

Article

# Hydrodechlorination of Different Chloroaromatic Compounds at Room Temperature and Ambient Pressure—Differences in Reactivity of Cu- and Ni-Based Al Alloys in an Alkaline Aqueous Solution



# Tomáš Weidlich <sup>1,\*</sup>, Barbora Kamenická <sup>1</sup>, Klára Melánová <sup>2</sup>, Veronika Čičmancová <sup>3</sup>, Alena Komersová <sup>4</sup> and Jiří Čermák <sup>5</sup>

- <sup>1</sup> Chemical Technology Group, Institute of Environmental and Chemical Engineering, Faculty of Chemical Technology, University of Pardubice, Studentska 573, 53210 Pardubice, Czech Republic; st38856@student.upce.cz
- <sup>2</sup> Joint Laboratory of Solid State Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 84, 53210 Pardubice, Czech Republic; klara.melanova@upce.cz
- <sup>3</sup> Center of Materials and Nanotechnologies, Faculty of Chemical Technology, University of Pardubice, Nam. Cs. Legii 565, 53002 Pardubice, Czech Republic; veronika.cicmancova@upce.cz
- <sup>4</sup> Department of Physical Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentska 573, 53210 Pardubice, Czech Republic; alena.komersova@upce.cz
- <sup>5</sup> VUOS a.s.—Research Institute for Organic Syntheses, č.p. 296, 53354 Rybitví, Czech Republic; jiri.cermak@vuos.com
- \* Correspondence: tomas.weidlich@upce.cz; Tel.: +420-46-603-8049

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**Abstract:** It is well known that the hydrodechlorination (HDC) of chlorinated aromatic contaminants in aqueous effluents enables a significant increase in biodegradability. HDC consumes a low quantity of reactants producing corresponding non-chlorinated and much more biodegradable organic compounds. Two commonly used precious metals free Al alloys (Raney Al-Ni and Devarda's Al-Cu-Zn) were compared in reductive action in an alkaline aqueous solution. Raney Al-Ni alloy was examined as a universal and extremely effective HDC agent in a diluted aqueous NaOH solution. The robustness of Raney Al-Ni activity is illustrated in the case of HDC of polychlorinated aromatic compounds mixture in actual waste water. In contrast, Devarda's Al-Cu-Zn alloy was approved as much less active for HDC of the tested chlorinated aromatic compounds, but with a surprisingly high selectivity on cleavage of C-Cl bonds in the meta and sometimes the ortho position in chlorinated aniline and sometimes chlorinated phenol structures. The reaction of both tested alloys with chlorinated aromatic compounds in the alkaline HDC reaction mixture is very useful for subsequent treatment of HDC products by coagulation and flocculation of Al(OH)<sub>3</sub> caused by simple neutralization of the alkaline aqueous phase after the HDC reaction.

**Keywords:** hydrodechlorination; chloroaromatic compounds; Raney Al-Ni alloy; Devarda's Al-Cu-Zn alloy

# 1. Introduction

Chlorinated aromatic compounds (Ar-Cls) are used on a large scale as industrial solvents or intermediates in the synthesis of specialty organic chemicals, in other words, dyestuffs, pesticides and drugs. In addition, Ar-Cls are produced as by-products in processes based on radical

chlorination of aliphatic compounds (for example, formation of hexachlorobenzene during production of tetrachloroethylene) [1–5].

As Ar-Cls have been so widely used they can be found in nearly all major environmental compartments. Ar-Cls contaminate aqueous industrial effluents and subsequently polluted ground and underground water which is caused by their high stability in the environment with a tendency to accumulate in animal tissues [6,7]. The toxicity of Ar-Cls mainly arises from bound chlorine(s), while chlorine-free aromatic compounds are not only less toxic but can also be completely degraded by biological processes (or possibly recycled as industrial raw materials) [7].

Due to the above-mentioned reasons, the treatment of aqueous effluents contaminated with Ar-Cls using hydrodechlorination (HDC) by appropriate HDC reagent serves as a promising method producing hydrogen chloride and biodegradable dechlorinated aromatic compound Ar-H. For effective HDC, a suitable base is usually added to the aqueous Ar-Cl solution for neutralization of the produced HCl to prevent deactivation of the HDC catalyst. It was demonstrated that the base plays not only the role of a proton scavenger of the produced HCl but also takes part in the HDC reaction [8].

For effective HDC reaction, researchers have tested monometallic (Al, Fe, Mg, Zn) [4–6,8] or bimetallic metal systems by plating of electropositive metal surfaces with platinum or palladium (Pt/Fe, Pd/Fe, Pd/Mg, Pd/Al) [3,5,8–13]. In the case of non-plated electropositive metal application, the kinetic of HDC of Ar-Cls is extremely slow even using nanoparticles. This means that effective HDC requires a significant excess of used metallic reductant [5,12,13]. Use of bimetallic HDC systems makes it possible to dechlorinate Ar-Cls effectively. Electropositive zero-valent metal produces nascent hydrogen and additional metal (usually from platinum group metals) works as a hydrogenation catalyst which leads to the formation of metal hydride bonds [9–12].

Platinum group metals, in contrast, used for plating of electropositive metals as HDC catalysts are rare, very sensitive to poisoning and quite expensive [3,7–12].

Due to these above-mentioned reasons, less expensive bimetallic reductants have been tested in recent years based on nickel or copper in the role of HDC catalysts for plating of electropositive metals Cu/Al, Cu/Fe, Ni/Fe, Ni/Zn and Cu/Zn [3,6,14–17].

Apart from bimetals, several Al-based metallic alloys containing Cu or Ni (Al-Cu and Al-Ni) have been published as very effective for HDC of Ar-Cls [18–26] due to the high quantity of Ni (or Cu, respectively) working as HDC catalysts compared with bimetals where electropositive metal (source of reductant) is covered with a thin layer of HDC catalyst. Raney Al-Ni alloy (which contains 50 wt.% of Al and 50 wt.% of Ni) in a diluted aqueous base seems to be an especially effective HDC reagent exploiting both the reduction potential of Al in the alkaline aqueous solution with the high HDC activity of in situ produced Raney Ni [18-24,27-29]. The role of the base in the HDC reaction mediated by the Al-Ni alloy was studied in several works [21,24,28,29]. It was observed that the limiting step of HDC is the solubility of Al from the Al-Ni alloy. Using alkali metal hydroxide solutions or alkaline solutions of complexing agents (EDTA or citric acid sodium salts), rapid HDC was observed in the case of the studied chlorinated anilines or 2-chlorophenol. Using an excess of sodium fluoride instead of NaOH and a high (more than 100-times above stoichiometry) excess of Al-Ni, efficient HDC of 2-chlorophenol was observed by Yang and co-authors [28]. Al-Ni is the most expensive reagent, however, in this HDC system which disfavored the application of this technique even in the case of three-times repeated Al-Ni recycling. We observed that using NaOH or KOH and Al-Ni alloy for HDC of Ar-Cl in molar ratio 10:2:1, the HDC is completed within 120 min in the case of monochloroanilines and the quantity of used Raney Al-Ni alloy could even be lowered by addition of glucose in some cases [23].

In contrast, Al-Cu alloys were not often described in the chemical literature as efficient HDC agents. Rapid hydrodebromination of 2,4,6-tribromophenol using Devarda's Al-Cu-Zn alloy and HDC of only several Ar-Cls in the alkaline NaOH solution using Al-Cu alloy were observed [25,26]. Al-Cu alloys are a well-known reducing agent for inorganic nitrate reduction (Devarda's alloy) or for HDC of much more reactive halogenated methanes [30]. Devarda's Al-Cu-Zn alloy (which contains

50 wt.% Al, 45 wt.% Cu and 5 wt.% Zn) was reported as an effective HDC agent only by co-action of excess NaBH<sub>4</sub> at an elevated temperature for DDT and 2,4,6-trichlorophenol HDC [31].

