$).

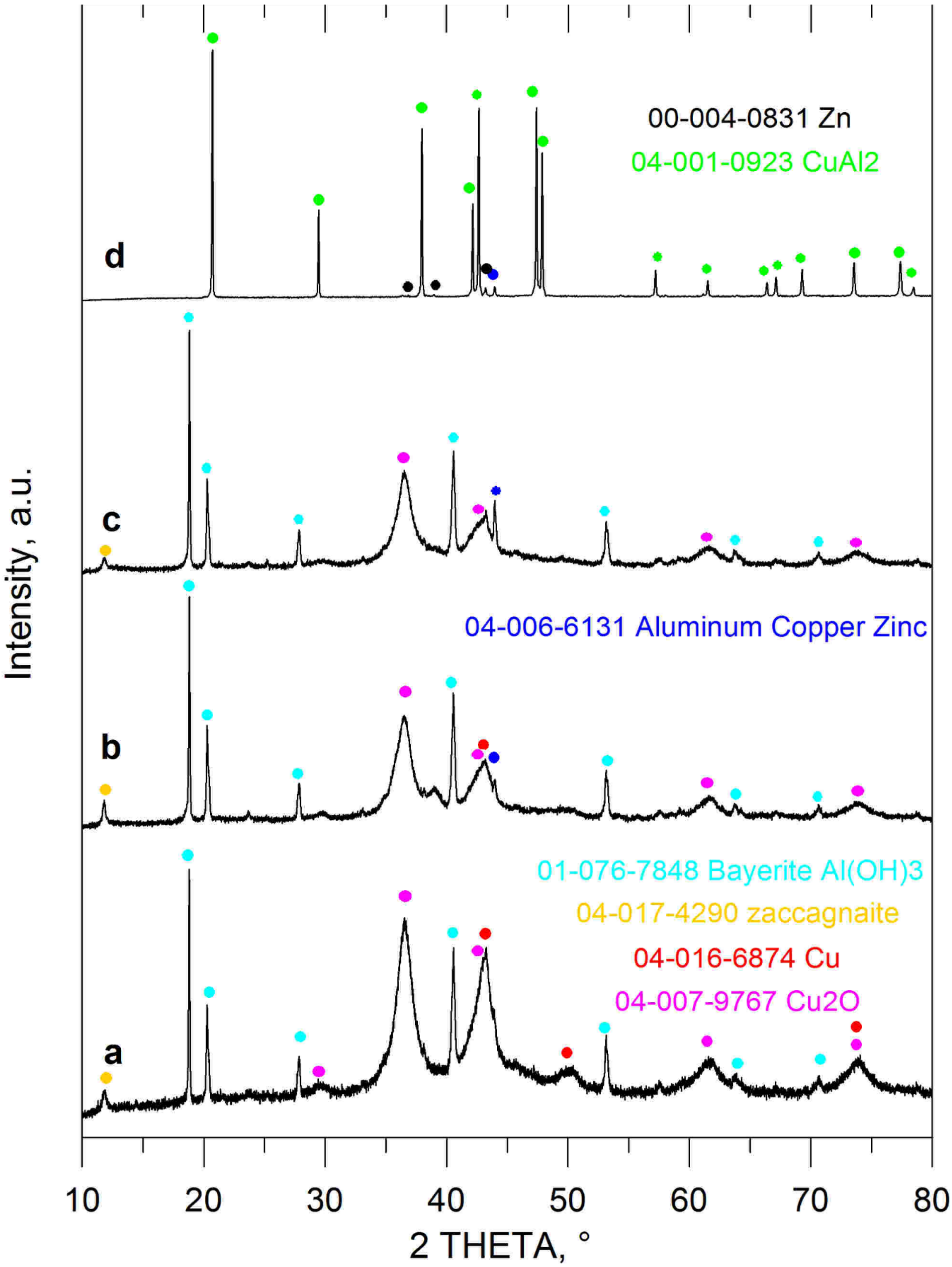


Figure 4. The comparison of powder X-ray diffractograms of Dev. alloy (**d**) unused; (**c**) used for overnight HDB of 5 mM BRX in aq. 100 mM NaOH; (**b**) recycled from step *c* and subsequently used for overnight HDB of 5 mM BRX in aq. 100 mM NaOH and coaction of $NaBH_4$; (**a**) recycled from step *b* and used for overnight reaction with 5 mM BRX dissolved in 100 mM NaOH and coaction of $NaBH_4$.

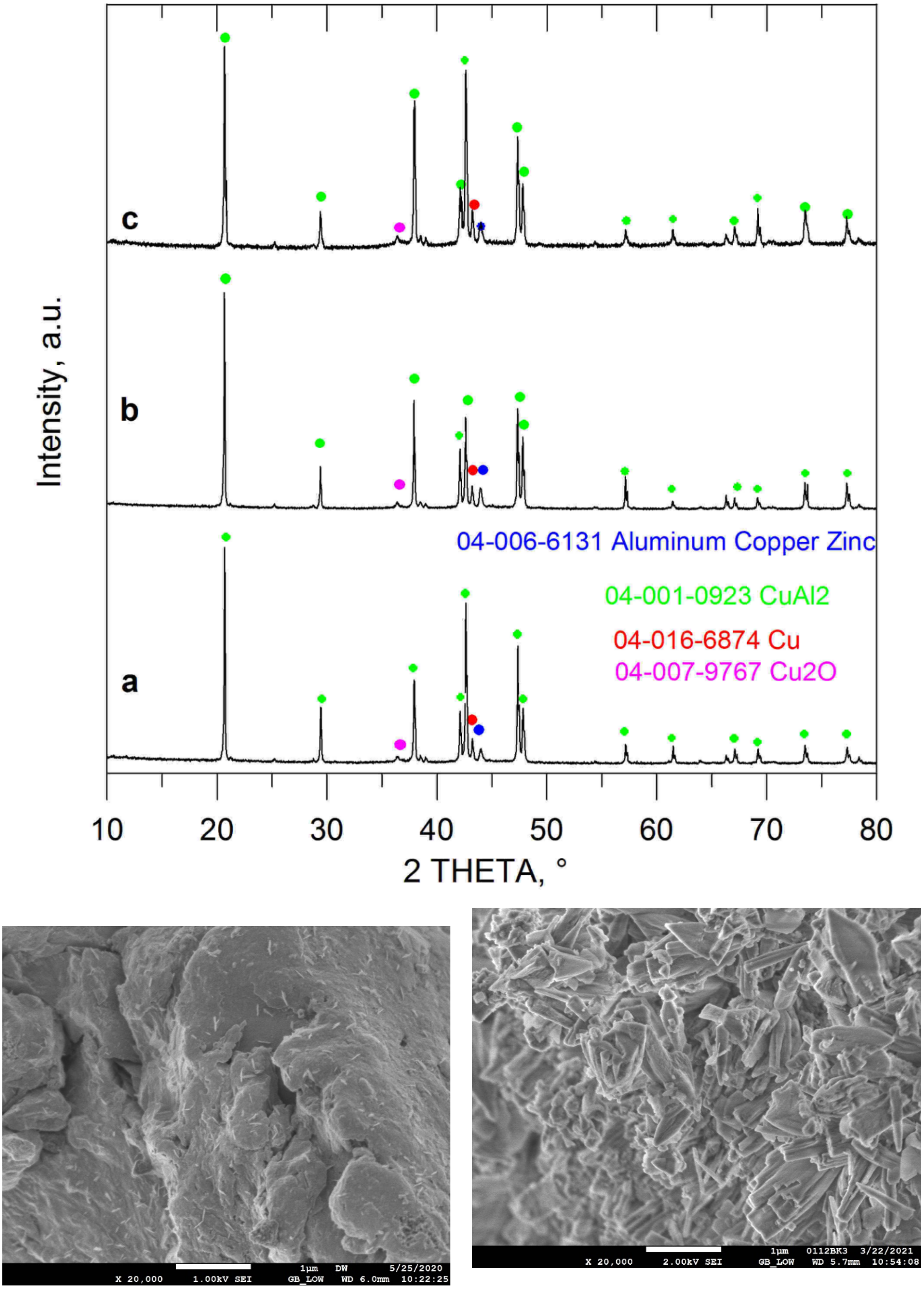


Figure 5. Powder X-ray diffractograms (**top**) of undissolved residue of Dev. alloy (0.7 g) after (**a**) 2 h; (**b**) 4 h and (**c**) 6 h of reaction with 5 mM aq. BRX dissolved in 20 mM NaOH (100 mL) and the coaction of $NaBH_4$ (0.8 g) and the SEM images of unused Dev. alloy (**bottom left**) and insoluble part of Dev. alloy after 6 h of reaction with 5 mM aq. BRX dissolved in 20 mM NaOH (100 mL) with coaction of $NaBH_4$ (0.8 g) (**bottom right**).

