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Effect of mechanical activation and thermal processing of Al-Ni mixtures on
hydrodehalogenation of AOX dissolved in aqueous solutions

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Abstract

The presented thesis deals with the possibility of the application of mechanically activated metal mixtures (aluminum and nickel), and their thermally processed products, for the reductive degradation of halogenated aromatic compounds from an aqueous environment. Mechanical activation is a process, in which the compounds are activated by ball milling, mainly due to an increase in a specific surface and the formation of various defects in their crystal structure. Thermally treated activated Al/Ni mixtures, retaining the features of mechanically activated materials, may provide a significant decrease in the total costs of reductive dehalogenation process for studied compounds in comparison with the commercially available Al-Ni alloys; such as the 50:50 wt.% Al:Ni Raney-type alloy. Materials prepared via this way, due to their unique structural properties, provide fast dehalogenation kinetics accompanied with high removal efficiency. The process of hydrodehalogenation, in general, is a robust method for removal of halogenated compounds from an aqueous environment at ambient conditions. In basic environment of sodium hydroxide, various halogenated contaminants (preferably brominated or chlorinated) have been shown to be completely degraded upon the action of Al-Ni alloys.

Abstrakt

Předkládaná práce se zabývá možností aplikace mechanicky aktivovaných směsí neušlechtilého kovu (konkrétně hliníku) a hydrogenačního katalyzátoru (niklu) pro hydrodehalogenační odbourávání aromatických halogenovaných látek z kontaminovaných vod. Mechanická aktivace představuje časově a ekonomicky nenáročný proces, při kterém dochází mletím k aktivaci kovů, hlavně vlivem zvětšování specifického povrchu i vznikem různých defektů v jejich krystalové struktuře. Termicky upravené aktivované směsi Al/Ni mohou několikanásobně snížit celkové náklady na reduktivní dehalogenaci studovaných halogenovaných aromatických sloučenin oproti doposud využívané komerčně dostupné Raney slitině (50:50 wt.% Al:Ni). Materiály připravené touto cestou, díky jejich výjimečným strukturním vlastnostem, poskytují rychlou dehalogenaci spojenou s vysokou účinností odstranění kontaminantů. Proces hydrodehalogenace je ve všeobecnosti robustní metodou na odstranění širokého spektra kontaminantů (převážně bromovaných a chlórovaných) za běžných reakčních podmínek.

Keywords

mechanical activation, binary Al-Ni alloys, Raney nickel, reductive dehalogenation, pollutants removal

Klíčová slova

mechanická aktivace, binární slitiny Al-Ni, Raney nikl, redukční dehalogenace, odstraňování polutantů

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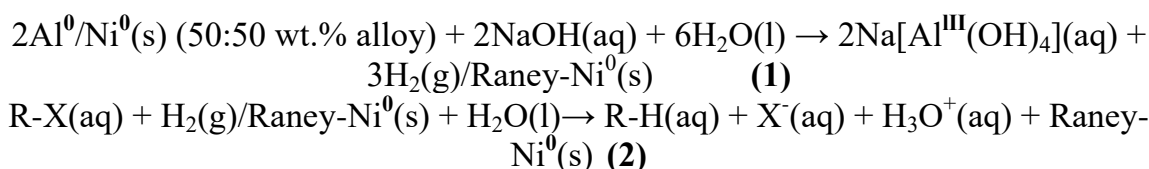
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1 Introduction

Organic halogenated aromatics represent a large group of chemical substances that were vastly produced and used in the 20th century, mostly as solvents, dyestuffs, pigments, flame retardants, biocides, pesticides, or medical drugs. Their production was many times connected to a leakage of unreacted starting materials or side products into waste- or groundwater, where they are still found due to their low biodegradability and high chemical stability of C-X bond (X = F, Cl, Br, I). Since most of the halogenated organic compounds are classified as persistent organic pollutants (POPs) that can bioaccumulate in the environment and cause harm to living organisms, their production has been eliminated or at least restricted (e.g. Stockholm convention on persistent organic pollutants [1]). Still, there are more than 300 000 sites contaminated sites in the European Union, out of which around 10% is reported to be contaminated by chlorinated organics [2].

Numerous methods for the degradation of halogenated organics have been developed over the years. Whereas, in the case of simple aliphatic halogenated compounds (e.g. chlorinated ethylenes), the oxidative dehalogenation was found to provide promising results, it showed only limited efficiency for halogenated aromatics degradation. Generally, the oxidation route is exhaustive because the C-H and C-C bonds are much more prone to oxidation. Thus, a large excess of oxidizing agents is needed for the oxidation of organics down to inorganic products till organically bound halogen atoms are finally removed and transformed into inorganic halogenides. On the other hand, reductive methods are more selective to C-X bond cleavage. In the process, organically bound halogens are subsequently substituted with hydrogen atoms. Most of the times, catalysts based on precious metals have been utilized under high temperature and pressures [3]. Other, more economically feasible solutions have been provided, too. These included metal sodium/potassium reduction or usage of strong reducing agents (e. g. NaBH_4 , N_2H_4). All of the mentioned processes are, however, technologically demanding. Thus, the focus of interest has turn to more simple alternatives. Zero-valent iron nanoparticles or their nanocomposites with Ni or Pd [4–6] have proved to be efficient dehalogenation reagents. Several studies were published also on supported Pd/Pt catalysts at ambient conditions. While the catalyst showed acceptable removal rates and total removal of contaminants, it was found that a number of life cycles is relatively low and only low levels of contaminants were tested.

A hydrodehalogenation reaction (HDH) using Al-Ni alloy (50:50 wt.% Al-Ni) has been found as one of the most efficient and cost-effective methods for removal of a broad range of organic halogenated pollutants from an aqueous environment [7–12] (Table 1). The mechanism of the reaction itself has not been described explicitly till now. Depending on the conditions and the compound being eliminated, it may slightly differ. It was found that the reductive strength of the alloy is even higher in dilute NaOH solutions, capable of reducing aromatics [13], or in specific cases cleaving the C-C bond [14], as well. In general, aluminum is leached out of alloy in basic environment followed by hydrogen gas evolution (equation 1) and the formation of the porous Raney Ni catalyst with a high surface area on which the hydrogenation reaction takes place in the next step (equation 2). The alloy then acts both as a reagent and a source of catalyst. After the reaction, the halogen atoms stay in the solution in a form of inorganic halides.



Moreover, the alloy is easy to handle and widely used for the preparation of the Raney Ni catalyst. Compared to financially demanding heterogeneous catalysts based on precious metals (Pd, Pt, Rh), no special apparatus is needed for the HDH reaction and it can be performed at room temperature and atmospheric pressure. The alloy is as well an air-stable material and thus overcomes the storage problems of the Raney nickel or n-ZVI iron. Its utilization in a basic environment also excludes the leaching of toxic nickel metal.

Table 1. A brief overview of up-to-date published papers on the HDH reaction of aromatic pollutants utilizing the Raney Al-Ni alloy.

Compound	Al:substrate molar eq.	Temperature (°C)	Time (h)	Reference
Monochlorobiphenyl	4-40	60-90	2-8	[13]
TBBPA	18-46	90	4-8	[14]
TBBPA, TCBPA	9.5-46	60-90	5-8	[15]
X-PhOH	5-18.5	90	4-6	[16]
XAN	5-15	25	17	[17]
XAN	2.5-5	25	17	[8]
TBP	3-5	25	16	[9]
Triclosan, Chlorophene	4-20	25	o/n	[11]
2-CP	100-1500	25	1	[18]
2-CP	500	25	0.75	[19]
Cl-B	480	25	o/n	[20]

TBBPA = tribromobisphenol A, TCBPA = trichlorobisphenol A, X-PhOH = halogenated phenols, XAN = halogenated aniline, TBP = tribromophenol, 2-CP = 2-chlorophenol, Cl-B = chlorinated benzenes; o/n = overnight

Despite the mentioned positives, several negative points such as a high excess of aluminum to substrate molar ratio, elevated temperatures, or long reaction times were reported previously for the complete dehalogenation of contaminants; utilizing the Raney-type Al-Ni alloys. But the major drawback of the technology is the cost of the Al-Ni alloy prepared via the metallurgical route, which requires working with high temperatures and molten metals. Moreover, crushing of ingots must be then utilized to isolate the alloy in a form of powder. Therefore, the potential large-scale applicability of the Al-Ni alloys is for now economically unfavorable; especially in the case of low contaminated waters.