Raney Al-Ni alloy is used in chemical technology in high quantities as a source of Raney nickel hydrogenation catalysts and Devarda's Al-Cu-Zn alloy is applied for nitrates reduction to ammonia in contaminated waters.

In this article, we attempt to compare the HDC activity of two commercially available and well-defined Al alloys, particularly Raney Al-Ni alloy and Devarda's Al-Cu-Zn alloy at room temperature and ambient pressure in an alkaline aqueous solution for HDC of Ar-Cls. Exclusively room temperature and ambient pressure was used due to the minimization of capital costs and the environmental impact of this method in assumed industrial application for treatment of water contaminated with Ar-Cls. In this study, the long reaction time (around 16 h) was used usually in describing HDC experiments to achieve completion of the HDC reaction (at least more than 10 half-lives of HDC reaction) [21,26]. A concentration of diluted aqueous NaOH solution and an excess of both tested Al alloys were chosen on the basis of our earlier published results by studying the hydrodehalogenation of halogenated anilines and phenols [21–24,26]. Changes in the structures of both mentioned alloys are presented during a HDC reaction in the diluted aqueous NaOH solution.

#### 2. Results

#### 2.1. Dechlorination of Chlorinated Anilines

Chlorinated anilines (Cl-ANs) are common chlorinated contaminants in the specialty organic chemicals production sector due to their sparing aqueous solubility. A broad spectrum of Cl-ANs is used, for example, for preparation of dyes and pigments and for production of phenylurea herbicides. In addition, Cl-ANs are often degradation products of herbicide metabolization due to low biodegradability or the biocidal properties of Cl-ANs. For this reason, the facile method available for rapid HDC of Cl-ANs in water is of high interest.

A set of 12 different Cl-ANs was used in the HDC experiments for a comparison of reductive efficiency of Raney Al-Ni and Devarda's Al-Cu-Zn alloy in aqueous NaOH. HDC of Cl-ANs in water using Raney Al-Ni alloy proceeds in a straightforward manner not only in 1% NaOH solution but even in alkaline buffers at pH above 10 [21]. In contrast, practically no regioselectivity or bound halogen selectivity of this HDC was observed, as could be seen in Table 1. The important exception to this claim is the more difficult cleavage of quite stabile C-F bonds by the action of Al-Ni which is applicable for selective HDC of chlorinated  $CF_3$ -anilines [21,22].

Starting Cl-AN	Content of Anilines after Al-Ni/NaOH Treatment <sup>2</sup>	Content of Anilines after Al-Cu-Zn/NaOH Treatment <sup>2</sup>
2-chloroaniline	100% aniline	100% aniline
3-chloroaniline	100% aniline	100% aniline
4-chloroaniline	100% aniline	100% 4-Cl-aniline
2,3-dichloroaniline	100% aniline	100% aniline
2,5-dichloroaniline	100% aniline	6.9% aniline + 93.1% 2,5-diCl-aniline
2,6-dichloroaniline	100% aniline	43.7% aniline + 56.3% 2,6-diCl-aniline
2-chloro-5-CF <sub>3</sub> -aniline	3-CF <sub>3</sub> -aniline + 3-CF <sub>x</sub> H <sub>v</sub> -aniline $^2$	10.4% 3-CF <sub>3</sub> -aniline + 89.6% 2-chloro-5-CF <sub>3</sub> -aniline <sup>2</sup>
4-bromo-2-chloroaniline	100% aniline	100% aniline
2,4,5-trichloroaniline	100% aniline	10% 4-Cl-aniline + 90% 2,4,5-trichloroaniline
3,4-dichloroaniline	100% aniline	100% 4-chloroaniline
3,5-dichloroaniline	100% aniline	100% aniline
2,6-dichloro-4-CF <sub>3</sub> -aniline	4-CF <sub>3</sub> -aniline + 4-CF <sub>x</sub> H <sub>v</sub> -aniline $^3$	100% 2,6-dichloro-4-CF <sub>3</sub> -aniline <sup>3</sup>
3-chloro-4-fluoroaniline	100% aniline	100% 4-fluoroaniline

**Table 1.** Comparison of HDC reactivity of Raney Al-Ni and Devarda's Al-Cu-Zn alloys toward different chloroanilines (Cl-ANs)<sup>1</sup>.

<sup>1</sup> The experimental procedure is described in Section 4.2.1. <sup>2</sup> According to the <sup>1</sup>H NMR spectra of the obtained CDCl<sub>3</sub> extracts of the reaction mixture. <sup>3</sup> According to the <sup>1</sup>H and <sup>19</sup>F NMR spectra of the obtained CDCl<sub>3</sub> extracts of the reaction mixture.

When using Devarda's Al-Cu-Zn alloy with co-action of 1% aqueous NaOH for reductive treatment of different Cl-ANs, a much higher regioselectivity of HDC was observed. We observed that chlorine bound in the meta or eventually ortho position toward the amino group in the Cl-AN structure is reduced smoothly by the action of Devarda's Al-Cu-Zn alloy via HDC (Figure 1). HDC was not observed at all, however, in the para position (see Table 1) in case of chloroanilines.

In addition, attempts to recycle an already used Devarda's Al-Cu-Zn alloy for subsequent HDC of 3- or 2-chloroaniline completely failed.



Figure 1. The reaction scheme of *m* and *o*-chloroanilines HDC using the Devarda's Al-Cu-Zn alloy.

Weidlich et al. [23] published a method available for reducing the minimal quantity of Al-Ni alloy for HDC of several Cl-ANs. This method is based on the addition of glucose which works as an oxidation inhibitor of Raney Al-Ni in the diluted NaOH solution. Due to the inhibition of Al dissolution caused by added glucose, the HDC reaction slows down, although, the minimal dose needed for complete HDC of tested Cl-ANs was diminished to less than one half compared with the action of Al-Ni/NaOH without the addition of glucose (Figure 2).

A first order model was chosen for the kinetic evaluation of the HDC process, as is frequently the case in literature for reactions of Ar-Cls with electropositive metals [3,4,6,9–12,14–16]. High values of  $R^2$  (Table 2) obtained fitting of the time dependences for HDC of Cl-ANs using the Raney Al-Ni alloy without glucose, confirm the fact that this reaction follows the first order kinetic model. The observed rate constants  $k_{obs}$  were determined to be approximately 0.087 min<sup>-1</sup> for 2-chloroaniline and 0.080 min<sup>-1</sup> for 3-chloroaniline (using 2.5 mol Al in Al-Ni for HDC of 1 mol of chloroaniline) at 25 °C. The value of the observed rate constant for 2-chloroaniline is slightly higher than for 3-chloroaniline, but the difference is statistically insignificant as evidenced by the overlapping curves on Figure S3 in the Supplementary Materials. The addition of glucose and the application of a decreased Al-Ni amount caused, in contrast, a significant decrease in the studied chloroaniline) using only 1.2 mol of Al in Raney Al-Ni alloy per mol of chloroaniline and 0.023 min<sup>-1</sup> for 3-chloroaniline) using only 1.2 mol of Al in Raney Al-Ni alloy per mol of chloroaniline and 5 mol of glucose. Lower values of  $R^2$  for the same reaction with the glucose addition and decrease in Raney Al-Ni quantity were found which in all probability demonstrates a more complicated kinetic model for HDC at these experimental conditions.

