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Combined degradation methods of halogenated pollutants focused on decay of halogenated phenolic compounds

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Abstract

We could find halogenated organic compounds especially chlorinated phenolics almost in every aspect of human activity in today´s world. Many of them are dangerous to living organisms and the environment. Such compounds are among persistent organic pollutants which bioaccumulate in the environment and are highly resistant against any kind of degradation. This PhD thesis deals with the degradation of widely used antibacterial agents based on chlorinated phenols such as triclosan and chlorophene by various methods and approach. Main studied degradation approach was using several metallic alloys such as Raney Al-Ni (50% Al, 50% Ni), Devarda's Al-Cu-Zn alloy (45% Al, 50% Cu, 5% Zn), and Arnd's Cu-Mg alloy (60% Cu, 40% Mg) for reduction of above mentioned antibacterials while generating dechlorinated compounds which might be easily biologically degraded. Electro-Fenton process was studied as another approach of degradation for triclosan remediation from aqueous solution. Various conditions such as different concentrations of added iron(II) as Fenton reagent, different concentrations of sodium sulfate electrolyte, different flow rates, current density values and different pH values. Both ways of degradation gave satisfactory results which were evaluated in this thesis.

Abstrakt

Halogenované organické látky, zejména chlorované fenolické sloučeniny, můžeme nalézt v dnešním světě takřka v každém odvětví lidské činnosti. Mnoho z nich představuje nebezpečí pro živé organismy a obecně pro životní prostředí. Tyto látky patří mezi perzistentní látky, které jsou schopny bioakumulace v životním prostředí a jsou vysoce odolné vůči mnohým způsobům degradace. Tato disertační práce se zabývá tématem degradace běžně používaných antibakteriálních činidel na bázi chlorovaných fenolů, jako jsou triclosan a chlorophene, za využití odlišných metod a přístupů. Hlavním studovaným způsobem degradace výše zmíněných látek je zde redukce pomocí různých slitin kovů jako například Raneyovy Al-Ni slitiny (50 % Al, 50 % Ni), Devardovy Al-Cu-Zn slitiny (45 % Al, 50 % Cu, 5 % Zn), Arndovy Cu-Mg slitiny (60 % Cu, 40 % Mg) za vzniku dechlorovaných látek, které mohou být lépe biologicky odbouratelné. Jako další způsob odstranění antibakteriálního činidla triclosanu z vodného roztoku byla využita tzv. elektro-Fentonova oxidace. Při tomto způsobu degradace byly studovány různé podmínky jako například různé koncentrace železnatých iontů přidávaných jakožto Fentonovy reagenty, různé koncentrace elektrolytu síranu sodného, různé hodnoty průtoku, proudové hustoty či pH.

Key words

antibacterial agents, chlorinated phenolic compounds, reduction, electrochemistry, metal alloys, electro-Fenton process

Klíčová slova

antibakteriální činidla, chlorované fenolické sloučeniny, redukce, elektrochemie, kovové slitiny, elektro-Fentonův proces

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Introduction

Organohalogens are widely spread around many different things that we are using in our everyday lives. We are encountering these compounds consciously or unwittingly on almost every step. Many of them are dangerous to human health and to living organisms (e.g. polychlorinated biphenyls - PCBs) and their use and production has been eliminated or restricted with different kinds of agreements (e.g. Stockholm Convention on Persistent Organic Pollutants) to protect the environment. There should be an encouragement towards so called environmental friendly alternatives, which would have preferably no harmful impacts on Nature. Chlorinated organics are among persistent organic pollutants, which bioaccumulate in the environment, and are highly resistant against degradation, and also enter the bodies of living organisms where they could change the DNA structure and cause cancer.[1-3]
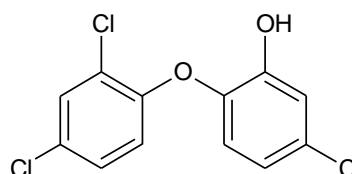
1. Chlorinated phenols