1.1 Chlorinated organics as emerging contaminants

Chlorinated organic pollutants represent a wide range of chemical entities; out of which, the majority are classified as persistent organic pollutants (POPs). POPs, in general, are organic compounds, which to various degrees resist degradation (photolytic, biological or chemical). Along with chlorinated hydrocarbons, polycyclic

aromatic hydrocarbons (PAHs) and all other halogenated organic compounds (fluorinated and brominated), which are also classified as POPs [3]. The chlorinated organic pollutants can be further divided into three main categories; depending on their structure:

- a) aliphatic (chlorinated methanes and ethanes; with relatively short half-lives)
- b) aromatic (chlorinated anilines, benzenes, chlorophenols, benzoic acids, biphenyls, dioxins, furans, etc.)
- c) polycyclic (chlorinated PAHs; formed as byproducts of combustion processes) [21, 22].

Even though some of the chlorinated organic pollutants can emerge from natural sources, e.g. metabolites of polychaete species [23], mostly they originate entirely from anthropogenic activity (targeted or unintentional emission). The sum parameter characterizing the level of organically bound halogen atoms present in soil or water matrix is called AOX (adsorbable organic halides) and is usually given in mg/L [24].

The measure of POPs persistence in the environment is usually defined as a time needed to break down the compound into a less hazardous one (or the one more prone to degradation). In the case of POPs, half-lives ($t_{1/2}$) are usually 6 months and more.

There are however two other factors, which add more emphasis to the early detection and tracking of POPs. Mostly, POPs have low water solubility and are highly lipophilic (preferably dissolve in fats and lipids), which can lead to their bioaccumulation in fats. This tendency causes bioconcentration of the compounds and finally its biomagnification up through the food chain. The phenomena of bioconcentration and biomagnification result in the highest exposure to the organisms at the top of the food chain.

Moreover, some of these compounds (especially the higher halogenated congeners) might be semi-volatile, which allows them to be transported for long distances due to significantly increased mobility. Long-range transport of the chemicals is mediated by the atmosphere as the primary medium. Volatilization is supported via surface use of the chemicals (pesticides on plants and soil) and is highly dependent on a number of meteorological parameters such as temperature and vapor pressure. Thus, these substances may volatilize from hot areas and will condense and tend to remain in colder regions.

Short-term exposure of a living organism to high concentrations of POPs may result in acute illness or in some cases to death. Long-term exposure to POPs may also be associated with a wide range of adverse health and environmental effects. Investigation on the environmental impact of POPs revealed that they might be involved with such phenomena as endocrine disruption, immune and reproduction system dysfunction, neurobehavioral and development disorders [25].

The chlorinated organic compounds are historically important compounds with many applications as starting reagents, solvents, or intermediates in organic chemistry or other industries [3]. They have proven to be most resistant to degradation and have had the widest production, use and release characteristics of all halogenated hydrocarbons. Historically, trichloroacetaldehyde was one of the first organochlorines to be synthesized in 1832. This was later on used as a key reagent in the production of strong insecticide 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane, known as DDT.

During the world wars, chlorine-based toxic gases, such as chloropicrine (CCl_3NO_2), diphosgene (ClCOOCCl_3), and phosgene (COCl_2) were developed and used in large quantities. This was accompanied by the production of chlorinated benzenes started in 1909 in England and was rapidly increased during World War I. Back then, chlorinated benzenes were used as intermediate products to phenols; used as explosives. This group of halogenated aromatic substances is represented by 12 individual compounds out of which a few have become of great industrial importance [26]. There exist no natural sources of these compounds and their occurrence in nature is therefore exclusively connected with industrial production. Monochlorobenzene is widely used in the manufacture of pesticides, and as an intermediate compound to other chemicals. Even though its production in the US has declined, it is still listed as a high-volume chemical (over 450,000 kg annually by 2012). Other higher chlorinated benzenes, such as 1,2,4-trichlorobenzene, penta- or hexachlorobenzenes were mostly used as lubricants, decreasing agents or intermediate compounds in herbicide production. Acyclic short-chain organic halides have been widely used as solvents or degreasing agents; the principal representatives being the chlorinated solvents methylene chloride, tetrachloroethylene, and trichloroethylene. In the 1940s early organochlorine pesticides usually with cyclodiene-type or cyclonorbornane type structures emerged. To mention a few, aldrin, dieldrin, heptachlor, chlordane, or lindane were produced in vast quantities. Despite being later on identified as serious harm to humans, they also helped to save millions of lives. For example, in some countries, DDT is still used to control the mosquito population.

In contrast to the aforementioned chemicals, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin is considered to be “*the most toxic man-made chemical*”; being more toxic than strychnine or sodium cyanide. Also, it is the most potent cancer promoter known. Chlorinated dioxins and furans are generated in the combustion process of municipal or chemical waste. 2,3,7,8-TCDD was also present as an impurity in the production of a defoliating agent so-called Agent Orange during the Vietnam war and led to severe health issues in soldiers.

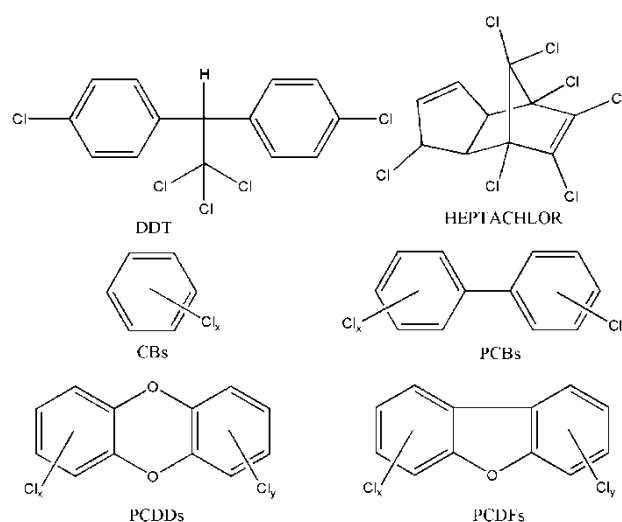


Figure 1. The structures of the two selected organochlorine pesticides (DDT and Heptachlor) and general structures of the most common organochlorine aromatic pollutants.

Among others, during the interwar decades, polychlorinated biphenyls were created. Polychlorinated biphenyls are represented by a group of 209 congeners containing diphenyl core, to which 1-10 chlorine atoms are attached. The congeners substituted at the 3,4-ortho- positions were found to be the most toxic. Their physical properties depend mostly on a degree of chlorination and cannot be generalized. Due to their excellent properties, such as high thermal stability, non-flammability, high electrical resistivity, and dielectric constant it found world-wide use as oil in capacitors or dielectric in capacitors [27]. Their acute toxicity is low (0.5 g/kg to 11.3 g/kg of body weight) and most of the effects result in chronic exposure to the PCBs. As for chlorinated benzenes, no natural source of PCBs is known. In the 1970s, due to evidence of adverse environmental effects, their production was gradually stopped. Chlorobenzoic acids (CBAs) represent a newly emerging class of POPs, which can be released to the environment from various sources. For example, 2,3,6-trichlorobenzoic acid (TCBA or *trysben*) or 3,6-dichloro-2-methoxybenzoic acid (*dicamba*) have been widely used as herbicides (synthetic auxins) in agriculture [28, 29]. Other CBAs can be formed by microbial degradation of higher chlorinated congeners, by the degradation of various pharmaceutical compounds (e. g. indomethacin, bupropion), or as the final products of degradation of other chemicals; such as polychlorinated biphenyls or DDT [30]. In many cases, 4-chlorobenzoic acid has been identified as the intermediate or the final product of the degradation of these substances; as in the degradation pathway of indomethacin. It was reported that some CBAs can persist in soils from months up to several years [31, 32], and can be found in effluent waters or groundwater. Especially, TCBA (Figure 2) was found to persist in upper parts soils for prolonged period of time [33].

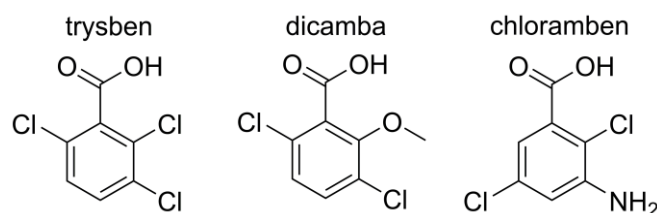


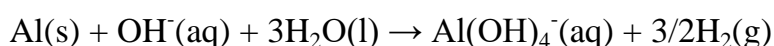
Figure 2. Chemical structures of pesticides under investigation - 2,3,6-TCBA (*trysben*), 3,6-dichloro-2-methoxybenzoic acid (*dicamba*), and 3-Amino-2,5-dichlorobenzoic acid (*chloramben*).