**Table 2.** Observed rate constants for HDC of Cl-ANs using the Raney Al-Ni alloy described in Figure 2(and [23]), evaluated based on a non-linear regression analysis (applying a pseudo-first order model).

Reactant	+1.2 eq. of Al (Added as RANEY Al-Ni) + 5 eq. Glucose		+2.5 eq. of Al (Added	as Raney Al-Ni)
2-chloroaniline 3-chloroaniline	$\begin{split} k_{obs} &\pm \text{SD} \ (\text{min}^{-1}) \\ 0.0178 &\pm 2.6 \times 10^{-3} \\ 0.0227 &\pm 2.7 \times 10^{-3} \end{split}$	R <sup>2</sup> 0.9410 0.9772	$\begin{split} k_{obs} &\pm SD \; (min^{-1}) \\ 0.0872 &\pm 5.6 \times 10^{-3} \\ 0.0803 &\pm 2.6 \times 10^{-3} \end{split}$	R <sup>2</sup> 0.9943 0.9985

Interestingly, the effect of glucose on decreasing of Raney Al-Ni supply was observed only in the case of more via HDC reactive Cl-ANs such as *o*- and *m*-chloroaniline, but not for *p*-chloroaniline or 2,5-dichloroaniline. As we observed, Cl-ANs reducible via HDC by Devarda's Al-Cu-Zn alloy are reducible even by the action of a low excess of Raney Al-Ni with the co-action of glucose and aqueous NaOH.



**Figure 2.** A comparison of the reaction rate of *o*- and *m*-chloroaniline (Cl-AN) by Al-Ni/NaOH with and without co-action of glucose (ratio of reactants: 2 mmol of studied Cl-AN, 0.13 g Al–Ni alloy, 10 mmol glucose, and 25 mmol NaOH in 200 mL water; stirring at 500 rpm and 25 °C, for more details see [23]).

#### 2.2. Dechlorination of (Poly)Chlorinated Benzenes

(Poly)chlorinated benzenes are another group of Ar-Cls, broadly analyzed in contaminated water streams from chemical plants, especially aqueous effluents from the sector of organic technology where chlorinated benzenes are valuable inert solvents, reactants for production of phenolic compounds or sometimes industrial by-products [2–4,9,19].

2.2.1. Dechlorination of Chlorinated Benzenes Using Devarda's Al-Cu-Zn Alloy

The HDC reaction (Figure 3) of nonpolar and in water very sparingly soluble polychlorobenzenes was performed in a methanol-H<sub>2</sub>O mixture to achieve sufficient solubility of these Ar-Cls in the reaction mixture.



**Figure 3.** The proposed pathway of hexachlorobenzene and (poly)chlorinated benzenes HDC using studied Al alloys.

As can be seen from Figure 4 and Table S1 in Supplementary Materials, using a higher excess of Devarda's Al-Cu-Zn alloy, hexachlorobenzene (HCB) was completely reduced producing tetrachlorobenzenes (tetraCBs) and dichlorobenzenes (DCBs) produced as the main reduction products after 16 h of excess of Devarda's Al-Cu-Zn alloy action. However, no benzene (B) was observed in the reaction mixture, the HDC was completed by production of chlorobenzene (CB). For comparison, Shih et al. [4] published much slower HDC of HCB using a high excess of nanoiron. By the action of a thousand-times excess of nanoiron, only approximately 65% of HCB was reduced producing pentachlorobenzenes (pentaCBs), tetraCBs and trichlorobenzenes (triCBs), predominantly. Using a lower excess of Devarda's Al-Cu-Zn alloy (Figure 3, HCB\*), similar results with those published by Shih et al. [4] were observed. The conversion of HCB was very low, only pentaCBs, tetraCBs and triCBs were determined in the obtained liquid phase. The concentration of other less chlorinated chlorobenzenes was below the detection limit (less than 1  $\mu$ g/L).



**Figure 4.** The composition of obtained reaction mixtures after HDC of different polychlorinated benzenes using Devarda's Al-Cu-Zn alloy (for more details see Supplementary Materials, Table S1). The experimental procedure is described in Section 4.2.2.

Subsequent experiment testing HDC of pentaCB also indicated a higher stability of tetraCBs in comparison with other chlorinated benzenes. PentaCB was hydrodechlorinated with a high conversion to the mixture of less chlorinated benzenes and a low quantity of benzene using a high excess of Devarda's alloy. Apart from tetraCBs, 1,2,4-triCB, DCBs and CB were identified in the obtained reaction mixture after 16 h of Devarda's Al-Cu-Zn alloy action together with 1% NaOH in H<sub>2</sub>O/MeOH 1/1 solution. In the reaction mixture, a mixture of tetraCBs was the dominant product (over 69% of the determined aromatic products), accompanied by a lower quantity (below 9%) of 1,2,4-triCB, DCBs (below 12%), CB (below 6%) and a low quantity of benzene (below 3.5 molar% of aromatic compounds). Interestingly, no 1,2,3- and 1,3,5-triCBs were observed in the reaction mixture.

Attempts to directly reduce tetraCBs via HDC using an excess of Devarda's alloy in the methanolic aqueous NaOH solution resulted in unreacted tetraCBs as the main chlorinated aromatic compound occurring in the reaction mixture after overnight reaction. This experiment illustrated that tetraCBs are quite resistant to the Devarda's Al-Cu-Zn alloy action used even in high excess. As can be seen in Figure 4 and Table S1, the observed conversion of tetraCBs to the lower chlorinated products is slightly below 50%, with a predominant quantity of 1,2,4-triCB. Apart from CB (presented in 10.8% of the overall chlorinated benzenes content), the other HDC products are presented in less than 10% occurrence in the obtained reaction mixture after more than 16 h reaction time. Comparing abundance

of triCBs, 1,2,4-triCB is the most stable one even in the case of HDC of tetraCBs using the Devarda's Al-Cu-Zn alloy.

Testing HDC of the triCBs mixture, it was observed that practically no 1,2,4-triCB was reduced using the Devarda's Al-Cu-Zn alloy, only 1,2,3- and 1,3,5-triCBs were partially dechlorinated with a low conversion producing low concentrations (below 3%) of each of the less chlorinated benzenes.

A mixture of DCBs is also reduced with the Devarda's Al-Cu-Zn alloy very sparingly. Low quantities of CB and B were observed in the obtained reaction mixture.

With the testing action of the Devarda's Al-Cu-Zn alloy on the technical quality 1,2-DCB, the result was very similar, with only a few percent of CB and B being observed apart from DCB even after overnight stirring with an excess of reductant.

Low conversion of CB was obtained after overnight stirring of excess Devarda's Al-Cu-Zn alloy in aqueous NaOH.

In summary, only HCB is reduced completely by the Devarda's Al-Cu-Zn alloy, however, most other chlorinated benzenes are produced with only a very low content of biodegradable non-chlorinated benzene. Comparing the reactivity of chlorinated benzenes, especially tetraCBs, 1,2,4-triCB and DCBs seems to be resistant to the reductive HDC action of the Devarda's Cu-Al-Zn alloy in the alkaline aqueous/MeOH solution.

#### 2.2.2. Dechlorination of Chlorinated Benzenes Using the Raney Al-Ni Alloy

The HDC of nonpolar and in water very sparingly soluble polychlorinated benzenes was performed in the methanol-H<sub>2</sub>O mixture. Furthermore, 1,2-Dichloro- and monochlorobenzene were reduced with Al-Ni in the aqueous NaOH solution. In case of the action of Raney Al-Ni together with aqueous NaOH solution, benzene was the only product detected in the resulting liquid phase even after washing of Ni slurry with methanol (after HDC according to the Figure 3, sometimes with observed minute quantities of unreacted starting polychlorinated benzene in all probability due to its sorption of the wall of the reaction vessel above the reaction mixture).