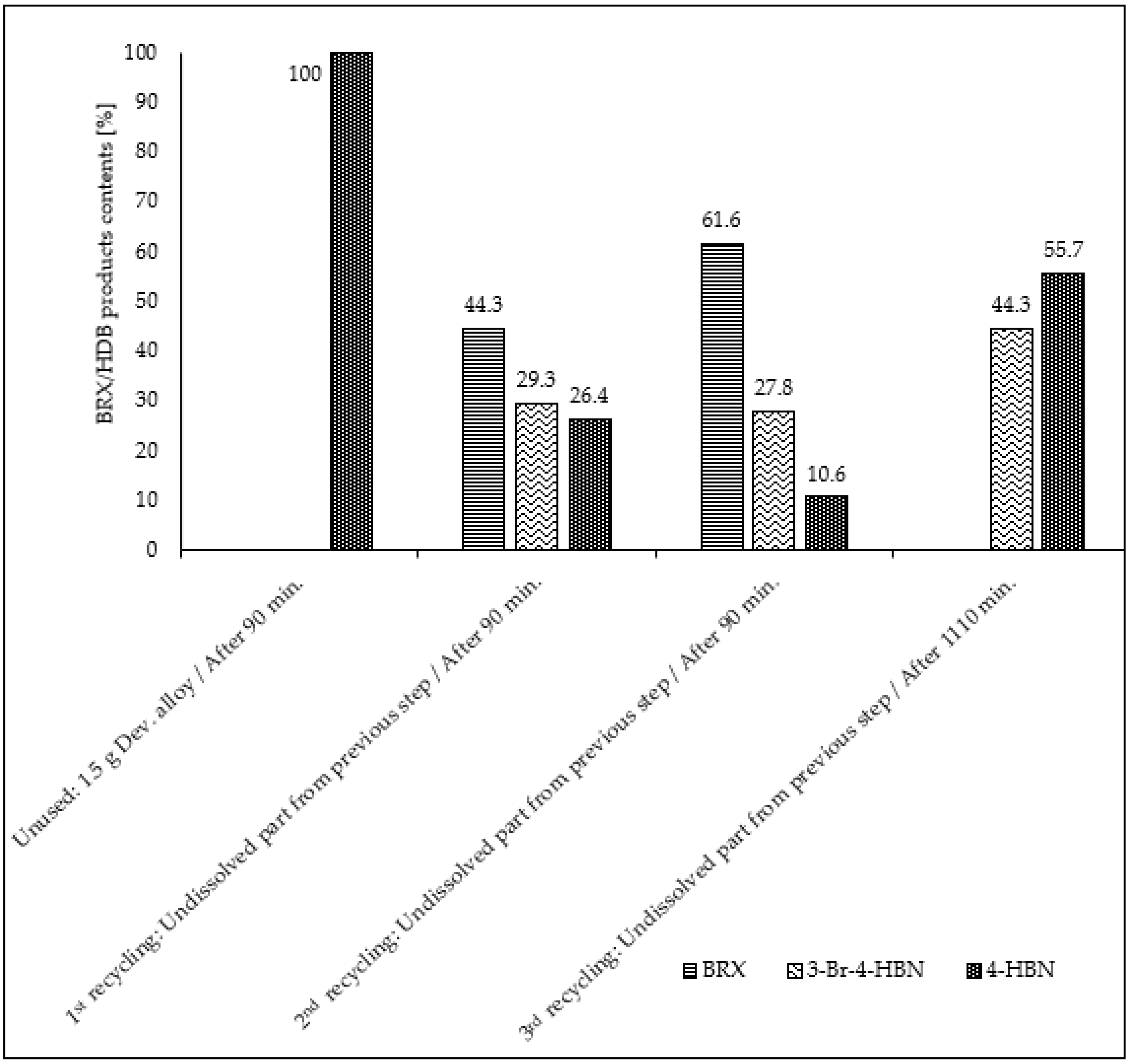


Figure 6. Comparison of HDB efficiencies involving unused and/or recycled Dev. alloy added to the solution of 2.5 mmol BRX + 50 mmol NaOH in 100 mL H_2O.

Dev. alloy is composed of the mixture of khatyrkite $CuAl_2$ as the main component (ca. 96%) with crystallite size around 1000 Ångströms (Å), zinc (ca. 2% with crystallite size ca. 680 Å) and aluminium-copper-zinc ternary system $Cu_{1.14}$ $Zn_{0.20}$ $Al_{0.66}$ (ca. 2% and crystallite size ca. 530 Å) (Figure 4d).

The observed decrease in the activity of the used Dev. alloy within the HDB of BRX is presumably a consequence of a lack of remaining aluminium metal in the undissolved part of the Dev. Alloy, which is necessary for completion of the HDB process (Supplementary Materials Table S3).

As we described earlier [5], the Dev. alloy mixed with diluted NaOH solution is gradually converted to the aluminium hydroxide ($Al(OH)_3$), zaccagnaite (zinc aluminium carbonate hydroxide hydrate, $Zn_4Al_2(CO_3)(OH)_{12}(H_2O)_3$) and cuprite ($Cu_2O$) or even tenorite (CuO), which is accompanied with hydrodehalogenation of some halogenated aromatic compounds occuring in aqueous solution. Oxidation of the original metals forming Dev. alloy is accompanied by significant changes on structure of this Cu-based reductant, of course. Figure 3 compares changes in composition of different quantities of the Dev. alloy after 16 h of action on 5 mM BRX in 100 mM aqueous NaOH solution (complete HDB conversion was observed in all cases). Figure 3a,b illustrate undissolved residue obtained from 0.5 g (or 0.6 g, respectively) of Dev. alloy in 100 mL of 5 mM BRX dissolved in 100 mM aqueous NaOH producing 42.1% of 4-HBA and 57.9% of 4-HBN as the

HDB products (see Schemes 1 and 2). As evidenced by the powder X-ray diffractogram in Figure 3c, addition of $NaBH_4$ to the Dev. alloy inhibits the corrosion of Cu-Al significantly, and thus, no metallic Cu was observed in the undissolved residue after 16 h of action of 5 mM BRX in 100 mM aqueous NaOH.

The powder XRD analysis of separated residue even after four-times used Dev. alloy identifies still ca. 8% of unreacted Al-Cu-Zn trimetallic alloy together with 85% of Cu_2O, 6% of elemental Cu and 1% of zaccagnaite ($Zn_4Al_2(CO_3)(OH)_{12}(H_2O)_3$) produced within overall 1290 min (21.5 h) lasting corrosion of the original Dev. alloy using 5 mM BRX dissolved in aqueous 100 mM NaOH solution (Supplementary Materials Figure S1a and Table S3, Entries 5–7).

Powder XRD analyses of samples obtained from the once re-used Dev. alloy (that caused 100% conversion BRX to 4-HBN after overnight action) show the composition of ca. 3 % Al-Cu-Zn alloy, 65% Cu_2O, 7% Cu, 16% Al-Zn and 9% zaccagnaite (Supplementary Materials Figure S1c, Table S3, Entry 2) while the same used Dev. alloy after subsequent overnight action on 5 mM BRX dissolved in aqueous 100 mM NaOH (afforded only 77% conversion of BRX in this third HDB step, Figure S1b, Table S3, Entry 3) contained still ca. 2% Al-Cu-Zn alloy, 24% Cu_2O, 2% Cu, 7% zaccagnaite and, in addition 65 % CuO as the major species.

With this information in hand, the application of some reductant in excess capable to reduce both produced copper oxides and C–Br bonds serves as the potential technique for recycling of used Dev. alloy. Promisingly, applying of prolonged reaction times, together with the addition of external reductant $NaBH_4$, led to the complete conversion of starting BRX to the mixture of 3-bromo-4-hydroxybenzonitrile (3-Br-4-HBN) and 4-hydroxybenzonitrile (4-HBN), even in the case of the already three-times used undissolved part of the original Dev. alloy (Figure 7, Supplementary Materials Table S4, Entries 1–3). Subsequent experiments were focused on exploring the conditions that enable the HDB of BRX. These attempts involved (i) use of different amounts of $NaBH_4$ and (ii) changing the reaction time at room temperature (Supplementary Materials Table S4, Entries 4–6). Unfortunately, the complete HDB of BRX to 4-HBN was not achieved in these cases.

The effects of the coaction of $NaBH_4$ and commercially available unused Dev. alloy on the HDB of BRX were investigated using different amount of both involved reduction agents. For this set of experiments, aqueous solution of 5 mM BRX in a slightly lower excess (20 mM) of NaOH was used with the aim to suppress the known stabilizing effect of NaOH to $NaBH_4$. The obtained results (Supplementary Materials Table S5, Entries 1–3; 6–8) documented that a decrease in the added amount of NaOH, along with the addition of $NaBH_4$ to the unused Dev. alloy significantly decreases the HDB rate, together with the dissolution rate of aluminium metal. This seems to be a benefit for a potential recycling of the Dev. alloy, albeit, as demonstrated in the Table S5 (Supplementary Materials, Entry 5), the second recycling of the used Dev. alloy (even under coaction of $NaBH_4$) fails in quantitative conversion of the BRX even after 68 h of action. Moreover, an extension of the reaction time causes subsequent reduction of the cyano group instead of the desired HDB process, which was confirmed by the NMR spectroscopy (Figures S7–S9) and GC-MS analysis (Figures S10 and S11). The HDB rate of BRX has been examined (Figure S3) based on the data obtained in these experiments. The measured data imply that the complete conversion of BRX using the Dev. alloy and $NaBH_4$ was achieved within less than 1 h but the following HDB of 3-Br-4-HBN is the key rate-determining step. The changes in structure of the Dev. alloy during HDB of BRX in coaction of $NaBH_4$ are supported by the X-ray diffractograms and SEM images in Figure 5. Comparing the XRD data of the Dev. alloy used together with $NaBH_4$ after 2–6 h of action, decrease of content of probably most reactive $CuAl_2$ is remarkable along with the formation of low quantities of metallic copper and Cu_2O, both in the form of nanoparticles.