1.2 Principle of the proposed technology

The proposed HDH technology is based on catalytic heterogeneous hydrogenation on a surface of the Raney-Ni catalyst, which is produced *in-situ* during the reaction. The Raney nickel is a much-employed hydrogenation catalyst and it represents a cheap alternative to Pd and Pt catalysts. It can be prepared easily from Raney Al-Ni alloy (typically Al-Ni 50:50 wt%) by leaching out aluminum and washing the catalyst to remove alkali. The main phases for the preparation of Raney nickel are:

1. pyrometallurgical preparation of Al-Ni alloy by addition of nickel into molten aluminum
2. pulverization of produced alloy ingots to obtain powdered materials
3. extraction of aluminum in alkaline medium at elevated temperature
4. washing and storing of the catalyst.

The properties of the Raney nickel depend on the conditions such as duration of leaching, temperature, and alkali concentration [34]. The Al leaching step can be written as



The main difference between conventional hydrogenation reactions and the proposed HDH technology lies in the use of hydrogen gas being evolved during the leaching step (Figure 3). As the Raney-Ni catalyst is being generated *in-situ* during the leaching, evolved hydrogen gas can be immediately used for HDH reaction with contaminant already present in alkaline aqueous medium. Up to our best knowledge, no efforts have been carried out globally to implement this technology; even though our group has published several papers on the topic [8, 10–12, 35]. The technology itself being low-cost however still has some drawbacks:

1. Excess of alkali is needed to effectively leach out aluminum out of the commercial samples of 50:50 wt.% Raney Al-Ni alloy.
2. Alkali needs to be neutralized after the reaction is done, which leads to the formation of a large amount of salt.
3. Pre-treatment of water is needed if it contains easily reduced compounds (i.e. unsaturated C=C bonds) or catalytic poisons.

Moreover, the preparation of alloys from the Al-Ni binary system is an energetically/technologically demanding task due to the relatively high melting point of elemental aluminum and the exothermic character of the reaction. Typically, all of the mentioned intermetallics are prepared by pyrometallurgical methods. As published before, this obstacle can be overcome by mechanical alloying [36]. Mechanical alloying is a ball-milling process where a powder mixture placed in the ball mill is subjected to high energetic collisions from the balls [37, 38]. The process does not differ from mechanical activation but is mostly connected with metallic or ceramic powders [39]. Besides the common processes for the preparation of alloys, this represents an alternative, which came into attention during the 1970s. The two most important events are repeated welding and fracturing of the material. The mechanical alloying can be continued only if the rate of one event balances the other one and the average particle size stays relatively coarse. From the viewpoint of microstructure evolution, the mechanical alloying can be further divided into four stages:

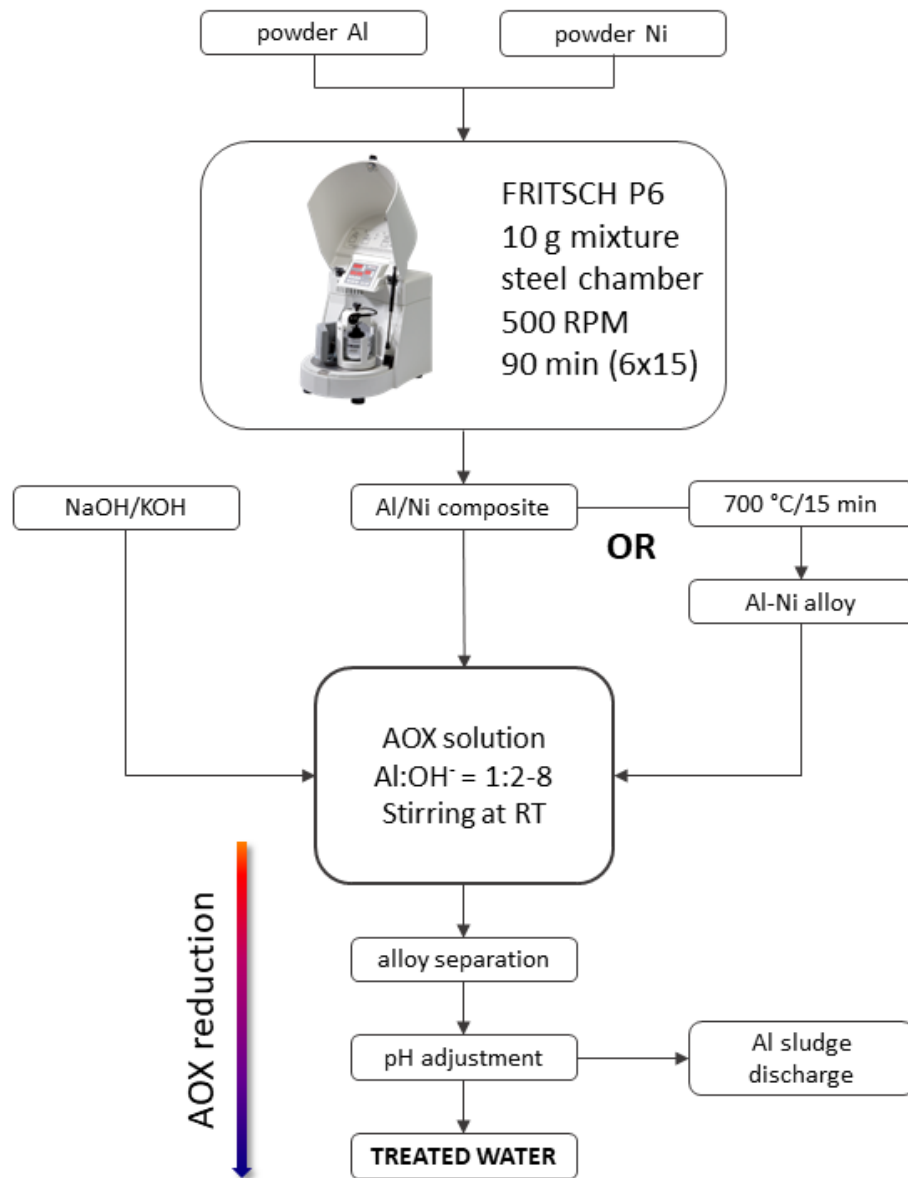


Figure 3. Schematic representation of the proposed hydrodehalogenation technology utilizing the ball-milled samples or mechano-thermally prepared alloy materials (scheme for 50:50 wt.% Al-Ni).

a) *Initial stage* – during the initial stage, powders particles are usually flattened by compression forces due to the collisions of the balls. Almost no welding can be observed at this stage, only particle shape changes because of micro-forging. For ductile-ductile system, layered structure with separation between the two different elements can be observed as well. For very short duration of milling, large variations in composition, particle size, and shape might be found. For ductile-brittle systems, the hard particles usually remain untouched and the ductile particles act as a binding agent to form agglomerates.

b) *Intermediate stage* – increasing the milling time, significant changes are observed. Cold welding becomes dominant and greater plastic deformations lead to the formation of pronounced layered structures. Fracturing appears which is indicated by the random orientation of lamellae and their thickness is decreased. Even though, dissolution might have appeared, the powder is not homogenous.

c) *Final stage* – in the final stage, no layering is observed anymore and the material becomes homogenous even at micro-scale. The formation of the true alloy can have already taken place. Homogeneity of the prepared material is an outcome of the balance between fracturing and cold welding. The particle size is also the result of the balance of the forces that cold weld particles together and the forces required to fracture them. Depending on the system, crystallite size can reach nanometric size.

c) *Completion stage* – extremely deformed metastable structure is formed, real alloy is formed.