The comparison of the HDC reaction rate of trichloro- and dichlorobenzenes was elucidated in a set of additional experiments and the results are depicted in Figures 5 and 6. As could be seen, the reaction rate is very similar with only a minute occurrence of less chlorinated benzenes as by-products in collected samples which indicates higher reaction rates of HDC of less chlorinated benzenes in comparison with more chlorinated benzenes, using Al-Ni/NaOH reagent.

Removal of 1,2,3-triCB via HDC follows the first order kinetic model with  $R^2$  equal to 0.9999. Kinetic model of the first order was confirmed also based on calculated value of  $c_0$  which is in accordance with experimental values. The mechanism of the 1,2,4-triCB and 1,3,5-triCB removal does not follow the first order kinetic model so clearly. The differences could be caused by the inaccuracy of the experimental points. Despite experimental inaccuracies being possible, the values of observed rate constants (Table 3) show about a three times higher reaction rate for 1,2,3-triCB.

Table 3. Observed rate constants (kobs) for removal of trichlorobenzenes (triCBs) via HDC described ir
Figure 5, evaluated based on a non-linear regression analysis (fitted to the first order kinetic model).

Reactant	Rate Constant of Tricb Removal $k_{obs} \pm SD$ (min <sup>-1</sup> )	c <sub>0</sub> (μg/L) Calculated	c <sub>0</sub> (μg/L) Determined	<b>R</b> <sup>2</sup>
1,2,3-triCB	$0.3205 \pm 1.6 \times 10^{-3}$	27,602	27,600	0.9999
1,2,4-triCB	$0.1008 \pm 2.48 \times 10^{-2}$	29,775	26,790	0.9130
1,3,5-triCB	$0.1122 \pm 2.08 \times 10^{-2}$	20,114	18,800	0.9500

The mechanism of DCBs removal via HDC can be described by the first order kinetic model which was confirmed by high values of  $R^2$  and by the conformity of the values  $c_0$  calculated and experimental. The values of rate constants (Table 4) show that the rate of 1,2-DCB and 1,3-DCB removal are comparable and the difference is statistically insignificant. The rate of 1,4-DCB removal is slightly

lower in comparison with 1,2-DCB and 1,3-DCB mentioned above. The mechanism of CB removal was not analyzed using non-linear regression analysis because of the lack of experimental points.

The kinetics of aluminum dissolution has also been described by the first order kinetic model. The observed Al dissolution rate constant is  $0.0775 \pm 0.013 \text{ min}^{-1}$  with a coefficient of determination  $R^2 = 0.952$ .

Additionally, as could be seen in Tables 3 and 4 and Figures 5 and 6 and on Figures S4 and S5 in Supplementary Materials, the observed HDC removal rate constants of DCBs is higher than the HDC rate of triCBs using Raney Al-Ni alloy. This is in sound agreement with the above-mentioned observation of complete HDC of studied polychlorinated benzenes caused by the action of the Raney Al-Ni alloy (no less chlorinated benzenes were detected after the HDC reaction using Raney Al-Ni).

**Table 4.** Observed rate constants for removal of dichlorobenzenes (DCBs) via HDC described in Figure 5, using the Raney Al-Ni alloy, evaluated based on a non-linear regression analysis (fitted to the first order model).

Reactant	Rate Constant of DCB Removal $k_{obs} \pm SD \ (min^{-1})$	c <sub>0</sub> (μg/L) Calculated	c <sub>0</sub> (μg/L) Determined	R <sup>2</sup>
1,2-DCB	$0.1861 \pm 5.7 \times 10^{-3}$	4374	4358	0.9984
1,3-DCB	$0.1841 \pm 5.7 \times 10^{-3}$	5993	5975	0.9983
1,4-DCB	$0.1593 \pm 6.5 \times 10^{-3}$	4724	4683	0.9968



**Figure 5.** HDC rate of trichlorobenzene (TCB) mixture with the Raney Al-Ni alloy. The experimental procedure is described in Section 4.2.4.



**Figure 6.** HDC rate of dichlorobenzene (DCB) mixture using the Al-Ni alloy. The experimental procedure is described in Section 4.2.4.

#### 2.3. Dechlorination of Chlorinated Phenolic Compounds

Chlorinated phenols are common aquatic pollutants due to their biocidal properties and solubility in water [5–7,10,12,14,15,17,18,20,26–29,31]. Due to this reason the possible reductive degradation of several chlorinated phenols was studied via HDC process testing both Devarda's Al-Cu-Zn and Raney Al-Ni alloys. The results are presented in Table 5. It is clear, that in the case of polychlorinated phenols, the Devarda's alloy fails in role of HDC agent. Only in the case of a highly chlorinated pentachlorophenol mixture of less chlorinated products was HDC reactivity 2,4,6-trichlorophenol toward the Devarda's alloy observed and testing and low conversion to 4-chlorophenol was documented. Additional tested polychlorinated phenols are inert to the Devarda's alloy action in all probability due to the deactivation of tested chlorophenols by other bound chlorine atoms, CF<sub>3</sub> or carbonyl groups in the ortho or para position with respect to the other Cl substituents in the tested polychlorophenol structures.

**Table 5.** Comparison of HDC reactivity of Raney Al-Ni and Devarda's Al-Cu-Zn alloys toward different chlorinated phenols <sup>1</sup>.

Starting X-AN	Content of Phenols after Al-Ni/NaOH Treatment <sup>2</sup>	Content of Phenols after Al-Cu-Zn/NaOH Treatment <sup>2</sup>
pentachlorophenol	100% phenol	Mixture of chlorinated phenols
2,4,5-trichlorophenol	100% phenol	100% 2,4,5-trichlorophenol
2,4,6-trichlorophenol	100% phenol	8% 4-chlorophenol + 92% 2,4,6-trichlorophenol
2-chloro-4-CF <sub>3</sub> -phenol	4- CF <sub>3</sub> -phenol + 4-CF <sub>x</sub> H <sub>v</sub> -phenol	100% 2-Cl-4-CF <sub>3</sub> -phenol
Triclosan (5-Chloro-2-(2,4-dichlorophenoxy)phenol	100% 2-phenoxyphenol	100% Triclosan
2-hydroxy-5-chlorobenzaldehyde	Salicylaldehyde and 2-hydroxybenzylalcohol	2-hydroxy-5-chlorobenzylalcohol
2-hydroxy-5-chloroacetophenone	2-ethylphenol + 5% of 2-( $\alpha$ -hydroxy)-ethylphenol	2-(α-hydroxy)-ethyl-5-chlorophenol

<sup>1</sup> The experimental procedure is described in Section 4.2.1. <sup>2</sup> According to the <sup>1</sup>H NMR spectra of obtained CDCl<sub>3</sub> extracts of the reaction mixture.

#### 2.4. Application of Al-Ni Alloy for HDC of Polychlorinated Compounds Mixture in Actual Waste Water

The robustness of Al-Ni HDC activity was tested on technological aqueous stream obtained from the production of azo pigments based on reactions of 2,5-dichloroaniline. According to the routine screening GC-MS analysis based on extraction of contaminated water sample with dichloromethane and GC-MS analysis of obtained organic phase, the technological aqueous stream is contaminated with different chlorinated anilines and chlorinated phenols accompanied by low concentrations of chlorinated biphenyls, chlorinated azobenzene and chlorinated aminobiphenyls (see Table 6, column Ar-Cls analyzed in wastewater).