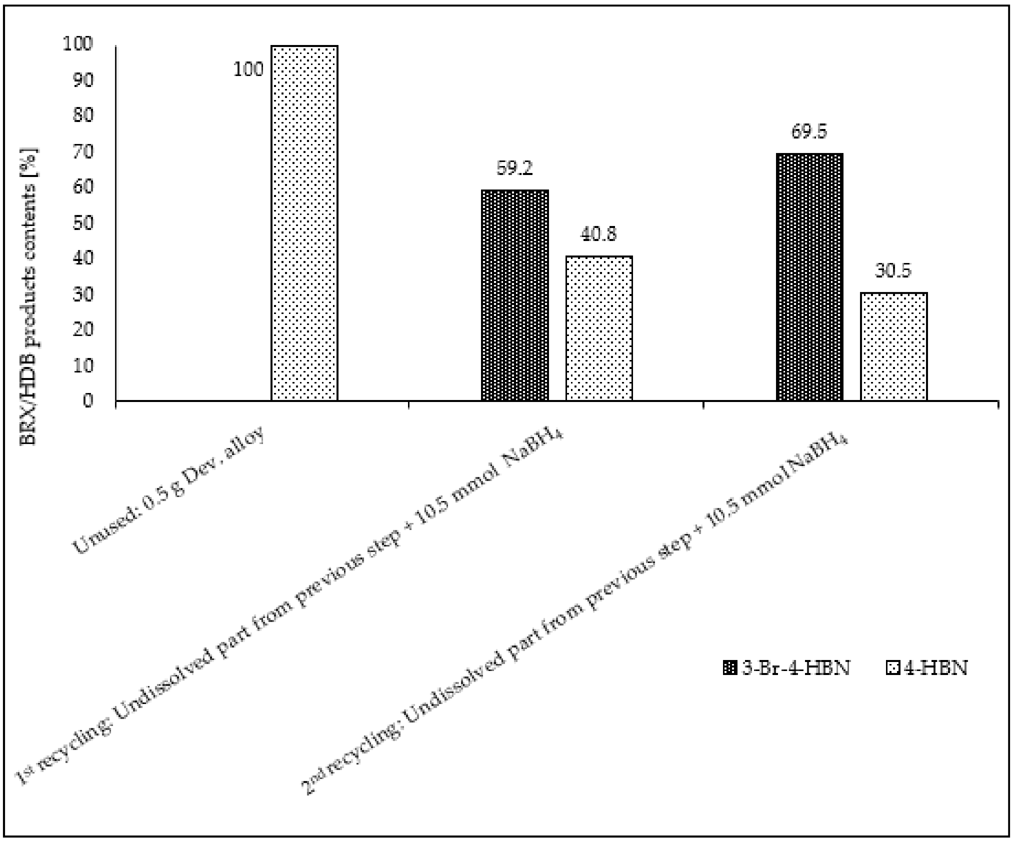


Figure 7. Effect of Dev. alloy recycling on the HDB of BRX using $NaBH_4$ after 18 h of vigorous stirring. Dev. alloy was added to the solution containing 2.5 mmol BRX + 50 mmol NaOH in 100 mL H_2O.

In accordance with the above observed, it was found that once under a coaction of $NaBH_4$ the used Dev. alloy in the subsequent HDB step (Supplementary Materials, Table S5, Entry 9) is only slightly less active in comparison with the unused one in excess of NaOH (compare with Figure 1 and Table 1, Entry 4). As we observed in the aforementioned experiments, the increase of metallic copper content in the reused spend Dev. alloy (Figures 4 and 5) caused by $NaBH_4$-mediated in-situ reduction of Cu_2O has not significant catalytic effect on the HDB process.

It was also found that pure powdered copper exhibited poor HDB activity under the coaction of $NaBH_4$ (Supplementary Materials Table S2, Entries 4–8 and Figure S5). Employing Arnd's (Mg-Cu) alloy (Table S2, Entry 1) within the HDB of BRX provided results quite similar to the aforementioned synergistic effect of the Dev. alloy combined with $NaBH_4$ (compare with Table S5, Entry 1 and Figure 8).

Beside the experiments described vide supra, other potential Cu-based metal catalysts (e.g., bronze Cu-Sn, brass Cu-Zn) for the $NaBH_4$ mediated HDB of BRX have been explored (Figure 9, Table S2). However, the obtained results within the respective HDB processes using brass or bronze powders (Table S2, Entries 2 and 3) are much worse when compared to the results obtained within employing the Dev. alloy. Due to the low content of Zn metal in the Dev. alloy and negligible effect of the Cu-Zn alloy or powdered Zn on the HDB of BRX, the effect of zinc metal was neglected in proposed HDB mechanism.

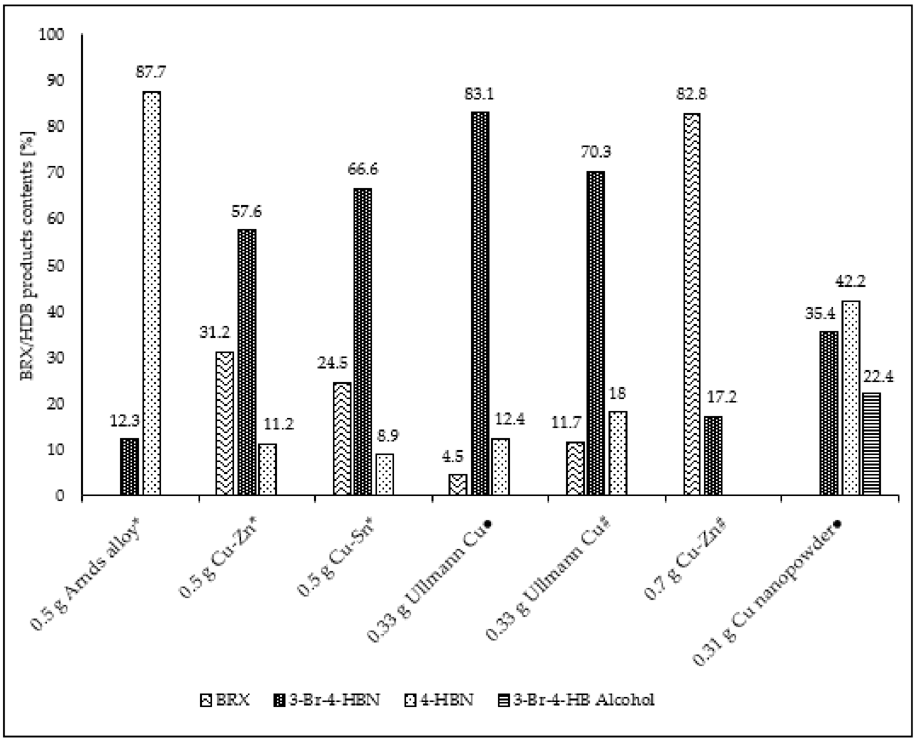


Figure 8. Effect of different sources of the Cu-catalysts on the HDB of BRX using $NaBH_4$ after 18 h. HDB agents were added to the solution containing 0.5 mmol BRX + 10 mmol NaOH in 100 mL H_2O + 5 mmol $NaBH_4$ (*) or 0.5 mmol BRX + 2 mmol NaOH in 100 mL H_2O + 21 mmol $NaBH_4$ (•); or 0.5 mmol BRX in 100 mL MeOH + 21 mmol $NaBH_4$ (#).

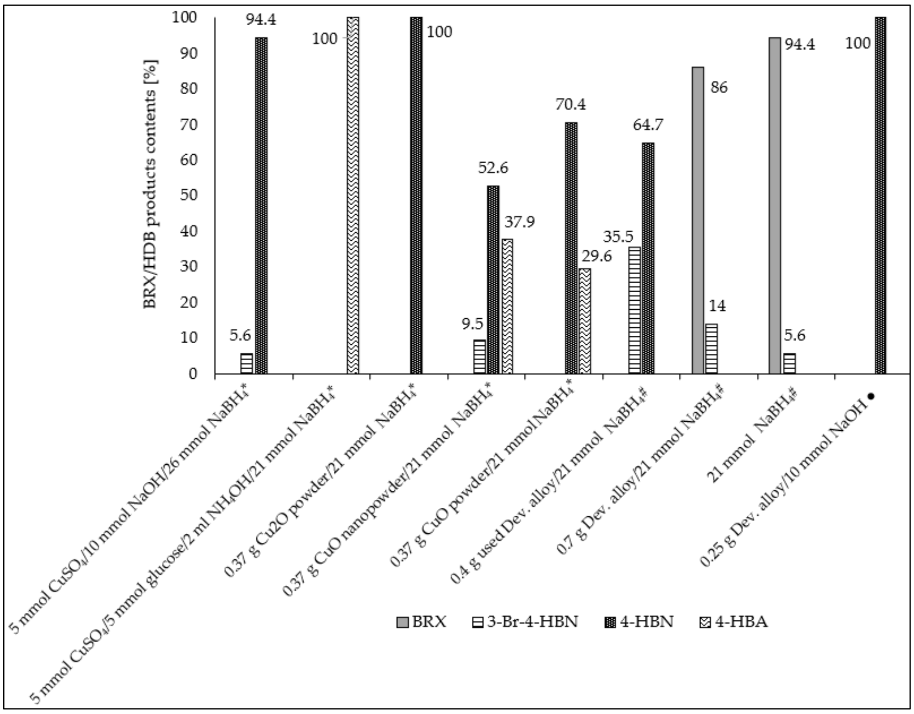


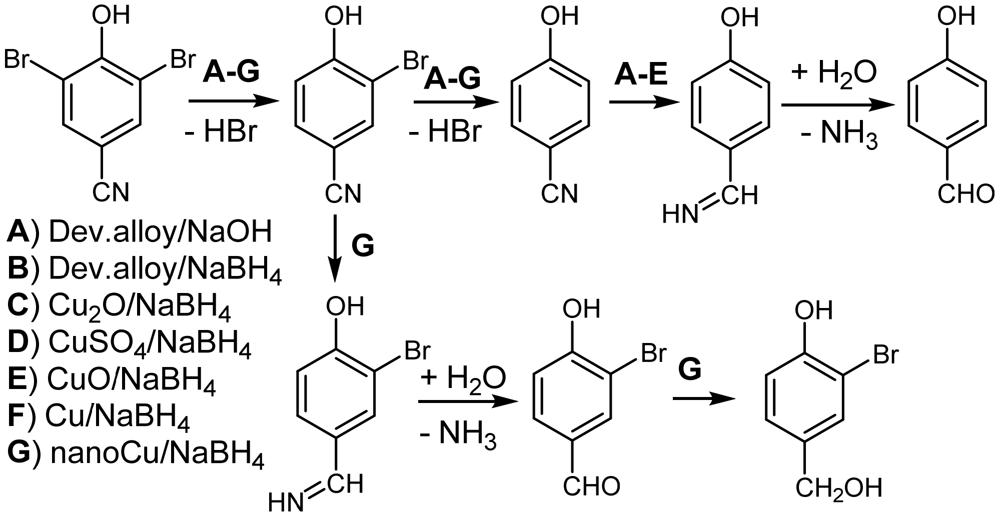
Figure 9. Effect of different sources of the Cu-catalyst with coaction of $NaBH_4$ on the HDB of BRX after 18 h of vigorous stirring. Comparison with HDB of BRX caused by the Dev.alloy/NaOH action. HDB agents were added to the solution containing 0.5 mmol BRX + 2 mmol NaOH in 100 mL H_2O (*), 0.5 mmol BRX + 10 mmol NaOH in 100 mL H_2O (•) and 0.5 mmol BRX in 100 mL MeOH (#).