Several works on the topic of the Al-Ni alloys have been published in the past. Due to a highly negative mix enthalpy of Al-Ni (-71 kJ/mol at 298 K), preparation of β -AlNi via ball milling should be accompanied by an abrupt increase in temperature after short milling. Before this reaction takes place, layered Al and Ni layer should be observed because of the low diffusion coefficient between the two metals. No gradual formation of the compound is observed and this also proves why the formation of another intermetallic compound from the Al-Ni system is not detected. The crystallization of Al_3Ni or Al_3Ni_2 phases is hindered by the fact that at a given composition these rapidly recrystallize to β -AlNi. Another explanation could be that the reaction enthalpy is the largest for β -AlNi phase. In the work of Atzmon et al. [40], an explosive character of the equimolar Al-Ni reaction was proven upon milling for only 120 mins. A thorough explanation of the reaction mechanism was proposed. The alloy is thought to be melted in the process of explosion and solidified on cooling. Another paper of Cardellini [41] demonstrated the preparation of the very same phase with slightly changed milling conditions in 3 hours confirming the explosive character under defined conditions. The utilization of mixer mill SPEX 8000 must be emphasized. Up to our knowledge, the mechanical alloying using another type of mill was done by Rafiei [42] but many parameters of milling are not provided (milling chamber volume, ball size), which is the main drawback of many published papers. Also, there was a paper published by Naeem, who reported successful preparation of β -AlNi phase after 4 hours of milling in the planetary ball mill Fritsch Pulverisette 5. [43]. Several other papers were published on mechanical alloying of AlNi_3 phase, which are however not of particular interest for the hydrodehalogenation application.

Likewise, the strategy proposed within this thesis utilizes mechanochemical activation of the Al-Ni mixtures. Mechanical activation of the metal mixture leads to enlargement of the active surface area and provides close contact/interdiffusion of metal particles. Thus, the materials can be processed at considerably lower temperatures, yielding the same alloys as the ones prepared via the pyrometallurgical way. This approach leads to a dramatic cut down on overall technology costs because it eliminates a need for high-temperature pyrometallurgical preparation of Al-Ni alloys. According to the analyses, the mixture rapidly reacts to form an alloy, which in turn provides even higher hydrodehalogenation efficiency than commercial products as will be discussed below in the experimental part. Moreover, after aluminum is leached out, the remaining nickel powder can be easily separated by magnets and regenerated.

2 Objectives of the thesis

The main objective of the present thesis is to further develop and optimize the hydrodehalogenation technology based on the reduction of halogenated organics using the Al-Ni alloys. This technology for degradation of a vast spectrum of halogenated organic compounds had been suggested back in the 1990s and since then it had been mostly overlooked by scientists. Even though it provides a cheaper solution than most of the precious metal-based catalysts and its realization does not require high pressures, temperatures, or complicated technological devices, it still possesses several disadvantages. First, utilization of aluminum must be increased because only a fraction of the metal is leached during the reaction. Second, as the Raney Al-Ni alloy acts both as a reagent and a catalyst, the way for its recycling and re-use must be developed; its market price is too high for a single-use operation. Therefore the work focuses on the reduction of the technology by the optimization of the Raney Al-Ni alloy solid-state preparation/properties and by possible scheme for its recycling. Below, a list of the partial tasks to achieve this is given:

- preparation of intermetallic phases from Al-Ni binary system, namely Al_3Ni and Al_3Ni_2 phases (or their mixture), via mechanical activation followed by subsequent thermal processing
- characterization of the prepared materials by common analytical techniques for solid-state materials characterization, such as X-ray diffractometry, scanning electron microscopy, particle size distribution, etc.
- demonstrate robustness and applicability of the HDH reaction using Al-Ni alloys
- test prepared materials for their hydrodehalogenation properties on the model solution of chlorinated contaminants
- demonstration of scale-up experiment with the selected organic pollutant
- scheme out the possible way for material regeneration and reuse via ball milling technique.

3 Experimental

3.1 Materials and methods

3.1.1 Chemicals and reagents

All chemicals were bought and used without further purification. The powdered metals (aluminum and nickel) were obtained from Fichema company (Czech republic) in technical grade purity (98+%). The commercial samples of 50:50 wt.% Al-Ni alloy (Sigma-Aldrich, Germany, mesh 300) and Al_3Ni phase (American elements, USA, mesh 150) were also purchased for comparison with the in-house prepared materials. Halogenated aromatic compounds used within the thesis were obtained from different suppliers and are listed in the table below (Table 4) along with their basic physic-chemical properties.

3.1.2 Mechanical activation of Al-Ni mixtures and thermal processing

A mixture of powdered elemental aluminum and nickel in corresponding weight ratio (either 50:50 or 58:42 Al-Ni wt.%) was co-milled in a Fritsch Pulverisette 6 planetary ball mill at 500 rpm in argon atmosphere at ambient temperature for different times. A milling chamber (250 cm³ in volume) and balls (10 mm in diameter) made of hardened steel were used. The ball-to-powder ratio was set to 10:1. Small amount of methanol or stearic acid (1-5 wt.%) was used as a process control agent (PCA) in order to avoid extensive cold welding of the material. The milling chambers were let overnight to cool down to room temperature before opening. Pre-milled metal mixtures were further processed by annealing either in air or under argon atmosphere for 15 minutes in alumina crucibles at either 500 °C or 700 °C. A tube furnace equipped with quartz glass tube was used.

3.1.3 Hydrodehalogenation of halogenated organics

Each of the laboratory experiments was carried out at ambient temperature using 100/250/500 ml Erlenmeyer flask enclosed by a drying tube filled up with 5 grams of granulated active carbon. Constant stirring was maintained during the reaction process. Typically, freshly prepared aqueous solution containing desired concentration of the studied contaminant was placed into the flask. Then, sodium hydroxide either in a form of solid or a solution was added and the resulting mixture was homogenized by stirring for 5 minutes. To this mixture, different amounts of the commercial Al-Ni 50-50 wt.% alloy, Al-Ni ball-milled mixtures, or mechano-thermally prepared alloys (of 50:50 wt.% Al-Ni or 58:42 wt.% Al-Ni) were added. The reaction mixtures were sampled through 0.45 µm nylon filters and acidified by concentrated nitric acid to prevent aluminum precipitation for ICP-OES analysis.

3.1.4 Analytical techniques

3.1.4.1 Characterization of the ball-milled metal mixtures and alloys

The qualitative identification of the alloys phase composition was performed by *X-ray powder diffraction (XRPD)* method with an Panalytical Empyrean diffractometer (Malvern Panalytical, UK) working in the Bragg - Brentano geometry Cu K_{α1,2} with doublet radiation. Rietveld refinements of the XRD data were performed using the *Fullprof* program. The XRD line broadening was analyzed by the refinement of regular Thompson-Cox-Hastings function parameters. In order to obtain proper geometry set-up and to eliminate instrumental broadening the instrumental resolution function was determined by refinement of LaB₆ standard specimen. The morphology of the samples was studied via *Scanning electron microscopy (SEM)*. SEM images of the samples were recorded using a MIRA 3 FE-SEM microscope (TESCAN, Czech Republic) equipped with EDX detector (Oxford Instrument, UK). Thermal behavior of ball-milled mixtures was studied via *difference scanning calorimetry (DSC)*. The measurements were carried out using a STA 449 Jupiter thermal analyzer (Netzsch, Germany). Approximately 85 mg of the sample was placed into an Al₂O₃ crucible and heated from ambient temperature °C up to 700 °C under argon atmosphere with a rate of 30 K/min. *The particle size distribution (PSD)* of the alloys was determined with the use of Malvern Mastersizer 3000 (Malvern Panalytical, UK). Demineralized water

and IGEPAL CA-630 as a dispersant were used. The sample was directly added into dispersion unit with stirring set up to 2,800 rpm and internal sonication with intensity 80% for 60 s was applied on sample before measurement. The Fraunhofer calculation model was used for evaluation of the final PSD from raw data. The analysis of *specific surface area (SSA)* was performed with the use of gas sorption analyzer Quantachrome Autosorb iQ. Each sample was degassed at 250°C for at least 240 min and subsequently the adsorption isotherm (11 equidistant points in range 0.05-0.30 p/p₀) of N₂ at 77 K was measured. The Brunauer-Emmett-Teller (BET) theory was used for determination of SSA.

3.1.4.2 Analysis of the water samples

The levels of selected compounds were determined by *high-performance liquid chromatography (HPLC)* using the Shimadzu Prominence HPLC (Shimadzu, Japan) machine equipped with a UV-Vis 2-channel detector and the Gemini C6-phenyl 3 μm 100 x 3 mm chromatographic column (Phenomenex, USA) at a flowrate of 1 mL/min. 0.1% aqueous solution of phosphoric acid (solvent A) and acetonitrile (solvent B) were used as mobile phases. Analyses were performed at room temperature (24-25 °C) with pre-defined injection volume of 1.3 μL. The compounds were detected at 230 nm. The calibration was performed in the range of 0-1 mmol/dm³. The *AOX (Adsorbable organic halides) level* was determined using AOX XPlorer analyser (TE Instruments, Netherlands). The samples for measurement were prepared by adsorption of contaminants on active charcoal at pH 2 for 1 hour and washing with 25 mL 0.01M sodium nitrate solution. The sample sorbed on the charcoal is subsequently burned in an oven at 1000 °C followed by evolution of HX gases which are trapped in the titration cell by a reaction with acetic acid. The amount of halogenides was determined by coulometric titration with standardized AgNO₃ solution. The levels of selected metals in the water samples were determined utilizing *Inductively coupled plasma atomic emission spectroscopy (ICP-OES)* with Spectrometer iCAP 7400 D (ThermoFisher Scientific, USA); CID86 detector. The instrument was calibrated on the certified reference material AN 9090(MN) representing a mixture of metal ions stabilized in 5% HNO₃ (v/v).