For saving the HDC reagent, Raney Al-Ni in co-action with a commercial mixture of 12 wt.% NaBH4 in 14M NaOH instead of sole NaOH was proved as the source of the base (NaOH) and as a possible co-reductant for reducing azo groups, et cetera, in reducible contaminants [5]. Using NaBH<sub>4</sub> pretreatment and subsequent Al-Ni/NaOH based HDC procedure, chlorinated aromatic compounds observed in technological water sample were removed, which is documented by GC-MS and even by significant decrease of AOX value determination. As could be seen by comparison of GC-MS spectra described in Figure S6a–e in Supplementary Materials, signals of chlorinated aromatic compounds (mainly 2,5-dichloroaniline, chlorinated biphenols, etc.) observed in technological water samples disappear with subsequent formation of non-chlorinated aromatic or alicyclic products (aniline, cyclohexylamine, phenylcyclohexanol and cyclohexylphenol) (compare the upper GC chromatogram of wastewater sample 9110VVUOS with GC chromatogram after HDC treatment (sample 1211TW, bottom trace) in Figure S6a in Supplementary Materials and subsequent data depicted in Figure S6b–e). Besides this, the chemical oxygen demand (COD) value of both starting technological and treated water is quite similar which supports the main effect of HDC process for Ar-Cls reductive removal with only minor role of adsorption on separated insoluble part (Ni and AlO(OH)). The determined

non-zero value of AOX parameter (content of total organically bound halogens) measured after HDC procedure may be caused by the presence of inorganic chlorides wide-spread in this type of wastewater in multigram quantities and influences AOX determination [32].

**Table 6.** Results of Ar-Cls contaminants HDC in wastewater obtained from production of azo pigments using Al-Ni/NaOH+NaBH<sub>4</sub>. The experimental procedure is described in Section 4.2.5. For more details see Supplementary Materials, Figure S6.

Ar-Cls Analyzed in Wastewater Sample	Conversion of HDC Reaction	Identified Products of HDC Reaction
2,5-dichloroaniline	>99%	aniline or cyclohexylamine
tetrachloroazobenzene	>99%	aniline or cyclohexylamine
trichloro-hydroxy-biphenyl	>99%	phenylcyclohexanol or
$Cl_x$ $Cl_y$ $x + y = 4$ $OH$	>99%	phenylcyclohexanol or cyclohexylphenol cyclohexylaniline
Tetrachloro-hydroxy-biphenyl Tetrachloro-amino-biphenyl	>99%	

# 3. Discussion

#### 3.1. Possible Mechanism of Tested Al Alloys HDC Action

Both studied Al alloys are able to cleave chlorine bound on aromatic carbon ( $C_{aromatic}$ -Cl) bond. The difference in the HDC action of both studied Al-alloys are abysmal, as was documented in the above-mentioned chapter. To elucidate the role of the metals represented in the studied alloys, the reaction of chlorinated benzenes with Cu and Ni was tested (Figures 7–10 and Table S2). As could be seen, hexachlorobenzene HCB is quite reactive via HDC even using in situ generated Cu or Ni through an excess of NaBH<sub>4</sub>. In the case of NiSO<sub>4</sub>/NaBH<sub>4</sub>, benzene was obtained as the dominant HDC product. Using CuSO<sub>4</sub>/NaBH<sub>4</sub> for in situ production of Cu, the HDC reaction is completed with the production of tetrachlorobenzene as the main HDC product, similarly to the Devarda's Al-Cu-Zn alloy. In contrast, the sole NaBH<sub>4</sub> is quite effective for HDC of HCB although, pentachlorobenzene is produced as the main product in this case.



**Figure 7.** The composition of reaction mixture at the end of HDC of HCB using in situ generated Cu (CuSO<sub>4</sub>/NaBH<sub>4</sub>), Ni (using NiSO<sub>4</sub>/NaBH<sub>4</sub>) and comparison of action of the sole NaBH<sub>4</sub> (for more details see Supplementary Materials, Table S2). The experimental details are described in Section 4.2.3.



**Figure 8.** The composition of reaction mixture at the end of HDC of tetrachlorobenzenes using in situ generated Cu (CuSO<sub>4</sub>/NaBH<sub>4</sub>), Ni (using NiSO<sub>4</sub>/NaBH<sub>4</sub>) and comparison of action of the sole NaBH<sub>4</sub> (for more details see Supplementary Materials, Table S2). The experimental details are described in Section 4.2.3.



**Figure 9.** The composition of reaction mixture at the end of HDC of 1,2,4-trichlorobenzene using in situ generated Cu (CuSO<sub>4</sub>/NaBH<sub>4</sub>), Ni (using NiSO<sub>4</sub>/NaBH<sub>4</sub>) and comparison of action of the sole NaBH<sub>4</sub> (for more details see Supplementary Materials, Table S2). The experimental details are described in Sections 4.2.2 and 4.2.3.



**Figure 10.** The composition of reaction mixture at the end of HDC of chlorobenzene CB using in situ generated Cu (CuSO<sub>4</sub>/NaBH<sub>4</sub>), Ni (using NiSO<sub>4</sub>/NaBH<sub>4</sub>) and comparison of action of the sole NaBH<sub>4</sub> and Al (for more details see Supplementary Materials, Table S3). The experimental details are described in Sections 4.2.2 and 4.2.3.

Tetrachlorobenzenes are quite inert if  $CuSO_4/NaBH_4$  for in situ production of Cu and possible HDC reaction was used. Only a low quantity of trichlorobenzenes was identified in the obtained reaction mixture. In addition, the role of Cu seems to be negligible because the HDC activity of CuSO<sub>4</sub>/NaBH<sub>4</sub> is practically equal to the application of the sole NaBH<sub>4</sub> (Figure 8).

1,2,4-Trichlorobenzene is converted mainly to the benzene only using NiSO<sub>4</sub>/NaBH<sub>4</sub> (Figure 9).

Chlorobenzene practically does not react with aluminum or CuSO<sub>4</sub>/NaBH<sub>4</sub> in the alkaline aqueous solution. High conversion to benzene was observed, in contrast, using NiSO<sub>4</sub>/NaBH<sub>4</sub> for in situ production of Ni (Figure 10 and Table S3 in Supplementary Materials).

The observed HDC efficiencies indicate in summary that the application of Ni is crucial for effective complete HDC of chlorinated benzenes to benzene at room temperature and ambient pressure. Application of in situ produced copper is much less effective for the subsequent HDC of HCB.

#### 3.1.1. Possible Pathway of Devarda's Al-Cu-Zn Alloy HDC Action

Interestingly, the observed Devarda's alloy mediated HDC of chlorinated benzenes (Figures 5–7) corresponded quite well with the observed Cu<sup>0</sup>-mediated dechlorination results described by Bureš et al. [33] and Gao et al. [34]. Bureš et al. and Gao et al. concluded that Cu<sup>0</sup> takes place in the HDC in the role of reactant not catalyst. A comparison of XRD results promotes this idea, Cu slurry obtained at the end of HDC is composed mostly from corresponding oxides of Cu and Al (concretely contains 24% of cuprite Cu<sub>2</sub>O, 60% of bayerite Al(OH)<sub>3</sub> and 16% of Cu<sub>0.951</sub>Zn<sub>0.049</sub>, see Figure 11d,e). Formation of Cu<sub>2</sub>O could be explained by oxidation Cu in the starting khatyrkite CuAl<sub>2</sub> with (poly)chlorobenzene (Ar-Cl) and producing CuCl by Equation (1) which is hydrolyzed to Cu<sub>2</sub>O in the alkaline aqueous solution Equation (2). Subsequent formation of bayerite Al(OH)<sub>3</sub> is based on the action of water on aluminum in a CuAl<sub>2</sub> couple according to the equations and Figure 12:

$$Ar-Cl + CuAl_2 + 6 H_2O \rightarrow CuCl + Ar-H + 2 Al(OH)_3 + 3 H_2$$
(1)

$$2 \operatorname{CuCl} + 2 \operatorname{NaOH} \rightarrow \operatorname{Cu_2O} + \operatorname{H_2O} + 2 \operatorname{NaCl}$$
(2)