Similarly, as in the case of the proposed mechanism of action by the Dev. alloy mediated hydrodechlorination [36], the formation of Cu_2O during two-step HDB of BRX could be explained by oxidation of both Cu and Al in the starting $CuAl_2$ (khatyrkite) with BRX and producing CuCl as an intermediate, which is hydrolyzed to Cu_2O in the alkaline aqueous solution (Supplementary Materials Reaction in Scheme S1).

Except the above-mentioned facts, the crucial effect of copper-based HDB in coaction of $NaBH_4$ is not fully clear yet.

The control set of experiments comprising addition of a Cu powder to the aqueous $NaBH_4$ solution and BRX causes (after ca. 3 days) debromination of BRX to the first step but, quite unexpectedly, very slow HDB of the formed 3-Br-4-HBN intermediate which was not completed even after 96 h (Supplementary Materials Figure S5 and Table S2, Entries 4–8). On the other hand, without an employment of powdered copper, the HDB does not proceed at room temperature even after 96 h of $NaBH_4$ action (Table 1, Entry 16).

The application of the commercially available Cu nanoparticles instead of the copper powder increase the reaction rate of $NaBH_4$ mediated HDB (Table S2, Entries 6 and 7), which could be expected due to a much higher specific surface area. However, significant amount of a novel product, 3-bromo-4-hydroxybenzylalcohol was formed. In principle, the intermediates (i.e., 3-Br-4-HBN) formed within the described HDB process of BRX catalyzed by Cu nanoparticles may undergo subsequent reduction of cyano group. The by-products were identified as 3-bromo-4-hydroxybenzylalcohol (3-Br-4-HB Alcohol) and presumably 3-bromo-4-hydroxybenzaldehyde (Figures S7–S11). The proposed reaction pathway of such unexpected reduction is depicted in Scheme 3.



Scheme 3. Proposed reduction pathways for the studied BRX degradation.

For comparison, it was described by Raut et al. [37] that even hydrodechlorination of monochlorinated aromatic compounds in low concentration (in milligrams per liter) is possible using nanoparticles of metallic copper (1–3 g nanoCu/L) in a coaction of $NaBH_4$ (0.25–1.5 g/L). Our research group observed Cu-mediated hydrodechlorination in the case of hexa- or pentachlorobenzene using the Dev. alloy [36]. However, this dechlorination was non-complete and less chlorinated benzenes (especially tetrachloro-, trichloro- and dichlorobenzenes) were produced with simultaneous formation of Cu_2O and Al(III) salts (but not metallic Cu).

For the elucidation of possible influence of NaOH on the HDB efficiency caused by copper or copper-based alloys-catalyzed $NaBH_4$ action, 10 mM methanolic solution of BRX was used instead of 5 mM BRX solution in 20 mM aqueous NaOH (Supplementary Materials, Table S2, Entries 4-5 and 8-9 and Table S7). In this case the HDB efficiency of BRX in methanolic/aqueous solution is generally considerably slower (Figures 8 and 9).

Using Cu_2O as a Cu-based catalyst for the desired $NaBH_4$ mediated HDB of BRX, 100% conversion of BRX to 4-HBN was obtained after an overnight reaction (Figure 9). The HDB rate of BRX using $Cu_2O/NaBH_4$ is depicted in Figure 10. The complete HDB reaction is accompanied by formation of mixture of metallic copper and Cu_2O nanoparticles (Figures 11d and 12).

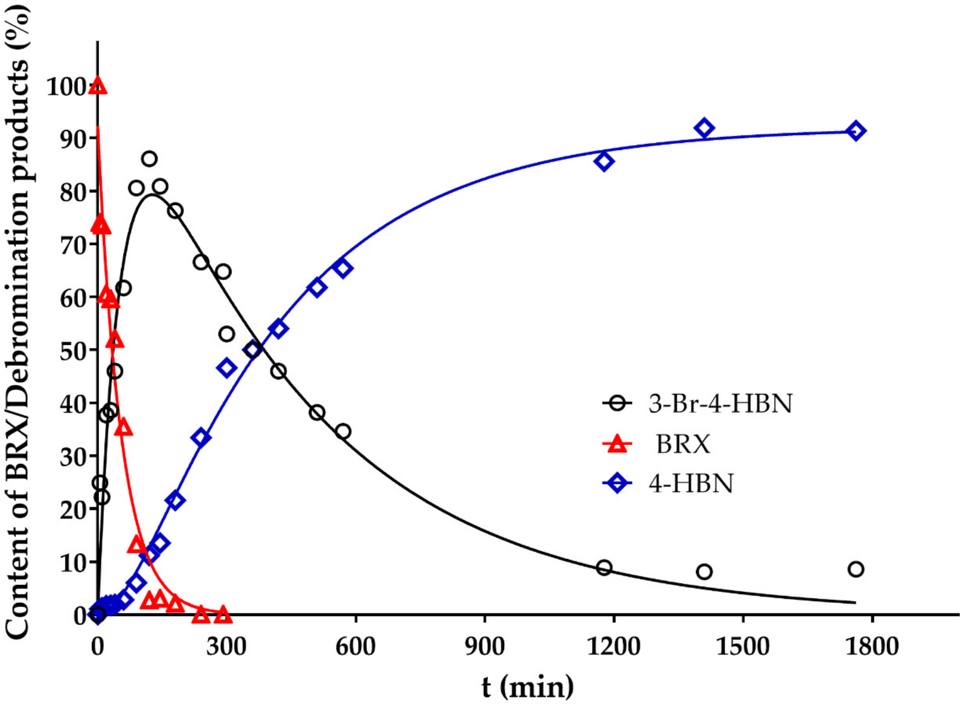


Figure 10. HDB rate of 5 mM BRX in 20 mM NaOH using Cu_2O (3.1 g/L) under the coaction of $NaBH_4$ (8 g/L).

Employing powdered CuO together with $NaBH_4$ for the HDB of BRX, mixture of 4-HBN and 4-HBA was formed after an overnight reaction (Figure 9). Interestingly, combination of nanoparticles of CuO with $NaBH_4$ is noticeably worse reducing system producing 9.5% of the 3-Br-4-HBN intermediate together with desired 4-HBN without any positive effect of higher specific surface area of nano CuO on HDB (compare results obtained using micro- or nano- particles of CuO (Figure 9 and Supplementary Materials Table S6, Entries 9 and 10). Due to the lower selectivity and worse HDB activity of $CuO/NaBH_4$ compared with the Dev. alloy or $Cu_2O/NaBH_4$ reduction systems, the $CuO/NaBH_4$ mediated HDB was not further investigated in details.

For comparison of the HDB activity of the tested Cu-based reduction systems, the evaluation of kinetics of studied BRX hydrodehalogenations was performed. The calculated values of rate constants (Table 2) confirmed that only the Dev. alloy in alkaline aqueous solution exhibits high HDB activity for studied BRX at room temperature. For Dev. alloy/NaOH/BRX, the process of 3-Br-4-HBN formation is significantly faster in comparison with $Cu_2O/NaBH_4$ and a few orders faster in comparison with $Cu/NaBH_4$. Total HDB of BRX using the Dev. alloy in aqueous NaOH solution proceeding via the 3-Br-4-HBN was finished ca. in 120 min (Figure 1). The comparable values of k_1 constant were obtained based on the time dependence of BRX and 3-Br-4-HBN concentration which confirmed that HDB process follows the kinetic model of subsequent reaction (Figure 1, Scheme 1). This fact was also confirmed by high R^2 values for the both reaction steps (Table 2).