3.2 Results and discussion

3.2.1 Mechanical activation and materials characterization

At the beginning of the present research, numerous mechanochemical experiments were carried out in a planetary ball-mill equipped with 250 mL stainless-steel milling jars. These experiments followed the pioneering works in the field of mechanical alloying in the Al-Ni system [40, 41]. It has been shown before that some intermetallics from the binary Al-Ni system (e.g. β-AlNi or Al₃Ni) can be prepared directly by co-milling the two elements or by a combined mechano-thermal approach. However, prevalently mixer mills (e.g. SPEX 8000) were utilized in these studies. The research was mostly focused on a general behavior of the Al-Ni system without detailed description of neither the material properties nor their application. This type of ball-mills is usually only used for small-scale synthesis.

Moreover, experimental details were often missing (material of the milling equipment, the volume of jars used, and frequency). For potential large-scale

fabrication of materials, it was inevitable to investigate whether same outcome could be obtained in another type of mill with higher material throughput. Generally, transferring the fabrication process between two types of mills may represent a challenge. Recently, it has been shown that the planetary or vibratory ball-mills can be successfully utilized for the scale-up of mechanochemical synthesis up to 100 g per batch [44, 45]. Possibly, the industrial scale mills could provide kilogram quantities of materials.

Within the thesis, attention was primarily focused on 50:50 wt.% Al-Ni system (equal to $\text{Al}_{69}\text{Ni}_{31}$ molar composition) as this Raney Al-Ni alloy solely has been used for hydrodehalogenation applications before [8–11, 17]. However, other Al-rich compositions of the Raney Al-Ni alloy (specifically 58:42 wt.% Al-Ni equal to $\text{Al}_{75}\text{Ni}_{25}$) were investigated due to their promising properties, too.

The prepared ball-milled samples and the samples of mechano-thermally prepared alloys were characterized in detail by X-ray powder diffractometry. The X-ray powder patterns of 50:50 wt.% Al-Ni metal mixtures milled for 15 to 90 minutes are shown in Figure 4a. The qualitative phase analysis of the measured patterns revealed the presence of starting reagents – elemental aluminum and nickel – in all samples; regardless of the milling time. The identical result was obtained for the 58:42 wt. % Al-Ni system (Figure 4b) after 90 minutes of ball-milling. No other phases from Al-Ni binary system or metal oxides could be detected. Based on the Rietveld refinement results, the nano-crystalline character of both aluminum and nickel was found with the crystallite size below/close to 50 nm at the end of the milling process. The change in the crystallite size was more pronounced for aluminum metal. The calculated wt.% composition of the mixtures was in an agreement with the set conditions.

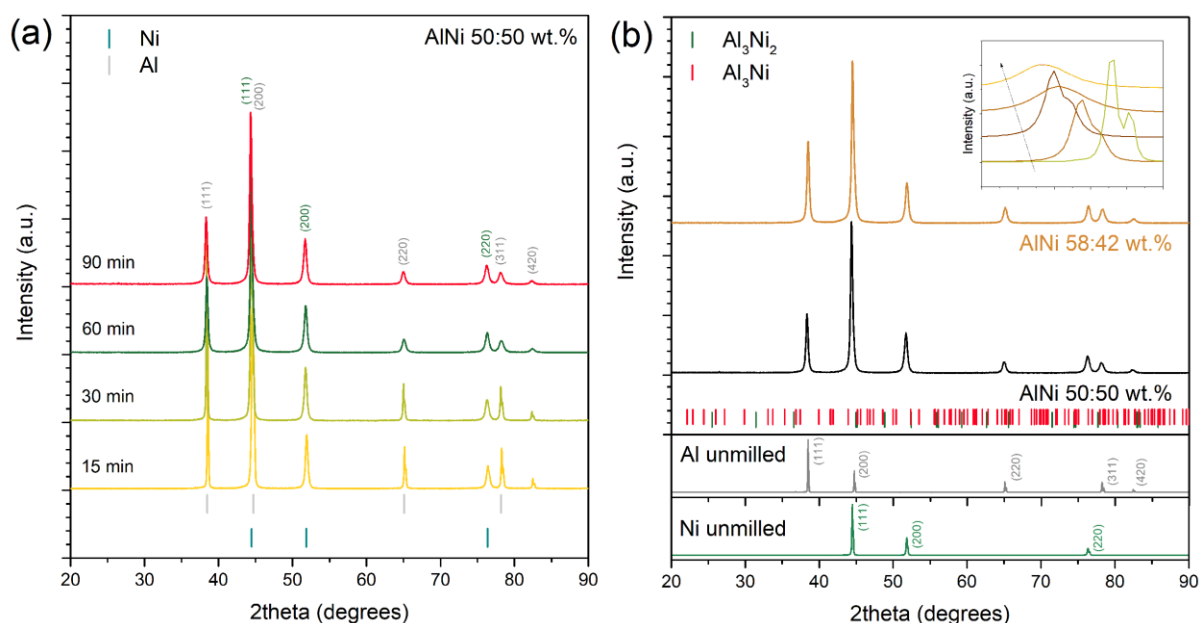


Figure 4. The evolution of the XRPD patterns for the ball-milled 50:50 wt. % Al-Ni mixture from 0 up to 90 minutes (a); the comparison of the XRPD patterns for 90 min activated mixtures (two different compositions) and the inset showing the evolution of aluminum (111) crystallographic plane – the arrow shows time progress.

Increased reactivity of the ball-milled materials was proved by the DTA measurements. For the unmilled Al-Ni mixtures, a sharp exotherm was observed in the pattern. This event was found to have a maximum at around 635 °C, around 25 °C below the melting point of pure aluminum metal, and was assigned to the crystallization of the alloy. The result was verified by XRPD measurement and the presence of intermetallic phases was confirmed (with no unreacted material left). It was concluded that the alloy with coarse grains could be prepared even without ball-milling for a given mixture of metallic particles. Such material, however, due to its non-homogeneity, is not applicable for the hydrodehalogenation purposes presented in the next chapters. Instead, highly homogenous ball-milled samples showed disappearance of the sharp exothermal peak, with thermal events shifted to a lower temperature range (below 500 °C). Treatment of the ball milled mixtures at either 500 or 700 °C provided dark grey powders, which were further analyzed.

Table 2. The calculated phase composition of the ball milled sample along with the crystallite size of aluminum and nickel metals followed in time.

sample (wt.% Al:Ni)	compositions (wt.%)		crystallite size (nm)		R_{wp} (%)
	Al	Ni	Al	Ni	
Al-Ni 50:50 0 min	48.1	59.1	216(3)	76	11.42
50:50 15 min	50.6	49.4	112(1)	37	10.10
50:50 30 min	50.8	49.2	134(2)	35	9.65
50:50 60 min	48.4	51.6	49	32	8.28
50:50 90 min	47.2	52.8	42	33	8.26
58:42 15 min	56.7	43.3	150(2)	41.4	9.52
58:42 30 min	55.4	44.6	89(2)	34.4	9.65
58:42 60 min	58.7	41.3	120.2	33.8	10.54
58:42 90 min	55.3	44.7	63.2	33.4	11.22

The XRPD patterns of the metal mixtures activated for 90 minutes after the thermal treatment are presented in Figure 5. The formation of new phases in the system and disappearance of elemental powder reflections is, even after short annealing at 500 °C/700 °C, self-evident. The Le-Bail analysis was performed starting with the expected phase composition to prove the formation of predicted intermetallic phases. The presence of orthorhombic Al₃Ni phase (JCPDS card no. 02-0416) with the unit cell parameters of $a = 6.62 \text{ \AA}$, $b = 7.37 \text{ \AA}$, and $c = 4.82 \text{ \AA}$ and rhombohedral Al₃Ni₂ phase (JCPDS card no. 03-1052) with the unit cell parameters of $a = 4.05 \text{ \AA}$ and $c = 4.90 \text{ \AA}$ was confirmed. The quantification of the samples was complicated due to the non-trivial preferred orientation of the Al₃Ni₂ phase. It is noteworthy that the observed phase composition for the materials is a good match with the phase diagram and previous studies. The presence of Al₃Ni₂ phase in 58:42 wt.% mixtures (equal to Al₃Ni) composition might have resulted from local inhomogeneity of the material.