The starting Devarda's alloy and its reaction products were studied by X-ray powder diffraction (see Figure 12). The crystalline phases present were determined by comparison with standards in the PDF-4+ database [35]. For multiphase samples the mass content of the individual components was calculated. Briefly after the beginning of the reaction, the original Devarda's alloy changes very slightly with content of individual phases (95% CuAl<sub>2</sub> (JCPDS No. 04-001-0923), 3% Zn (JCPDS No. 00-004-0831) and 2% Cu<sub>1.14</sub> Zn<sub>0.20</sub>Al<sub>0.66</sub> (JCPDS No. 04-010-7459) after 25 min, Figure 12b) differs slightly from Devarda's alloy (96% CuAl<sub>2</sub>, 2% Zn and 2% Cu<sub>1.14</sub> Zn<sub>0.20</sub>Al<sub>0.66</sub>). After a subsequent several minutes (40 min of action, Figure 12c), the isolated insoluble part of the original Devarda's alloy contains mainly poorly crystalline cuprite Cu<sub>2</sub>O (JCPDS No. 04-007-9767) and AlO(OH) (JCPDS No. 01-078-4587). Weak diffraction lines corresponding to Zn-Al layered hydroxide/carbonate (JCPDS No. 04-015-3264) were also observed. Originally presented khatyrkite CuAl<sub>2</sub> nearly disappeared, while the diffraction lines of the trimetallic alloy  $Cu_{1.14}Zn_{0.20}Al_{0.66}$  together with a  $Cu_{0.848}Al_{0.152}$  alloy (JCPDS No. 04-001-2629) are observable even after 60 min of reaction (Figure 12d). After the end of the reaction (Figure 12e), the isolated insoluble product contains mainly bayerite Al(OH)<sub>3</sub> (JCPDS No. 04-014-1754), cuprite and a small amount of the bimetallic Cu-Zn compound with significantly reduced Zn content (Cu<sub>0.951</sub>Zn<sub>0.049</sub>) (JCPDS No. 01-071-7928). The changes in surface morphology are documented by SEM (in Supplementary Materials, Figure S1).

Comparative experiments proved that the replacement of the Devarda's alloy with brass (Cu-Zn alloy) is not effective in the HDC process. Brass is not converted to the corresponding Cu or Zn oxides under used reaction conditions, only part of Zn (around 100 mg Zn/L) from brass is dissolved in the reaction mixture after 16 h of vigorous agitation with 1% aqueous NaOH solution contaminated with polychlorinated benzenes.



**Figure 11.** Powder X-ray diffraction patterns of commercial Devarda's Al-Cu-Zn alloy (**a**), of the used Al-Cu-Zn after 25 min of action (**b**), after 40 min (**c**), after 60 min (**d**) and at the end of HDC reaction (**e**) in 1 wt.% NaOH/HCB in  $H_2O:CH_3OH = 1:1$ .



Figure 12. Scheme of HDC mechanism using the Devarda's Al-Cu-Zn alloy (G=Cl<sub>5</sub>; *m*-NH<sub>2</sub> or *o*-NH<sub>2</sub>).

3.1.2. Possible Pathways of Raney Al-Ni Alloy HDC Action

In contrast to the Devarda's alloy action, the catalytically acting nickel from Raney Al-Ni alloy is not converted to the nickel oxides during HDC reaction and, as documented by Yang [28], the used Al-Ni alloy is principally recyclable in case either metallic aluminum in Al-Ni alloy is not consumed or if effective reductant substituting action of Al in Al-Ni alloy is added [23]. At least two reaction mechanisms are possible using Al-Ni as the HDC reagent. In most cases, Raney Al-Ni alloy in the

alkaline aqueous solution is a much more active HDC agent than the commercial Raney Ni catalyst in co-action of different reductants in the same reaction medium [18–25,28]. As mentioned by Yang et al. [28], the Al–Ni alloy is composed of a galvanic couple between the active Al anode and the stable Ni cathode after the dissolution of the Al<sub>2</sub>O<sub>3</sub> protection film by OH<sup>-</sup>. The Al surface exposed to OH<sup>-</sup>/H<sub>2</sub>O could directly provide electrons for HDC reaction of adsorbed chlorinated aromatic compounds catalyzed by Ni (Figure 13). The HDC reaction is actually in competition with H2 production caused by dissolution of Al<sup>0</sup> by action of OH<sup>-</sup>/H<sub>2</sub>O [28]. The competition between HDC reaction and H<sub>2</sub> evolution caused by oxidation of Al<sup>0</sup> in the Al-Ni alloy with H<sub>2</sub>O Equation (3) explains the higher consumption of Al-Ni than could be calculated from Equation (4) of the sole HDC reaction:

$$2 \operatorname{Al}^{0}(\operatorname{Ni}_{n}) + 6 \operatorname{H}_{2}O \rightarrow 2 \operatorname{Al}(OH)_{3} + n \operatorname{Ni}[H] + (3 - n/2) \operatorname{H}_{2}$$
 (3)

$$3 \operatorname{Ar-Cl} + 2 \operatorname{Al}^{0}(\operatorname{Ni}) + 5 \operatorname{OH}^{-} + 3 \operatorname{H}_{2}\operatorname{O} \to 3 \operatorname{Ar-H} + \operatorname{Ni} + 2 \operatorname{Al}(\operatorname{OH})_{4}^{-} + 3 \operatorname{Cl}^{-}$$
(4)



Figure 13. Scheme of HDC mechanisms using the Raney Al-Ni alloy.

The starting Raney Al-Ni alloy and its reaction products were studied by X-ray powder diffraction (see Figure 14). The crystalline phases present were determined by comparison with standards in the PDF-4+ database [36]. For multiphase samples the mass content of the individual components was calculated. The starting Raney Al-Ni alloy (see Figure 14a) contained 41% Ni<sub>2</sub>Al<sub>3</sub> (JCPDS No. 04-007-0402), 57% NiAl<sub>3</sub> (JCPDS No. 04-007-0403) and 2% aluminum (JCPDS No. 04-012-7848). Briefly after the beginning of the reaction (after 30 min, Figure 14b), the original Raney Al-Ni alloy changes relatively slightly, pure aluminum disappears and the proportion of NiAl<sub>3</sub> alloy decreases (34% NiAl<sub>3</sub>, 66% Ni<sub>2</sub>Al<sub>3</sub>). After 60 min of the reaction (Figure 14c), the NiAl<sub>3</sub> diffraction lines disappeared completely and the isolated solid products contains only Ni<sub>2</sub>Al<sub>3</sub>. At the end of HDC reaction (Figure 14d), the isolated solid contains besides the rest of Ni<sub>2</sub>Al<sub>3</sub> (18%) mainly Ni<sub>0.92</sub>Al<sub>0.08</sub> alloy (61%, JCPDS No. 04-007-0401) and pure nickel (10%, JCPDS No. 04-010-6148) and also a small amount of bunsenite (2%, JCPDS No. 04-007-0403). The changes in surface morphology are documented by SEM (in Supplementary Materials, Figure S2).