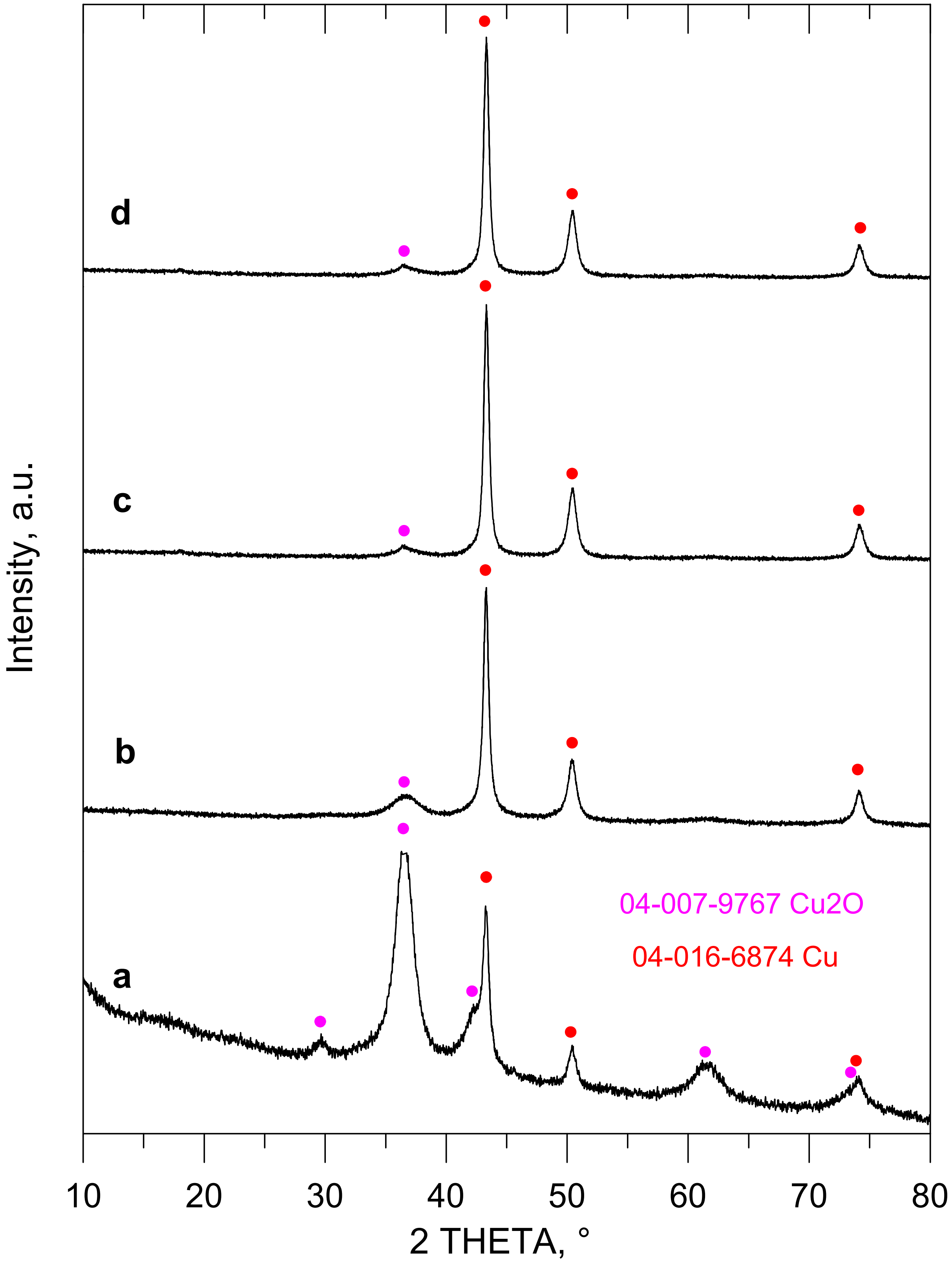


Figure 11. Powder X-ray diffractograms of insoluble part after HDB of BRX (5 mM solution in 20 mM aq. NaOH) mediated by: (**a**) $CuSO_4 \cdot 5\ H_2O$ (8.33 g/L) + NaOH (2.8 g/L) + $NaBH_4$ (6.67 g/L); (**b**) $CuSO_4 \cdot 5\ H_2O$ (8.34 g/L) + NaOH (2.6 g/L) + $NaBH_4$ (6.67 g/L); (**c**) $NaBH_4$ (8 g/L) + CuO nanopowder (3.7 g/L); (**d**) $NaBH_4$ (8 g/L) + Cu_2O (3.7 g/L).

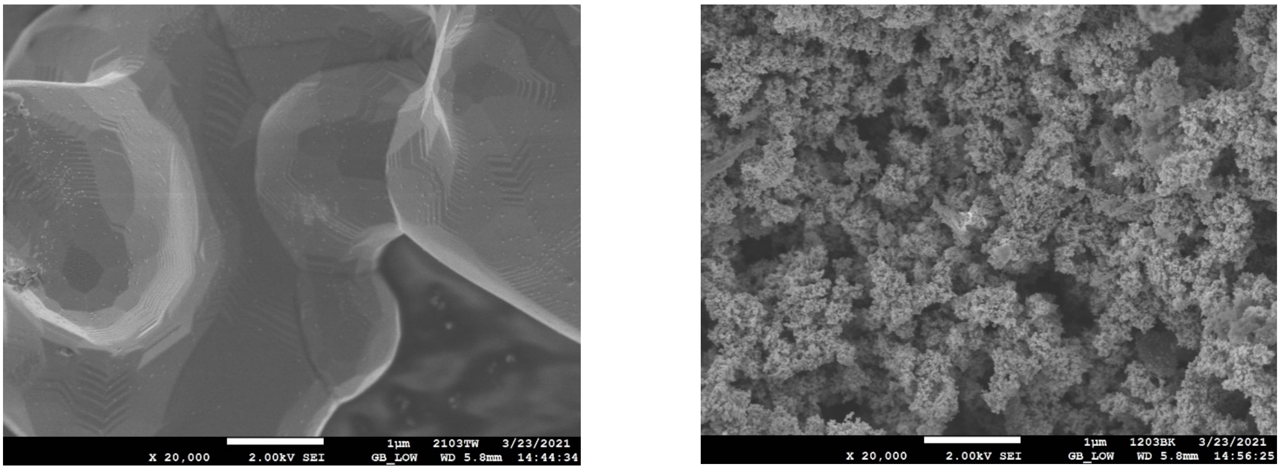


Figure 12. SEM images of the starting commercial Cu_2O after the treatment of 5 mM BRX solution in 20 mM aqueous NaOH without added $NaBH_4$ (**left**) and separated insoluble part (mixture of Cu and Cu_2O nanoparticles) after the HDB of BRX (5 mM BRX solution in 20 mM aqueous NaOH) using $Cu_2O/NaBH_4$ (**right**).

Table 2. Calculated kinetic constants (k_1 and k_2) for the HDB of BRX using different Cu-based HDB agents (k_1 represents the first order rate constant of the first reaction step and k_2 represents the rate constant of the second reaction step (see Scheme 1), SD is standard deviation and R^2 is coefficient of determination).

	$Cu/NaBH_4$	**$Cu_2O/NaBH_4$**	**Dev. Alloy/$NaBH_4$**	**Dev. Alloy/NaOH**
k_1 ± SD (min^{-1}) calculated based on the time dependence of BRX	$(8.8 \pm 0.4) \times 10^{-4}$	0.0183 ± 0.0018	0.07277 ± 0.0116	0.150 ± 0.0082
R^2	0.9960	0.9729	0.9620	0.9942
k_1 ± SD (min^{-1}) calculated based on the time dependence of 3-Br-4-HBN	$(7.4 \pm 0.2) \times 10^{-4}$	0.0192 ± 0.0026	* 0.06864 ± 0.0241	0.1630 ± 0.0343
k_2 ± SD (min^{-1}) calculated based on the time dependence of 3-Br-4-HBN	$(7.3 \pm 0.3) \times 10^{-5}$	0.00225 ± 0.0030	* 0.03874 ± 0.0163	0.0341 ± 0.0047
R^2	0.9981	0.9565	0.9842	0.9719

* calculated based on the time dependence of 4-HBN.

On the basis of the values of k_1 and k_2 constants (Scheme 1, Table 2), it is clear that when using $Cu_2O/NaBH_4$, the process of 3-Br-4-HBN formation is approximately by one order slower compared to the Dev. alloy/NaOH, which shows lower HDB efficiency of $Cu_2O/NaBH_4$ towards BRX (Figure 10). After 1800 min., approximately 90% conversion of BRX to 4-HBN was achieved. The HDB of BRX (5 mM BRX in 20 mM NaOH) using Cu_2O under the coaction of $NaBH_4$ also follows the kinetic model of subsequent reaction of the pseudo-first order which is presented on Figure 10 and confirmed by a compliance of k_1 values determined based on the time dependence of BRX and 3-Br-4-HBN concentration.

The HDB efficiency of $Cu/NaBH_4$ towards BRX is very low which was confirmed by the low values of k_1 and k_2 (Table 2), but the HDB process also follows the kinetic model of subsequent reaction (high value of R^2; compliance of k_1 values determined based on the time dependence of BRX and 3-Br-4-HBN concentration). After 72 h, approximately 24% conversion of BRX to 4-HBN was achieved (compare Figure S5 with Figure S3).

The comparison of rate of 4-HBN formation using studied Dev. alloy/NaOH, Dev. alloy/$NaBH_4$ and $Cu_2O/NaBH_4$ reduction systems mentioned in Table 2 is depicted in Figures 11 and S6 (reductive degradation rate of BRX). Using the Dev. alloy/NaOH system, during 120 min of the reaction all amount of BRX was converted to 4-HBN. In the case of the Dev. alloy/$NaBH_4$ catalysts, it is about 63% and for $Cu_2O/NaBH_4$ system the conversion (in 120 min) is only 11 % (Figure 13).