Furthermore, the process of the ball-milling was followed by scanning electron microscopy (SEM) to explore the microstructure of the ball-milled samples. The evolution of ball-milled system is demonstrated on 50:50 wt.% mixture. Selected SEM images of the non-milled elemental precursors and milled metal mixtures are shown in Figure 6. The elemental powders of aluminum and nickel showed a significant difference in their particle size and morphology, which corroborates

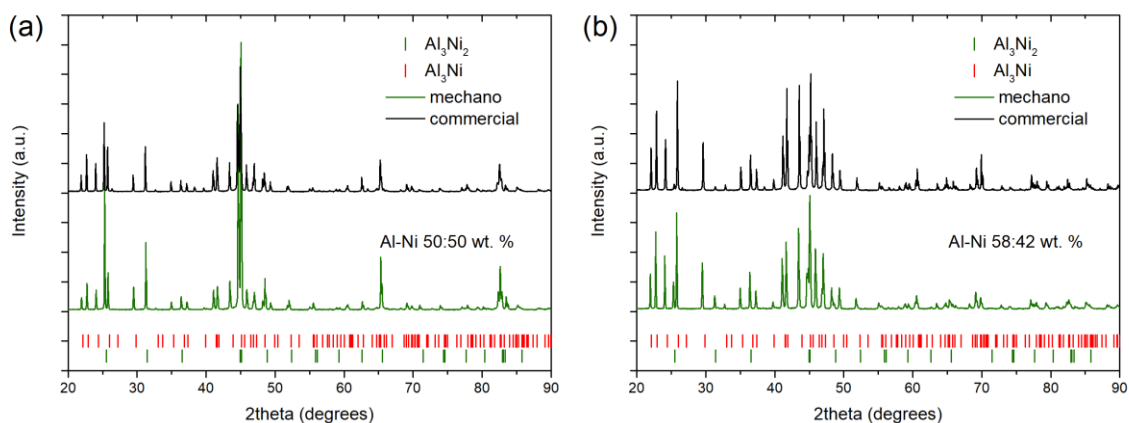


Figure 5. The XRPD patterns of mechano-thermally treated products revealing alloy formation – 50:50 wt.% Al-Ni (a) and 58:42 wt.% Al-Ni (b).

the findings from the XRPD measurements (average FWHM values of diffraction lines for the starting metals were higher for nickel). No contamination from abrasion of milling equipment was detected and the powders were only slightly oxidized on the surface. The presence of oxide phases could not be however, detected by X-ray powder diffractometry.

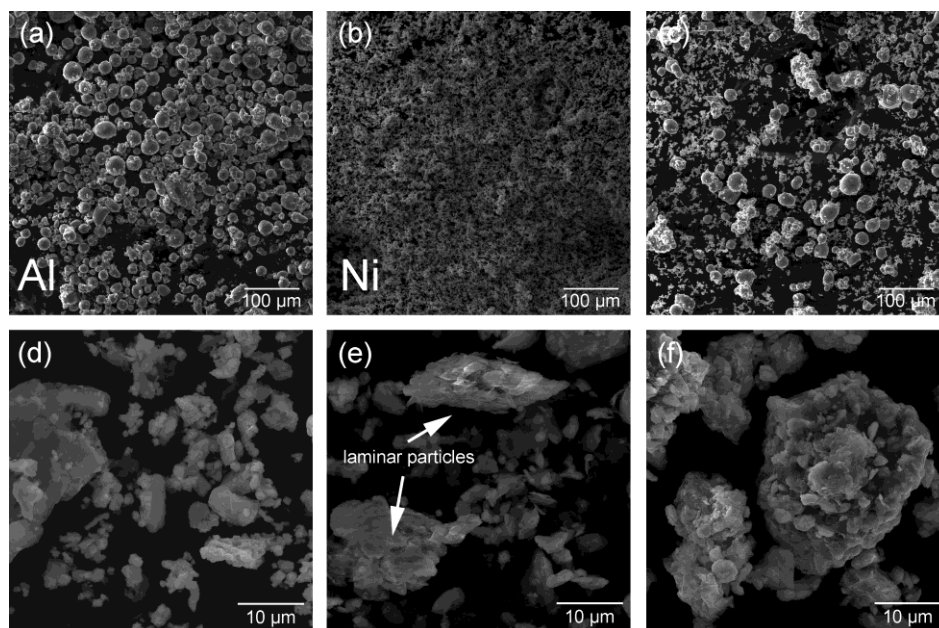


Figure 6. SEM images of the precursor materials (a, b), their physical mixture (c), and the mechanically activated 50:50 wt.% Al-Ni mixtures for 15, 30, and 60 min respectively (d, e, f).

The particle size distribution (PSD) measured for the alloy materials correlated well with the observation from the SEM analysis and surface area measurements. For the 50:50 wt.% alloy, a bimodal PSD curve was observed. While d_{50} value was determined to be around 36 μm . Due to the agglomeration effects, a small fraction of the material contained also bigger particles in the size range of 200-1000 μm . On the other hand, material with the composition adjusted to 58:42 wt.% had the particle distribution size almost identical to the commercial sample of the alloy. The d_{50} and d_{90} values were on average 37 and 107 μm . These values were also very close to the mechano-thermally prepared alloy with the 50:50 wt.% composition. Similar particle size distribution was beneficial for further comparison of the materials in terms of their catalytic properties.

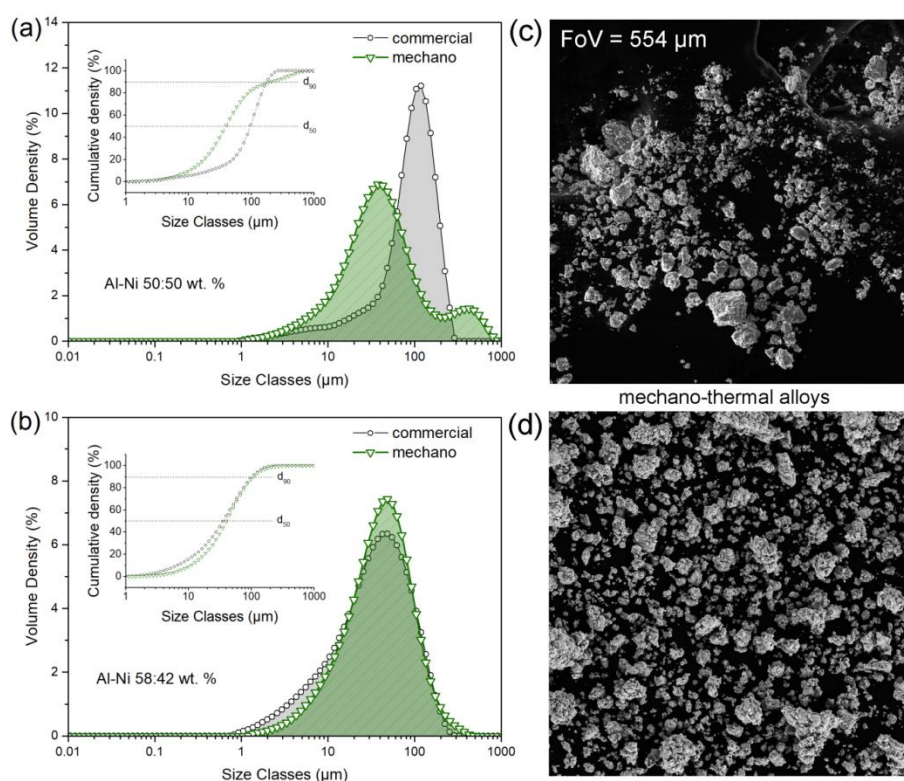
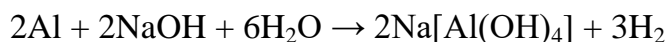


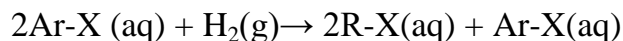
Figure 7. Particle size distribution (PSD) curves of mechano-thermally prepared alloys, compared to the commercially available analogues. SEM images at low magnification are shown in figures (c) and (d).