Chlorophene (2-benzyl-4-chlorophenol (**A1**)) and triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol (**C1**)) are chlorinated phenols used as antimicrobial agents either in household products, cosmetics, or as the basic antiseptics in hospitals, agriculture facilities, etc. **C1** is a widely used antibacterial agent with wide range of effect. We could find it in personal care products such as toothpastes, antibacterial soaps, shampoos, and cosmetics.[4,5] The European Union restricted **C1** in cosmetics since 2014 but it also can be found as an antibacterial preservative in plastics like kitchenware, toys, and as well in textile products like socks, beddings, and sports clothing.[6-8] **C1** has been also detected in human breast milk, and bodies of fish[9,10], it is commonly detected in the wastewater treatment plants and even though its degradation efficacy is quite high, trace concentrations go to effluents causing death of many aquatic organisms, such as algae, daphnids, phytoplankton, and fish.[11-13] In wastewater treatment plants or by incinerating **C1** contained clothing, **C1** could be transformed to even more toxic compounds (e.g. by photocatalysis of surface water, through biological methylation to methyltriclosan).[14,15] Use of **C1** in clothing has been banned by the European Union because of the concerns from bacterial resistance and generation of toxic metabolites, such as 2,8-dichlorodibenzo-*p*-dioxin.[16]

Chlorophene (**A1**) application is similar to **C1**, it is used in personal care products, household products, but also in the industry and agriculture (farming facilities) as an active agent in disinfectants.[17] Because of its use, **A1** goes to the aquatic environment and because of its toxicity and persistence it is accumulating in waters and soils.[18] It is assumed that **A1** toxicity to humans is low, but carcinogenicity and mutagenicity of **A1** to animals has been proven.[19] Recently, it was reported that **A1** displays antiandrogenic behavior while detected in fish bile together with **C1.** It showed about 50% more antiandrogenic effect compared to other chemicals.[20]
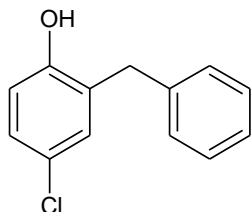
Chlorophene (**A1**)   Triclosan (**C1**)
Fig. 1 Chemical structures of studied antibacterial agents

1.1 Techniques used for chemical decay of biocidal halogenated phenols

1.1.1 Reductive dechlorination

Nowadays there is a continuous search for appropriate methods for remediation of organic pollutants, in particular chlorinated organics. Reductive dechlorination (RD) is an effective way for detoxification of chlorinated organics under relatively mild conditions without toxic byproducts formation. Unlike chemical oxidation where the pollutants are usually degraded to (if possible) CO_2 and H_2O under quite harsh conditions (and toxic byproducts could be produced), this method enables to replace chlorine in the molecule by hydrogen under relatively mild conditions and generate more easily biodegradable compounds due to their lower toxicity, i.e. no halogen in the molecule. Hydrogen could be introduced to the system in many different ways, e.g. by hydrogen gas bubbled to the solution or generated in situ from hydrides, hydroxides, or hydrazine by a reaction with metals (either by Pt or Pd on carbon, by a mixture of metals as a fly ash or in the form of metallic alloys). Those methods showed good results in the degradation of various chlorinated pollutants, such as toxic polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and trichlorobenzenes (TCBs)[21,22] under relatively mild conditions.

RD by activated zero valent metal (iron coated with Cu[23] or Zn powder coated with noble metals[24]) was successfully tested for the degradation of hexachlorobenzene[23] or 2,4,6-trichlorophenol (2,4,6-TCP).[24] Also metallic alloys (especially Raney Al-Ni and Devarda's Al-Cu-Zn alloys) had been used in the past for RD of chlorinated aromatics such as insecticide DDT and 2,4,6-TCP in $NaBH_4$ solutions[25] or in various alkali hydroxide solutions (monochloro- (MCB) and dichloro- (DCB) biphenyls)[26], respectively. Mainly products of RD had been obtained by replacing chlorine with hydrogen, however, in many cases the reduction of the aromatic ring in the molecule occurred.[26] Application of a high excess of Al-Ni alloy and its re-use in the RD of 2-chlorophenol was also reported with very promising results.[27,28] The hydrodehalogenation mechanism of halogenated aromatics by metallic alloys is not yet completely clarified – few different views on the problematic had been reported. The direct reduction of organically bound halogen ($C_{arom.}$-X bond) could either occur at the metal surface or there is the effect of adsorbed hydrogen activated on nickel sponge.[24,26] For a literature survey of the various methods see *Table 1*.