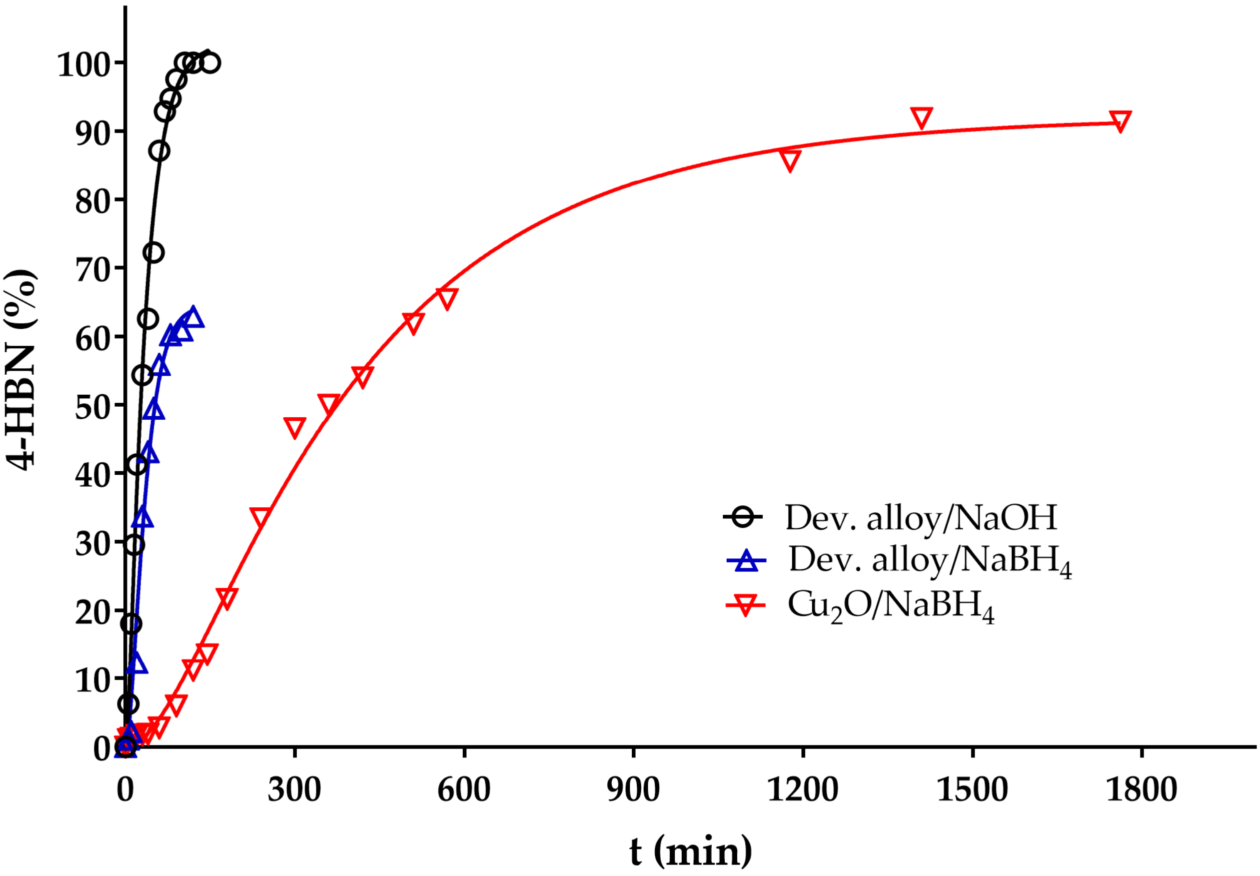


Figure 13. Time dependence of the 4-HBN formation by the HDB of BRX using different HDB systems.

Surprisingly, in-situ generation of copper/Cu_2O by the addition of aqueous solution of $CuSO_4$ to the alkaline solution of excess of $NaBH_4$ in aqueous BRX causes HDB process of BRX rapidly and the HDB is accompanied by the reduction of the cyano group (Supplementary Materials Table S6, Entries 2, 3, 5, 9–12 and Figures S7–S11). According to the powder X-ray analysis, using mentioned conditions, nanoparticles of both metallic Cu and Cu_2O are produced which significantly accelerates observed reduction processes (Figure 11a,b and Figure 14). The formation of metallic Cu(0) and Cu_2O was also observed in both cases by $Cu_2O/NaBH_4$ as well as by $CuSO_4/NaBH_4$ mediated HDB of BRX (Figures 11 and 14).

Taking into the account these findings, we propose the plausible reaction pathway comprising formation of Cu(I) salt of BRX (Cu^+BRX^-) in the first reaction step between CuOH and sodium salt of BRX. Cu^+BRX^- undergoes smooth reduction induced by the action of $NaBH_4$ producing thus sodium salt of 3-Br-4-HBN in the first reduction step. The sodium salt of 3-Br-4-HBN subsequently reacts with CuOH producing Cu^+(3-Br-4-HBN)$^-$. Nascent Cu^+(3-Br-4-HBN)$^-$ intermediate is reduced in the following HDB step to the 4-HBN. Both HDB steps are accompanied by the formation of metallic copper and hydrogen (Scheme 4).

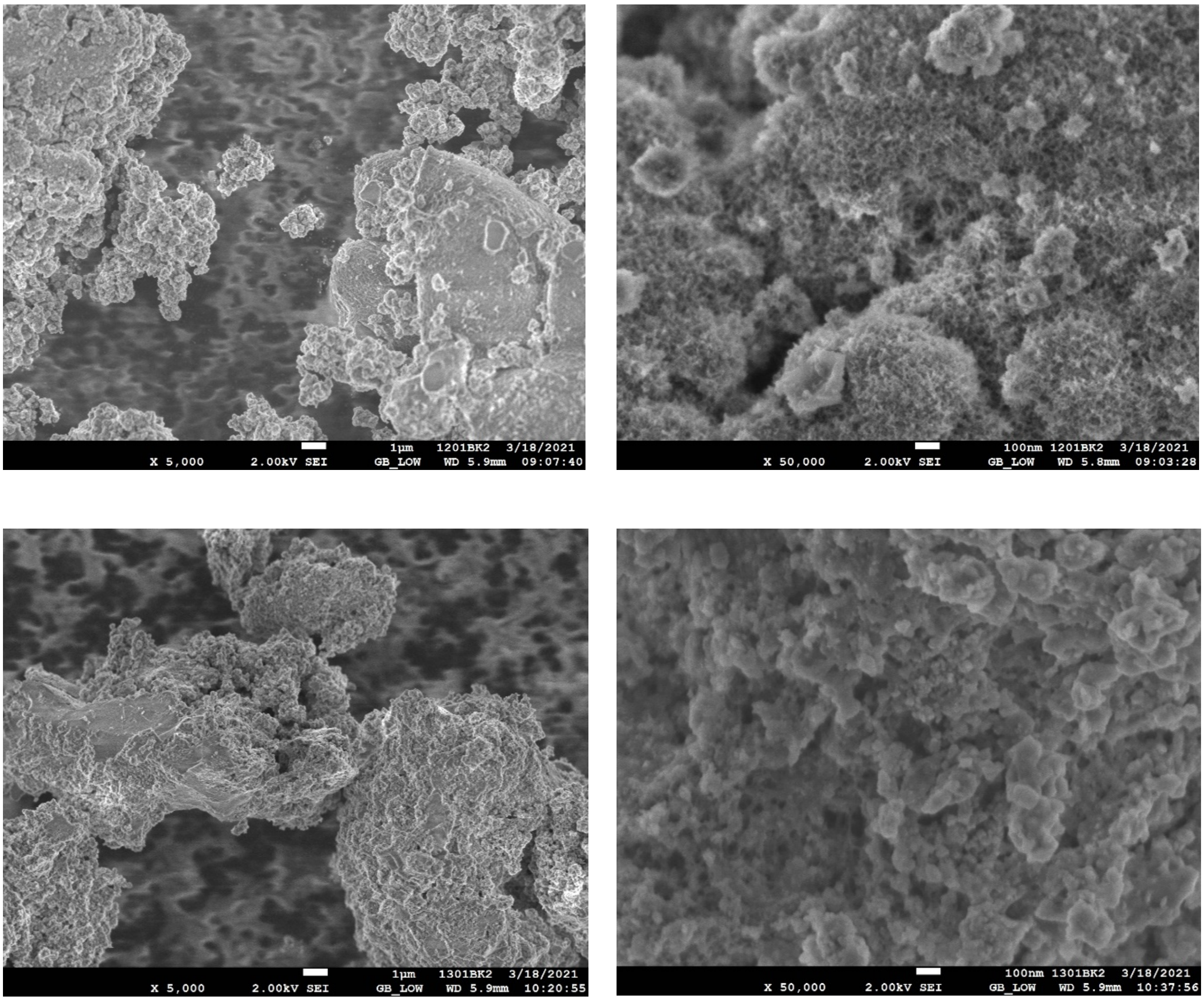
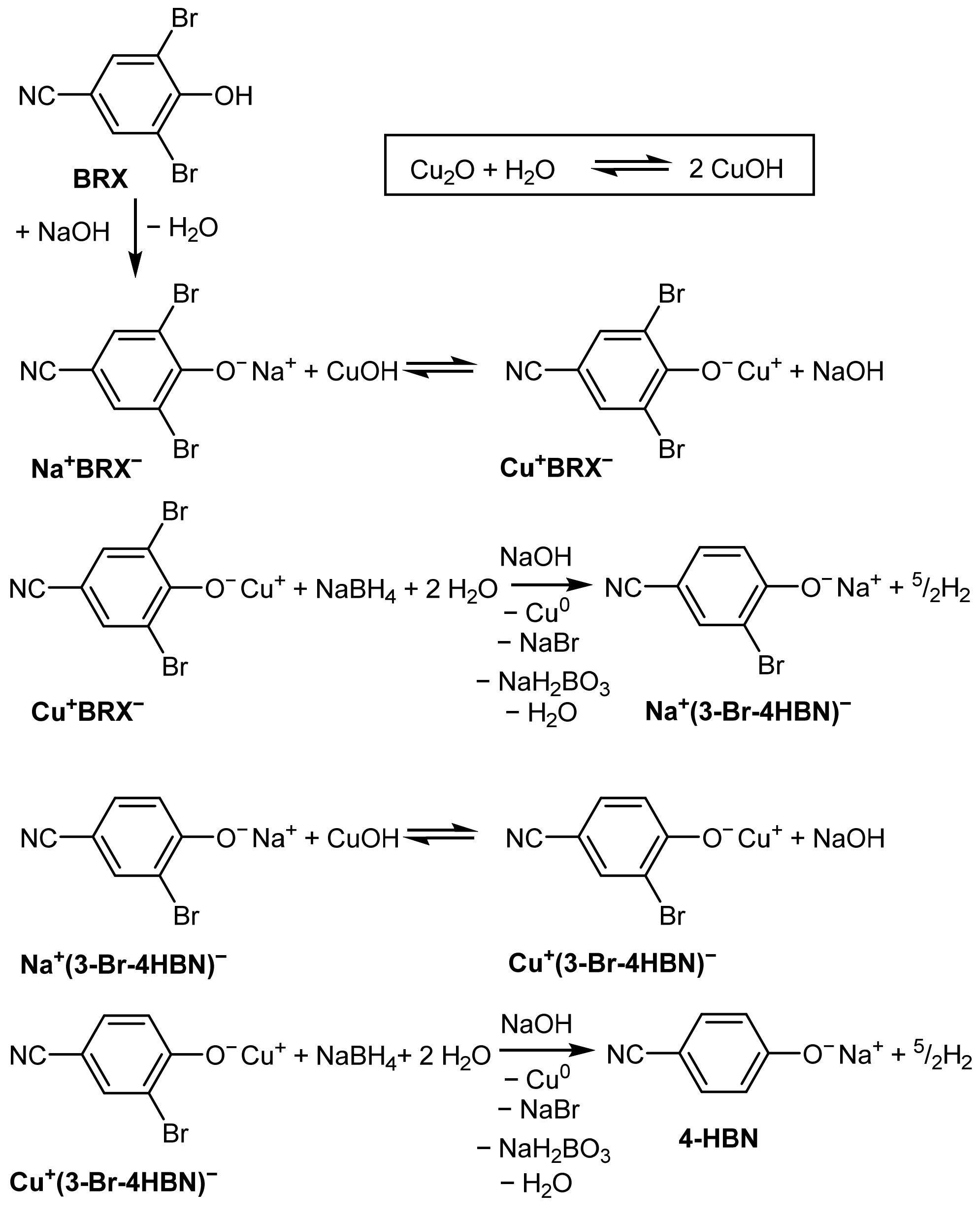