3.2.2 Hydrodehalogenation tests

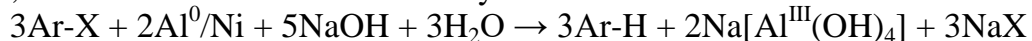
The most of the reactions were performed on 1 mM model aqueous solution, which represented hundreds of milligrams of pollutants per liter of solution. The concentration range lied in the solubility region for the substances in distilled water. All reaction were carried out all the reactions at normal conditions (atmospheric pressure and ambient temperature). The reactions were carried out in basic environment of sodium hydroxide as an optimal leaching agent. The sodium hydroxide dilute solutions (0.5-1 wt.%) were found to produce the environment with the pH levels well above 12.5, which secures high aluminum solubility and enough OH⁻ anions for the reaction with aluminum to produce hydrogen gas according to the equation



which is in turn utilized for the HDH reaction



So, the overall reaction stoichiometry for the HDH reactions can be written as



2-chlorobenzoic acid is easily dechlorinated under studied conditions and benzoic acid as the only product was determined by HPLC in the reaction mixtures (Table 3). The amount of alloy needed for conversion of over 90% for the pollutant was 0.8 g/L

Table 3. The results for hydrodechlorination of 2-chlorobenzoic acid in aqueous solution (1 mmol/dm³) with the studied alloy materials.

alloy (mg)	NaOH (mg)	molar ratio Cl:Al ⁺	Entry #	50:50 wt.%		Entry #	58:42 wt.%	
				removal	Al leached (mg/L)		removal	Al leached (mg/L)
80	200	1 : 14	1	>99 %	350	6	>99 %	396
80	100	1 : 14	2	>99 %	313	7	>99 %	375
40	100	1 : 7 :	3	>99 %	168	8	97 %	211
40	50	1 : 7	4	97 %	153	9	98 %	194
20	50	1 : 3.5	5	72 %	88	10	70 %	106

(15 mol eq.) in case of 50:50 wt.% alloys and 0.4 g/L (9 mol eq.) for 58:42 wt.% alloys. The often considered molar ratio of Al vs. contaminant, for the HDH reaction, typically lies in the range of 1-10. For lower dosages, even after 5 hours of stirring, the mixtures of benzoic acid with unreacted 2-chlorobenzoate formed. If the reaction times were increased, no further reaction progress was observed. The observed difference in efficiency can be unambiguously assigned to various leachability of aluminum from alloys materials. On average, around 25 % more aluminum could be leached from mechano-thermally prepared alloys of 50:50 wt.% composition (compared to the commercial material). Al-rich alloys, mainly consisting of Al₃Ni phase, showed difference of only 5 % in aluminum leachability. Better leachability of mechano-thermally alloys, in general, was also promoted by higher surfaces areas and considerably smaller crystallite size.

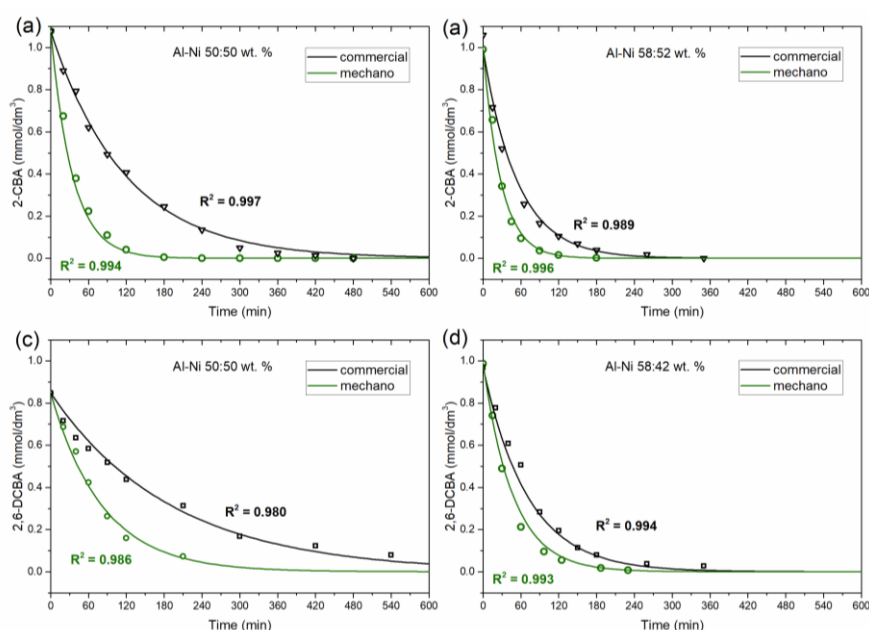


Figure 8. Decomposition kinetics of 2-CBA (a, b) and 2,6-DCBA (c, d) by mechano-thermally prepared alloys of two Al-Ni wt.% composition under identical reaction conditions (compared with their commercially available analogs).

The degradation of 2-chlorobenzoic acid was found to be considerably faster (Figure 8) in favor of the 58:42 wt.% Al-Ni alloy (both the commercial and mechano-thermally prepared materials). Using the mechano-thermally product, regardless of their elemental composition, practically full degradation was achieved under 3 hours

of the reaction time. The short reaction times are highly beneficial for the water treatment application as more contaminated wastewater could be cleaned per time unit.

For degradation of 2,6-dichlorobenzoic acid, a similar trend was observed. Higher efficiency was obtained for the 58:42 wt.% alloy materials. Here, the minimum amount of alloy needed for decomposition of contaminant evidently favored the mechano-thermally prepared alloy. At 0.4 g/L dosage, it could remove over 98 % of 2,6-DCBA during 5 hour run (191 mg 2,6-DCBA/1 L). Other materials needed at least 0.8 g/L alloy dosage to reach the same removal efficiency. If the concentration levels of contaminant were increased 10-fold times (10 mmol per dm³), after overnight mixing (Table 4), the same dosages of alloy (0.8 g/L) were sufficient to dehalogenate almost all amount of the present 2-CBA (ca 97-98 %). This represents a significant reduction and is caused more by the principles of heterogeneous catalysis (the probability of bimolecular reaction) than the amount of leached aluminum from alloy. In concentrated solutions, hydrogen gas evolved is being utilized more effectively for the HDH reaction. Comparing the found minimum molar excess for the successful HDH reaction to the reaction stoichiometry, at least 2 times molar excess was needed to complete the removal of chlorobenzoic acids. The molar excess determined within the present work in great accordance with the previously published results and can be taken as a rule of thumb for the HDH of Ar-X contaminants. Surprisingly, the phase composition of the used mechano-thermally prepared materials revealed that for 2,6-DCBA at higher concentration levels, utilization of 50:50 wt.% alloy provides higher removal. This is explained based on the phase composition and the kinetics of 2,6-DCBA decomposition (ca. two times slower compared to 2-CBA). It is suggested that while the decomposition is faster for 58:42 wt.% alloy, also aluminum leaching rate is rapid. In case of incomplete conversion, 50:50 wt.%, which provides slower aluminum leaching can in the end provide more hydrogen for the reaction in the course of 17 hours.

Table 4. Application of mechano-thermally prepared alloys for decomposition of 10 mM solutions.

alloy (mg, mmol Al)	NaOH (mg)	Entry #	mechano-thermal alloys		
			50:50 wt.% removal	Entry #	58:42 wt.% removal
270 (4.66)	400	1	>99 %	7	>99 %
135 (2.33)	400	2	>99 %	8	>99 %
135 (2.33)	200	3	>99 %	9	>99 %
80 (1.38)	200	4	97 %	10	81 %
80 (1.38)	100	5	98 %	11	97 %
40 (0.69)	100	6	41 %	12	45 %
			removal		removal
270 (4.66)	400	13	>99 %	19	>99 %
135 (2.33)	400	14	90 %	20	92 %
135 (2.33)	200	15	90 %	21	90 %
80 (1.38)	200	16	86 %	22	51 %
80 (1.38)	100	17	84 %	23	57 %
40 (0.69)	100	18	59 %	24	25 %

entries 1-12 correspond to 2-CBA, entries 13-24 to 2,6-DCBA, reaction conditions identical with experiments in Table 18.