As we published earlier [22], glucose works as an inhibitor of Al on Al-Ni surface oxidation and due to this reason the addition of glucose to the mixture of Ar-Cl and Al-Ni in aqueous NaOH enables a decrease in Al-Ni consumption for HDC reaction in some cases. The probable reason is the formation of stabilized Ni(H) nanoparticles acting as HDC agents (according to Equation (3)). Interestingly, the decrease in Al-Ni consumption caused by glucose addition works in the case of Ar-Cls which are

hydrodechlorinated even by the Devarda's alloy (simply reducible Ar-Cls such as 3-chloroaniline, 2-chloroaniline). Indirect HDC reaction of Ar-Cl with gaseous hydrogen activated with the catalytically acting Ni surface is the second possible mechanism for Al-Ni based HDC. As could be seen in our work [23], this mechanism is dominant only in the case of reactive chlorinated aromatics. In the case of less reactive 4-chloroaniline, only an inhibition of the HDC reaction is observed by the addition of glucose to the Al-Ni, the minimum quantity of Al-Ni is the same as without the glucose application (Ni(H) nanoparticles are not an effective HDC agent in this case).



**Figure 14.** Powder X-ray diffraction patterns of commercial Al-Ni alloy (**a**), of the used Al-Ni alloy after 30 min in 1 wt.% NaOH/Ar-Cl (**b**), after 60 min (**c**) and at the end of HDC reaction (**d**).

#### 4. Materials and Methods

The starting chlorinated aromatic compounds were purchased from commercial sources in a defined purity higher than 98% (Sigma Aldrich Co. (Prague, Czech Republic), Alfa-Aesar Co. (Thermo Fisher Scientific, Heysham, UK), TCI Europe (N.V. Zwijndrecht, Belgium), in the case of hexachlorobenzene (HCB the solution containing 200 µg HCB/mL MeOH). The industrial sample of o-dichlorobenzene used as the recycled solvent and a sample of technological water from the production of azo pigments were obtained from a local Czech chemical factory. Both aluminum alloys (Devarda's Al-Cu-Zn and Raney Al-Ni) and deuterated chloroform (CDCl<sub>3</sub>) were purchased from Sigma-Aldrich Co. Additional chemicals and solvents in 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 closed by a tube filled with granulated charcoal.

# 4.1. Chemical Analysis

The diffraction patterns (Cu K $\alpha$ ,  $\lambda = 1.5418$  Å) were recorded on powdered samples using a D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany) with Bragg-Brentano  $\theta$ - $\theta$  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  $\theta$ ) 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 [35]. For each selected pattern, EVA adjusts the scaling factor and width parameters by fitting, and the result is transformed into concentrations using the I/Icor factors from PDF-4+ database [36].

Aqueous samples for the analysis of the volatile compounds (dichlorobenzenes (DCBs), chlorobenzene (CB), benzene (B)), were placed in 100 mL dark glass containers and filled to the brim so that there were no bubbles in the container after closing. The containers were then cooled and transported to a laboratory. The analysis of these compounds was carried out by headspace GC/MS. Following that, 6 mL of the water sample was transferred to a 10 mL vial, placed in a heating box of a headspace system and incubated at 40 °C for 10 min. Released volatile compounds were analyzed by GC/MS Thermo trace GC Ultra system equipped with Restek RtX-624 capillary column (dimensions: 60 m × 0.25 mm × 1.4  $\mu$ m). The carrier gas was ultrapure helium (99.99%) set at the constant flow mode (1.5 mL/min). The temperature program was as follows: 10 min at 40 °C, then with heat ramp 1 °C/min to 50 °C and held for 10 min. The mass spectrometer with a single quadrupole (Thermo MS Trace DSQ) was operated in the electron-impact mode at 70 eV. The quadrupole operated in the scan mode in a range of molecular weights from 50 to 650. The temperature of the ion source was set at 200 °C.

GC-MS analyses of polychlorinated benzenes (tri-, tetra-, penta- and hexachlorobenzenes) were performed using *n*-hexane extracts (20 mL for 10 mL of aqueous sample for 0.5 h). Following that, 1  $\mu$ L of hexane extract was injected in the splitless mode with the injector temperature set at 330 °C and the detector set at 340 °C.

For analyses of extractable compounds in sample of technological water stream extraction with  $CH_2Cl_2$  was performed (300 mL of waste water sample was extracted repeatedly by  $3 \times 5$  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) using 30 m capillary column HP-5MS UI (HP) (I.D. 0.25 mm, 0.25  $\mu$ m film thickness). 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 fullscan mode.

The <sup>1</sup>H (eventually <sup>19</sup>F) NMR spectra were measured using solutions in CDCl<sub>3</sub> on a Bruker Ascend 500 spectrometer (equipped with Z-gradient 5 mm TBI 500 MHz S1 probe) at frequency 500.13 MHz for <sup>1</sup>H and compared with spectra of commercial standards.

The levels of selected metals in the actual water sample were determined utilizing ICP-OES Spectrometer iCAP 7400 D (Thermo Scientific, Dreieich, Germany) equipped with a CID86 detector. The instrument was calibrated on the certified reference material AN 9090(MN) representing a mixture of metal ions stabilized in 5% HNO<sub>3</sub> (v/v.). For experiments performed with model solutions, the levels

of toxic elements before and after the adsorption were determined by atomic absorption spectroscopy (AAS) using spectrometer 240 RS/2400 (Varian, Australia).

#### 4.2. HDC Procedures

#### 4.2.1. HDC of Chlorinated Anilines and Phenols Using Studied Al Alloys

The aqueous solution (1 mM, 100 mL, 0.1 mmol) of chlorinated aniline or chlorinated phenol was mixed with Raney Al-Ni or Devarda's Al-Cu-Zn alloy (0.27 g Al-Ni or 1.5 g of the Devarda's alloy was used per mmol of  $C_{arom}$ -Cl bound chlorine) and subsequently NaOH solution (0.5 M NaOH, 100 mL) was added slowly under vigorous stirring to the obtained suspension. The reaction mixture was stirred at 500 rpm at 25 °C overnight, filtered, and the filtrates were extracted with three portions of CH<sub>2</sub>Cl<sub>2</sub> (1 × 100 mL and 2 × 50 mL). Collected CH<sub>2</sub>Cl<sub>2</sub> extracts were evaporated and nonvolatile residue was dissolved in CDCl<sub>3</sub>. <sup>1</sup>H NMR spectrum of obtainedCDCl<sub>3</sub> solution indicating the conversion of the corresponding Ar-Cls to HDC products. (Note: In case of chlorinated phenols, the obtained filtrate of the reaction mixture was acidified to pH ~2 to 3 before CH<sub>2</sub>Cl<sub>2</sub> extraction.)

#### 4.2.2. HDC of Chlorinated Benzenes Using Studied Al Alloys or Al Foil

The aqueous or mixed methanolic/aqueous solution (100 mL) of the chlorinated benzene (10  $\mu$ mol) was mixed with Raney Al-Ni or Devarda's Al-Cu-Zn alloy (0.27 g Al-Ni or 1.5 g of the Devarda's alloy (or Cu-Zn alloy (brass)), eventually 0.4 g of Al foil was used) and subsequently NaOH solution (0.5 M NaOH, 100 mL) was added slowly under vigorous stirring to the obtained suspension. The reaction mixture was stirred at 500 rpm at 25 °C overnight, decanted and analyzed using GC-MS and eventually ICP-OES. When appropriate, the insoluble part of the used Al alloy was separated by filtration, washed with 3 × 200 mL of water and dried in the air overnight in hood.