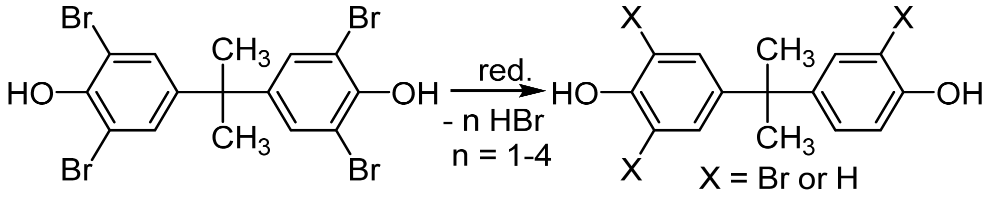
Figure 14. SEM images of the insoluble part after the treatment of 5 mM BRX solution in 20 mM aqueous NaOH with $NaBH_4/CuSO_4$ (top left 5000 times magnification, top right 50,000 times magnification) and with $CuSO_4/NH_4OH$/glucose/$NaBH_4$ (bottom left 5000 times magnification, bottom right 50,000 times magnification).

These findings were subsequently applied to verify the possibility of the HDB of tetrabromobisphenol A (TBBPA) which is well-known polybrominated pollutant widely used as flame retardant (Supplementary Materials Table S8, Scheme 5).

Both Dev. alloy/NaOH and $CuSO_4/NaBH_4$ work as an effective HDB agent producing pure bisphenol A under optimized reaction conditions (Supplementary Materials Table S8, Entries 3 and 4). Remarkably, using higher excess of the base, the HDB of TBBPA fails probably due to the high rate of Dev. alloy corrosion accompanied only by rapid liberation of hydrogen (Supplementary Materials Table S8, Entries 1 and 2). HDB of TBBPA using the Dev. alloy/$NaBH_4$ is significantly slower as could be seen within a comparison with the Dev. alloy/NaOH (Table S8, Entry 5). Interestingly, metallic Cu/$NaBH_4$ is quite comparable HDB agent for TBBPA with $Cu_2O/NaBH_4$ system (Supplementary Materials, Table S8, Entries 6 and 7). $NaBH_4$ without any Cu-based compounds is virtually ineffective within the target debromination of TBBPA (Entry 8).



Scheme 4. Plausible pathway for the $Cu_2O/NaBH_4$-based HDB of BRX.



Scheme 5. HDB of TBBPA using tested Cu-based reductants.

3. Materials and Methods

The starting brominated phenols Bromoxynil (abcr chemicals GmbH., Karlsruhe, Germany) and tetrabromobisphenol A (Alfa-Aesar Co., Thermo Fisher Scientific, Heysham, UK) were purchased from commercial sources in a defined purity higher than 95%. The aluminium alloys (Devarda's Al-Cu-Zn, 45–50–5%, p.a.; Arnd's Mg-Cu, 40–60%; brass, Cu-Zn powder—60 mesh; bronze, Cu-Sn spherical powder—200 mesh) and copper-based compounds CuO (CuO nanopowder < 50 nm and CuO powder < 10 μm, 98%), metallic Cu (Cu nanopowder 60–80 nm and Cu powder < 425 μm, 99.5%), Cu_2O (powder < 99.99%, anhydrous), $CuBr_2$ (99%), $NaBH_4$ (95%) and deuterated chloroform ($CDCl_3$) were purchased from Sigma-Aldrich Co. (Czech Republic). The Fe_3Al (97.5%) and silver brazing alloy (1.6 mm dia, Ag:Cu:Zn 30:38:32) was purchased from Alfa-Aesar Co. (Thermo Fisher Scientific, Heysham, UK). Additional chemicals and solvents in a p.a. quality were obtained from a local supplier (Lach-Ner Co., Neratovice, Czech Republic).

The comparative experiments were performed in 250 mL round-bottomed flasks equipped with magnetic stirring on Starfish equipment (Radleys Discovery Technologies, Saffron Walden, UK) installed on a magnetic stirrer Heidolph Heistandard for parallel reactions. The reaction flasks were fitted by a tube filled with granulated charcoal.

3.1. Chemical Analysis

The ^{1}H NMR spectra were recorded from solutions in $CDCl_3$ on a Bruker Avance 500 spectrometer (equipped with a Z-gradient 5mm ProdigyTM cryoprobe) at a frequency of 500.14 MHz or on a Bruker UltraShield^{TM} 400 spectrometer at frequency of 400.13 MHz at 295 K. The solutions were obtained by dissolving obtained evaporated residue (resulting from the work-up of reaction mixtures) in 1 mL of $CDCl_3$. The values of ^{1}H chemical shifts were calibrated to the residual signals of $CDCl_3$ ($\delta(^1H) = 7.27$ ppm). The mutual content of particular constituents in obtained mixtures was established via the integration of the corresponding area resonances. The identification of respective species in prepared samples has been done accordingly to the Spectral Database for Organic Compounds [38,39] or Online NMR Database accessible free of charge [40].

The diffraction patterns (Cu Kα, $\lambda = 1.5418$ Å) of powdered samples were recorded on a D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany) with Bragg-Brentano θ-θ goniometer (radius 217.5 mm) equipped with Ni-beta filter and LynxEye detector. The scan was performed at room temperature from 5° to 80° (2 θ) in 0.01° steps with a counting time of 1 s per step. The mass concentrations of the present phases were calculated by full pattern matching using EVA software (Bruker AXS GmbH, Karlsruhe, Germany) [34]. For each selected pattern, EVA adjusts the scaling factor and width parameters by fitting, and the result is transformed into concentrations using I/Icor factors from PDF-4+ database (Swarthmore, PA, USA) [35].

To analyze the extractable compounds in the sample of aqueous reaction solution, the extraction with CH_2Cl_2 (SupraSolv®DCM for GC/MS, Merck, USA) was performed (300 mL of waste water sample was extracted repeatedly by 3 × 5 mL of CH_2Cl_2) with subsequent concentration of obtained dichloromethane phase to approximately 1 mL. CH_2Cl_2 extract was injected in split (50:1) mode with the injector temperature set at 280 °C and detector set at 230 °C. The extract was analyzed on 6890GC/MSD 5973 Inert (Agilent Technologies, USA) using 30 m capillary Agilent J&W DB-5ms Ultra Inert column (I.D. 0.25 mm, 0.25 µm film thickness) (Agilent Technologies, USA). The temperature program started from 50 °C for 2 min, ramp at 10 °C/min to 300 °C. MS spectra were recorded using electron impact ionization (EI, 70 eV) in a full-scan mode.

3.2. HDB Procedures

3.2.1. HDB of Brominated Phenols Using Studied Al Alloys, Electropositive Metals or Cu-Based Catalysts and $NaBH_4$

The aqueous solution (5 mM, 100 mL) of BRX dissolved in aqueous NaOH solution (or 10 mM BRX solution in methanol) was mixed with Al-based alloy, electropositive metal or Cu-based catalyst (appropriate quantities are specified in Table 1 and in Supplementary Materials Tables S1–S8) and eventually other tested chemical was added slowly under vigorous stirring to the obtained suspension. The reaction mixture was stirred at 500 rpm at 25 °C for the appropriate time period, decanted, aqueous phase was filtered, and the filtrate was acidified to pH~2.5–3 using 16 wt.% H_2SO_4 and extracted with one portion of CH_2Cl_2 (1 × 100 mL) overnight under vigorous stirring. Collected CH_2Cl_2 extract was evaporated to dryness and approximately 30 mg of nonvolatile residue was dissolved in

$CDCl_3$. ^{1}H NMR spectrum of obtained $CDCl_3$ solution (and eventually GC-MS) indicates the conversion of the BRX to HDB products.

3.2.2. HDB of Brominated Phenols Using In Situ Generated Cu/Cu_2O

An appropriate quantity of $NaBH_4$ was dissolved in the solution (5 mM, 100 mL) of BRX dissolved in aqueous NaOH solution, and to this solution, appropriate quantity of additive and subsequently aqueous $CuSO_4$ solution (40 mM, 50 mL) was added dropwise under vigorous stirring (exact quantities are specified in Tables S6 and S8 in Supplementary Materials). The reaction mixture was stirred at 500 rpm at 25 °C overnight, filtered, acidified to pH~2.5–3 using 16 wt.% H_2SO_4 and extracted with one portion of CH_2Cl_2 (1 × 100 mL) overnight using vigorous stirring. The collected CH_2Cl_2 extract evaporated to dryness and approximately 30 mg of nonvolatile residue was dissolved in $CDCl_3$. ^{1}H NMR spectrum of obtained $CDCl_3$ solution (and eventually GC-MS) indicates the conversion of the BRX to HDB products.

For analyses of brominated compounds and products of their reduction in sample of aqueous solutions extraction with CH_2Cl_2 was performed (50 mL of aqueous phase acidified to pH = 2–3 was extracted by 50 mL of CH_2Cl_2 by overnight vigorous stirring) with subsequent evaporation of obtained dichloromethane phase to dryness.