Once the decomposition efficiency of 2-CBA and 2,6-DCBA was verified, 2,3,6-trichlorobenzoic acid (2,3,6-TCBA, *trysben*), which was commercially sold and used as a pesticide, was tested. The molecule of *trysben* contains three atoms of chlorine per molecule and thus hydrogen demand is three-fold compared to its monochlorinated analogue. Also, the position of chlorine atoms on benzene ring respective to carboxylic group may alter the decomposition. The compound can be degraded but at considerably lower reaction rates. In this case, superiority of the mechano-thermally prepared alloy material was pronounced. The alloy dosage of 0.8 g/L was found to be the lowest amount capable of decomposing chlorine-rich benzoic acid, with the kinetic rate constant of 0.01215 min^{-1} . The commercial product failed to provide full dechlorination under the same conditions. Therefore, the dosage was increased to 0.135 g/L and followed the decomposition. At this reagent dosage, it followed approximately the kinetics studied with mechano-thermally prepared alloy material. The applicability of 58:42 wt.% alloy was not studied in detail, since we were limited in the amount of available reagents. Anyway, we showed that especially for higher concentrations of pollutants, containing several chlorine atoms, fast leaching of aluminum from the alloy becomes a disadvantage.

Except for pure 2,3,6-TCBA, a mixture of 2,3,6-TCBA with other trichlorobenzoic acids isomers (technical grade quality) was dehalogenated. At the time, we had no available standards for quantification of each compound. However, we determined the removal efficiency in a sum (assuming similar absorption coefficients). The results were similar to that of pure compound with 0.8 g/L of alloy leading to close-to-complete dehalogenation.

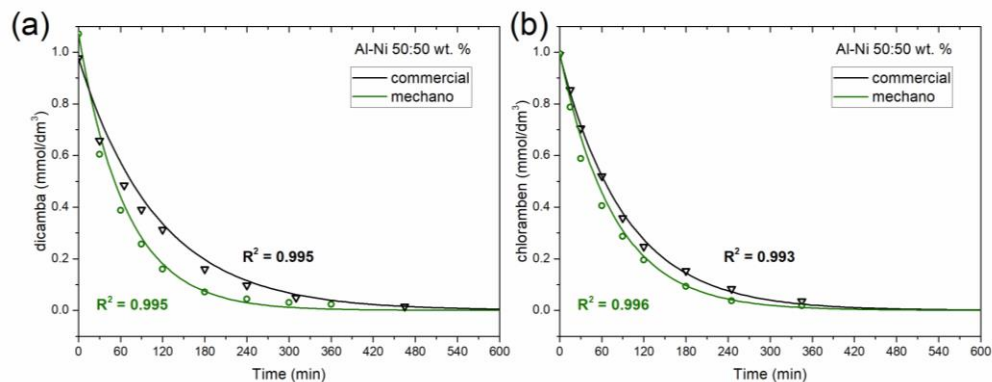


Figure 9. The decomposition kinetics of *dicamba* and *chloramben* under identical conditions (0.135 g/L 50:50 wt.% Al-Ni alloy + 2 g/L NaOH).

Two other studied analogs (*dicamba* and *chloramben*), containing only two chlorine atoms in different positions) provided good removal rates and acceptable reagent dosing (Figure 9). The observed difference in dehalogenation rates lies mostly in a number of halogen atoms bound to the aromatic benzene ring. No significant derivation for any studied compound was noticed. The removal rates were similar to that of 2,6-DCBA and are very favorable for applications. Our conclusion is that while structural aspects might play a role in the reaction kinetics, for analogs containing only one type of halogen, the removal rates will be alike and depend more on a number of halogen-bound atoms. The observed removal rates for all studied compounds herein showed similar values to catalyst based on supported-Pd/Pt. A direct reduction of the

compounds into their non-halogenated analogs is presumed. However, especially for *chloramben*, the product of dehalogenation could not be spotted with used HPLC method as it was detected in dead-time. Also, for *dicamba*, the two HPLC peaks were always detected in chromatograms. Additional HPLC-MS analysis did not solve the puzzle. The inability to assign the reaction products is considered as a minor drawback, since for HDH reaction the formation of unwanted halogenated by-products is improbable.

As the mechano-thermally prepared materials showed superior dehalogenation properties, other bases were tested as well for the 2-chlorobenzoic acid decomposition. Calcium hydroxide used as a leaching reagent provided complete dechlorination in the course of 20 hours with significantly smaller fraction of leached aluminum (0-70 mg/L). The efficiency comparable to that of sodium hydroxide is given by the pH levels securing solubility of the aluminum specimen. Surprisingly, utilization of potassium carbonate in the case of aluminum-rich alloy (58:42 wt.%) yielded led to 100% removal even at lower pH levels (around 10.5). Compared to $\text{Ca}(\text{OH})_2$, K_2CO_3 has 10x higher solubility in water and is able to promote the reaction via the following equilibria



The lowest efficiency was observed for ammonium hydroxide, which also showed the lowest values of pH and the precipitation of $\text{Al}(\text{OH})_3$. Experiments including NH_4OH also showed great variability in total removal (by 40-50%), probably due to its volatile nature.

While complexing agents, such as herein used EDTA provides reasonable efficiency at higher dosages, their utilization is mostly precluded by slow leaching of nickel metal as detected by visual inspection (the solutions have slightly blueish color) and ICP-OES measurement. Due to the complexing effect of similar compounds, this would result in carcinogenic Ni^{2+} ions leaching into the water, which makes their use improper for water treatment applications. The obtained data led us to conclusion that the decomposition of chlorinated contaminants in the environments with not sufficiently high pH or with bases, which extracts nickel, is not feasible. For most of the bases, after 17 hours reaction time, we detected precipitation of aluminum hydroxide. Once $\text{Al}(\text{OH})_3$ precipitates, it hinders the hydrodehalogenation reaction due to its crystals growing on alloy's particles.

4 Concluding remarks

Mechanical activation of the Al-Ni mixtures by ball-milling was proven to be an effective tool for the two-step, low-temperature, Al-Ni alloy preparation method. Via ball-milling in the planetary ball mill, nano-crystalline Al-Ni mixture can be prepared within 90 minutes under the argon atmosphere. The mixture showed excellent homogeneity and due to its structural properties, considerably lower crystallization temperatures of the intermetallic phases. After short annealing of the activated mixtures, Al-Ni alloy could be repeatedly prepared at 10 g scale. Possibly, this could be scaled up to hundreds of grams using vibratory ball-mills under optimized conditions. The prepared alloy materials of 50:50 wt.% Al-Ni or 58:42 wt.% Al-Ni composition, respectively, were characterized by available solid-state characterization techniques. The alloy prepared via proposed mechano-thermal way have characteristic surface morphology for ball-milled materials as detected by SEM. Their particle size distribution curves are relatively wide and materials possess higher surface areas when compared to the commercially available analogs. Owing to their properties, the prepared materials were evaluated as good candidates for hydrodehalogenation reactions in basic environment. The hydrodehalogenation tests confirmed their high efficiency and kinetic rates for the studied compounds. The tests were carried out on model aqueous solutions of chlorobenzenes and chlorobenzoic acids. The alloy materials were also compared to mechanically activated metal mixtures, which however showed only negligible removal efficiency and therefore were not of further interest. On the other hand, alloy materials showed excellent hydrodehalogenation properties, reaching complete removal of all studied pollutants within short times. The reaction conditions could be optimized to low excess of the used reagents. Moreover, the alloy can be recycled by the means of ball-milling after the use.

Regarding the HDH technology itself, its robustness using Raney Al-Ni alloy was verified based upon several observations

1. the reaction itself is not compound specific but rather C-Cl bond specific, while number of halogen atoms, and the compound's structure will affect the kinetics of removal
2. the reaction conditions for specific contaminant studied can be optimized experimentally in a few steps, for complex systems Design of Experiments (DoE) can be implemented
3. regardless of the contaminant, the reaction will be affected by temperature and stirring
4. the reaction can be scaled up several fold time but the process parameters will need to be adjusted in order to reach the same removal efficiency
5. the reaction can be applied to the samples of real wastewater showing high efficiency for halogenated benzenes removal
6. the Raney Al-Ni alloys provide an alternative to less efficient bimetallic couples or costly precious metal-based hydrogenation catalysts.

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List of Students` Published Works

1. Hegedüs, M. Gaborová, K. Weidlich, T. Kalivoda, P. Briančin, J. Tóthová, E. Rapid hydrodehalogenation of chlorinated benzoic acids using mechano-thermally prepared Raney alloy with enhanced kinetics. *Journal of Environmental Chemical Engineering*. 2021; 9(4) 105764.
2. Hegedüs, M. Lacina, P. Plotěný, M. Lev, J. Kamenická, B. Weidlich, T. Fast and efficient hydrodehalogenation of chlorinated benzenes in real wastewaters using Raney alloy. *Journal of Water Process Engineering*. 2020; 38; 101645.