# 4.2.3. HDC of Chlorinated Benzenes Using in Situ Generated Cu or Ni

The NaBH<sub>4</sub> aqueous solution (100 mM NaBH<sub>4</sub> in 10 mM NaOH, 50 mL) was added dropwise under vigorous stirring to the aqueous solution of CuSO<sub>4</sub> or NiSO<sub>4</sub> (40 mM, 50 mL). After completion of hydrogen liberation, the aqueous or mixed methanolic/aqueous solution of corresponding chlorinated benzene (100 mL, 10  $\mu$ mol) was added. The reaction mixture was stirred at 500 rpm at 25 °C overnight, decanted and analyzed using GC-MS.

# 4.2.4. HDC Kinetic Experiments Using Raney Al-Ni Alloy

Subsequently, the same quantity (1 mmol) of every dichloro- or trichlorobenzene isomer was dissolved in 1 L of methanol and mixed with 5.4 g of Al-Ni alloy. Subsequently, 1 L of 0.6 M aqueous NaOH solution was added under vigorous stirring and 50 mL portions of samples in appropriate time intervals were collected sequentially and analyzed by GC-MS.

The observed rate constants ( $k_{obs}$ ) for removal of Ar-Cls were evaluated based on non-linear regression analysis using GraphPad Prism 7.05. The time dependences of concentration were fitted to the first order kinetic model. Coefficient determination ( $R^2$ ) and absolute sum of squares (ASS) of residues were chosen as a criterion for assessing of quality of the fit.

#### 4.2.5. HDC of Real Wastewater Sample

A sample of technological water (1 L) produced in azo pigments manufacturing facility (chemical oxygen demand determined by chromate method using Hach cuvette tests LCK 514, COD = 710 mg  $O_2/L$ , content of adsorbable organically bound halogens AOX = 27.8 mg Cl/L, content of individual chlorinated aromatic compounds is mentioned in Table 6) was mixed with 2.7 g of Al-Ni alloy and 28 g (20 mL) of commercial aqueous 12 wt.% NaBH<sub>4</sub> in 14 M NaOH was added dropwise under vigorous stirring over 2 h. Subsequently, the obtained foaming suspension was agitated for 4 h. The obtained suspension was decanted, filtered and analyzed by GC-MS (see Supplementary Materials,

Figure S6a–e), ICP-OES and AOX. The measured values were AOX = 1.3 mg Cl/L and the content of Al 1268 mg Al/L and Ni less than 0.05 mg Ni/L. The organic compounds determined in the aqueous phase are summarized in Table 3. Subsequent neutralization of the treated aqueous phase using 36 wt.%  $H_2SO_4$  was accompanied by coagulation of AlO(OH). In the subsequently obtained filtrates COD and content of metals were measured, COD = 668 mg O<sub>2</sub>/L and content of Al and Ni were below Al: 0.5 mg Al/L and Ni: below 0.05 mg Ni/L.

#### 5. Conclusions

In conclusion, simply commercially available Cu- and Ni-based Al alloys produced in multiton amounts for application in the chemical industry were tested and compared for a new application in the area of HDC-based detoxification of common chlorinated aromatic aqueous contaminants.

The HDC activity of both Devarda's Al-Cu-Zn and Raney Al-Ni alloys was compared at room temperature and ambient pressure at pH above 12 caused by the addition of a diluted aqueous NaOH solution. The mentioned reaction conditions (ambient pressure and room temperature) were chosen due to environmental reasons as most economical to the energy supply projected for this technique for waste water treatment.

We demonstrated that the Devarda's alloy is an effective HDC agent only in the case of highly chlorinated hexa- and pentachlorobenzene and pentachlorophenol; however, even in this case only less chlorinated aromates are produced.

Apart from these chlorinated aromatics the Devarda's alloy is also a quite efficient HDC reagent for dechlorination of *m*- and *o*-chloroanilines. The results correspond well with the very limited HDC activity of copper demonstrated in the set of experiments using polychlorinated benzenes. Using the Devarda's alloy in the alkaline aqueous solution, Al, Zn and Cu are mainly converted to the corresponding (hydr)oxides and due to this reason Devarda's Al-Cu-Zn alloy cannot be directly reused in the subsequent HDC step.

In contrast to the above-mentioned Devarda's Al-Cu-Zn alloy, the Raney Al-Ni alloy is a universal, robust and very effective HDC agent for converting all the tested (poly)chlorinated aromatic compounds to the corresponding completely dechlorinated products. Using in situ generated Cu<sup>0</sup> and Ni<sup>0</sup> metals, we proved in the case of polychlorinated benzenes, that the action of Ni<sup>0</sup> is essential for effective HDC. It is in sound agreement with the observation of other research groups that the action of metallic nickel is crucial for effective HDC when platinum metals were not used [4,5]. The uncoverable catalytic role, of even slight nickel concentrations in zero-valent iron mediated HDC, was emphasized by Balda and Kopinke in recent work [37]. Our results, based on a comparison of HDC activity of Cu, Ni and Al, are in sound agreement with reference [37] because only nickel generated in situ from NiSO<sub>4</sub>/NaBH<sub>4</sub> is able to HDC of chlorobenzene to benzene.

We demonstrated, in contrast, that as late as alloying of aluminum with Ni<sup>0</sup> produces Raney Al-Ni alloy with powerful HDC activity even used in low excess for a broad spectrum of Ar-Cls even at room temperature and ambient pressure in the diluted aqueous NaOH solution, as could be seen from the high values of the observed rate constants for HDC of studied trichlorobenzenes, dichlorobenzenes and anilines.

The HDC reaction caused by Raney Al-Ni is accompanied by a reduction in other reducible (azo, carbonyl, etc.) groups. For this reason, application of another reduction agent could be useful for saving the HDC reagent [5]. Additionally, in HDC of an actual wastewater sample using the RaneyAl-Ni alloy, the addition of a commercial aqueous solution of NaBH<sub>4</sub> in NaOH as the co-reductant and source of NaOH was demonstrated as an effective treatment of the mixture of polychlorinated contaminants occurring in technological water produced at the azo pigments production site.

After the HDC reaction, the dissolved aluminum together with the appropriate Ni contamination and part of the dechlorination products are efficiently removed by neutralization and removal of insoluble Al(OH)<sub>3</sub>.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2073-4344/10/9/994/s1, Table S1: Composition of the reaction mixtures obtained by overnight action of 1.5 g the Dev. alloy and 2 g NaOH in 200 mL of aqueous (or 1:1 CH<sub>3</sub>OH:H<sub>2</sub>O) solution.; Table S2: Composition of the reaction mixtures obtained by overnight action of 5 mmol NaBH<sub>4</sub> and eventually 2 mmol of CuSO<sub>4</sub> or NiSO<sub>4</sub> on 50 µmol of corresponding chlorinated benzene in 200 mL solution of CH<sub>3</sub>OH:H<sub>2</sub>O = 1:1.; Table S3: Composition of the reaction mixtures obtained by overnight action of 5 mmol NaBH<sub>4</sub> and eventually 2 mmol of CuSO<sub>4</sub> or NiSO<sub>4</sub> or NiSO<sub>4</sub> on 0.1 mmol of chlorobenzene (CB) in 200 mL aqueous solution.; Figure S1. SEM images of Devarda's Al-Cu-Zn used in HDC process at 2000× magnification; Figure S2. SEM images of Raney Al-Ni alloy used in HDC process at 10,000× magnification. Figure S3. Time dependences for HDC of Cl-ANs using the Raney Al-Ni alloy with and without addition of glucose. Figure S4. Time dependences for HDC of triCBs using the Raney Al-Ni alloy. Figure S5. Time dependences for HDC of DCBs using the Raney Al-Ni alloy. Figure S6. GC/MS analysis of DCM extract of sample 8110VVUOS (technological water produced at the azo pigments production site)—upper trace and sample 1112TW (after HDC treatment)—bottom trace and MS spectra.

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

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