3.2.3. HDB Kinetic Experiments

To the 500 mL of 5 mM BRX solution in aqueous NaOH (100 mM NaOH using Dev. alloy or 20 mM NaOH using other reduction systems) the appropriate quantity of Cu-based reduction agent(s) (see description in corresponding Figures captions) was added under vigorous stirring (600 rpm). Subsequently, 50 mL portions of samples in appropriate time intervals were collected sequentially, filtered, filtrates were acidified to pH~2.5–3 using 16 wt.% H_2SO_4 and extracted with 50 mL of CH_2Cl_2 overnight for GC-MS and/or NMR analysis.

3.3. Evaluation of Kinetics of the HDB of BRX)

Rate constants (k_1 and k_2) of BRX debromination were evaluated based on non-linear regression analysis using GraphPad Prism 7.05 (GraphPad Software, San Diego, CA, USA). The time dependences of concentration of BRX and debromination products were fitted to the kinetic model of subsequent reaction of the first order (Figures 1, 7 and 11, Scheme 1 and Supplementary Materials Figures S3, S5 and S6) according to the equations:

$$c(\mathrm{BRX}) = c_0(\mathrm{BRX})\, .\, e^{-k_1.t} \quad (1)$$

$$c(3-\mathrm{Br}-4-\mathrm{HBN}) = \frac{k_1\, .\, c_0(\mathrm{BRX})}{k_1-k_2}\, .\, \left(e^{-k_2 t}-e^{-k_1 t}\right) \quad (2)$$

where $c(\mathrm{BRX})$ and $c(3-\mathrm{Br}-4-\mathrm{HBN})$ are the actual concentrations of BRX and 3-Br-4-HBN in time t, $c_0(\mathrm{BRX})$ is the initial concentration of BRX, k_1 and k_2 are the rate constants of the first and second reaction step.

The value of k_1 corresponding to the first step of subsequent reaction (the formation of 3-Br-4-HBN) was evaluated based on the time dependence of BRX concentration and compared with the value of k_1 calculated from the time dependence of 3-Br-4-HBN. The value of k_2 rate constant can be also evaluated based on the time dependence of 4-HBN concentration but this possibility was not used due to the difficulties with subsequent reaction of 4-HBN (which undergoes subsequent transformation to 4-HBA). Coefficient determination (R^2) and absolute sum of squares of residues were chosen as a criterion for assessing of quality of the fit.

4. Conclusions

To conclude, it was found that among the tested Cu-based agents and/or catalysts for the HDB of studied BRX (e.g., brass Cu-Zn, bronze Cu-Sn, Devarda's Al-Cu-Zn alloy with coaction of NaOH or $NaBH_4$, Cu/$NaBH_4$, Cu_2O/$NaBH_4$, CuO/$NaBH_4$), the best efficiency is achieved by the Dev. alloy in alkaline aqueous solution. The major drawback of this HDB reagent is its poor direct reusability due to the rapid and significant loss of the desired catalytic HDB activity. The main reason for this behavior is presumably the decrease in active $CuAl_2$ content during the HDB process in alkaline aqueous solution accompanied by the structural changes within the catalytically active Cu-species of the used Dev. alloy (i.e., formation of Cu_2O, zaccagnaite and other Al(III) compounds).

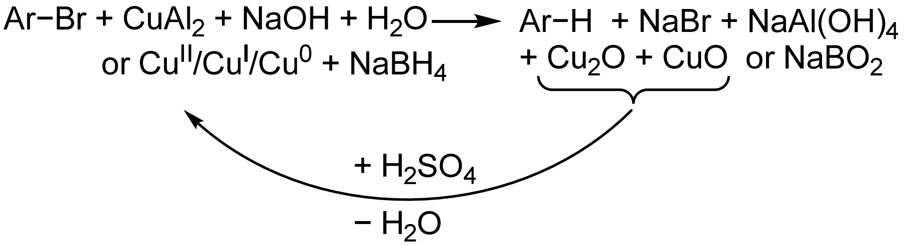
The possibility of addition of $NaBH_4$ as a replacement agent of consumed aluminium from the used Dev. alloy was investigated as well. The results are at least indicative of the possible employment of the used Dev. alloy/$NaBH_4$ mixture for partial HDB of starting BRX; however, such modified HDB process has never reached the desired completion.

We have also demonstrated that cooperative action of the Dev. alloy/$NaBH_4$ mixture of reagents within the HDB of alkaline BRX solution somewhat decrease the consumption of crucial aluminium bound within the Dev. alloy. Due to this reason, such cooperative action causes much slower HDB reaction rate and provides the same disadvantage resulting in a non-complete HDB process leading only to the formation of the 3-Br-4-HBN in case of attempted reuse of the partially spent Dev. alloy.

As one of the most interesting result, we have found that the Cu-based alloys are able of mediating the cyano group reductions in aqueous solutions at ambient temperature. To the best of our knowledge, such finding has not been described in the literature so far.

Finally, the possibility of employing the most promising HDB agent, the Dev. alloy with coaction of NaOH, has been auspiciously investigated within the environmentally desirable HDB processes of industrially important brominated flame retardant TBBPA, too.

Interestingly, though the Dev. alloy is not recyclable directly in studied HDB process, the in-situ formation of mixed Cu(0)/Cu_2O nanoparticles in coaction of $NaBH_4$ enables effective and complete HDB of both studied BRX and TBBPA (Scheme 6).



Scheme 6. Proposed sustainable method for studied Cu-based HDB of Ar-Br.

Based on new findings described in this article, for the complete HDB of both studied BRX and TBBPA, either the Dev. alloy in the coaction of excess of NaOH or combination of soluble Cu(II) salt under excess of $NaBH_4$ are the only efficient HDB agents. Due to this reason, for sustainability of the proposed HDB process based on $NaBH_4$, the crucial hydrometallurgical treatment of spent Cu catalyst (i.e., Dev. alloy, eventually Cu_2O or CuO, Scheme 6) with H_2SO_4 or HCl [33] is required.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/catal11060699/s1, Table S1: Effect of Cu^0, $CuBr_2$ and Cu(I) or Cu(II) oxides on 0.5 mmol BRX dissolved in 0.1 L of 0.1 M NaOH; Table S2: Effect of different sources of copper on the HDB of BRX under the coaction of $NaBH_4$; Table S3: Recyclability experiments of the Dev. alloy within the HDB of BRX; Table S4: Recyclability experiments of the used Dev. alloy under the coaction of $NaBH_4$; Table S5: Recyclability of Dev. alloy used under the coaction of $NaBH_4$; Table S6: Effect of different sources of copper on the HDB of BRX under the coaction of $NaBH_4$; Table S7: Effect of different sources of copper on the HDB of BRX in aq./methanolic solution without excess of NaOH; Table S8: HDB of TBBPA after overnight reaction using different HDB agents. Figure S1: Powder X-ray diffractograms of undissolved residues of reused Dev. alloys; Figure S2: Effect of repeated application of Dev. alloy in the coaction of $NaBH_4$; Figure S3:HDB rate of 5 mM aq. BRX dissolved in 20 mM NaOH mediated by the Dev. alloy (7.1 g/L) under the coaction of $NaBH_4$ (8 g/L);

Figure S4: Effect of added NaOH on the HDB of BRX after 18 h of vigorous stirring; Figure S5: HDB rate of 5 mM aq. BRX dissolved in 20 mM aq. NaOH using powdered copper (3.4 g/L) and under the coaction of $NaBH_4$ (8 g/L); Figure S6: Comparison of reductive degradation rates of BRX in aqueous NaOH using Dev. alloy or $Cu_2O/NaBH_4$; Figure S7: Comparison of the ^{1}H NMR spectra of evaporated residue of CH_2Cl_2 extracts obtained after the reaction of 5 mM BRX in aqueous NaOH with $Cu^0/NaBH_4$ (top), excess of Dev. alloy (middle) and nano $Cu^0/NaBH_4$ (bottom); Figure S8: Comparison of the ^{1}H NMR spectra (details of aromatic regions) of evaporated residue of CH_2Cl_2 extracts obtained after the reaction of 5 mM BRX in aqueous NaOH with $Cu^0/NaBH_4$ (top), excess of Dev. alloy (middle) and nano$Cu^0/NaBH_4$ (bottom); Figure S9: Comparison of the ^{1}H NMR spectra (details of aromatic regions) of evaporated residue of CH_2Cl_2 extracts obtained after the reaction of 5 mM BRX in aqueous NaOH with $Cu^0/NaBH_4$ (top), excess of Dev. alloy (middle) and nano $Cu^0/NaBH_4$ (bottom); Figure S10: GC-MS analysis of $CDCl_3$ extract of reaction mixture obtained after HDB of 5 mM BRX dissolved in 20 mM NaOH using nano $Cu/NaBH_4$ (Table S2, Entry 7) (retention times are given in minutes); Figure S11. (a) GC chromatogram of GC-MS analysis of $CDCl_3$ extract of reaction mixture obtained after reduction of BRX by in-situ prepared nano Cu + $NaBH_4$ (Table S6, Entry 12) (retention times are given in minutes). Figure S12: GC-MS analysis of CH_2Cl_2 extract of reaction mixture described in Table S8, Entry 2, HDB of TBBPA (retention times are given in minutes); Figure S13: GC chromatogram of GC-MS analysis of DCM extract of reaction mixture after complete debromination (using Dev. alloy/NaOH or $CuSO_4/NaBH_4$), Table S8, Entries 4, 5; Scheme S1: Proposed HDB of BRX using Dev. alloy and aqueous NaOH solution.

Author Contributions: T.W. conceived, designed and performed part of the experiments and wrote the paper; B.K. performed the experiments; L.B. performed powder X-ray measurements and analyzed the data; V.Č. performed SEM measurements; A.K. performed kinetic evaluations; J.Č. performed GC-MS measurements and analyzed the data; P.Š. performed NMR measurements. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Data is contained within the article or supplementary material. The data presented in this study are available in [insert article or Supplementary Material here].

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Conflicts of Interest: The authors declare no conflict of interest.

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