Table 1   Reaction conditions of hydrodehalogenation in various studies

Pollutant	Number of Cl atoms	Reductant	Ratio metal:substrate	Temp. (°C)	Reaction time (h)	Solvent	Special reactor	Reference
PCDBs, PCDFs	3 - 4	Pt /C or Pd/C + H$_2$	1(Pd or Pt) : 10	50	1.5 - 2	Aq./org.	Yes	lit[21]
TCPs	3	Pd/C +N$_2$H$_4$	1(Pd) : 1	RT - 60	0.083 - 3	Org.	[a]Yes	lit[22]
2,4,6-TCP	3	Zn(0), Zn/Pd, Zn/Pt etc.	12 – 61 (Zn) : 1	RT	20 -40 days	Aq.	No	lit[24]
DDT and 2,4,6-TCP	3 - 5	Devarda's alloy + NaBH$_4$	28 - 83(Al) : 1	80 – 100	1 - 4	Aq.	No	lit[25]
MCBs, DCBs	1 - 2	Al-Ni/OH⁻	19 (Al) : 1	60 - 90	1.5 - 8.5	Aq	[a]Yes	lit[26]
2-CP	1	Al-Ni/F⁻ (EDTA)	24 (Al) : 1	RT	0.75-2	Aq.	No	lit[27,28]
Chlorinated aromatics	1-3	Fly ash + alcohol	[b]	40 - 170	3 - 13	Aq./org.	Yes	lit[29,30]
2,4,6-TBP	3[c]	Devarda's alloy+ OH⁻	10 (Al) : 1	RT	2	Aq.	No	lit[33]
2,4,6-TBP	3[c]	Al-Ni/OH⁻	3.8 (Al) : 1	RT	1	Aq.	No	lit[34]

[a]Ultrasonic irradiation.
[b]Fly ash – individual metal contents in fly ash vary a lot, i.e. hard to define the ratios.
[c]Contains bromine atoms

The previous studies focused on reductive dehlaogenation were conducted either in non-aqueous solutions (in organic solvent alone, in a certain mixture of organic solvent/water respectively)[21,22,29], at non-ambient temperature or pressure[21,25,26,29,30], and with a high excess of metals/alloys against chlorinated organics[26-28]. Thus, our goal was to come up with a RD method under mild conditions, i.e. ambient temperature and pressure without need for special reactors or equipment.

1.1.2 Advanced oxidation processes

There are other ways for degradation of organic pollutants in addition to above mentioned, these are so called advanced oxidation processes (AOPs). These latter processes are all characterized by oxidation using $^{\bullet}$OH radicals as the main oxidizing species which are very strong oxidants capable of degrading a broad spectrum of organic molecules. The main aim is to degrade organic pollutants possibly to CO_2 and small(er) and non-harmful organic or inorganic compounds. Examples of these oxidation processes comprise TiO_2/UV photocatalysis[36,37], electrochemistry[38], sonoelectrochemistry[39,40], ozonation[41], chlorine dioxide[42], potassium permanganate[43] and Fenton based processes which are used in recent years in many different ways.

1.1.2.1 Fenton oxidation

Fenton reactions could be distinguished as follows: classical Fenton reaction uses combination of H_2O_2 and Fe^{2+} to generate $^{\bullet}$OH radicals[44], Fenton-like processes (H_2O_2 and Fe^{3+})[45], photo-Fenton (H_2O_2/ Fe^{2+} (Fe^{3+}) / UV[37] and also electro-Fenton which is the focus of this paper. Hydrogen peroxide in electro-Fenton process could be generated from the saturated oxygen solution on the electrodes of various materials, e.g. titanium[46], graphite[47], aluminum, stainless steel, copper[48], boron-doped diamond, platinum[49], or directly by injecting the gas to a gas diffusion electrode. In the electro-Fenton process hydrogen peroxide can be either added to solution or generated electrochemically.

Hydroxy radicals are very powerful oxidation species, considered as the second strongest oxidizing agent right after fluoride with a standard reduction potential E^0 ($^{\bullet}$OH /H_2O) = 2.8 V/SHE[50]. The main advantage is that this *in situ* generated radical acts in a nonselective way so it could degrade and eventually mineralize most of organic and organometallic pollutants.

Hydrogen peroxide could be generated at the cathode as it is illustrated in the bellow equation (*Eq. 1*). Either this generated hydrogen peroxide or the externally added one is reacting with added Fe^{2+} to generate $^{\bullet}$OH via the Fenton reaction (*Eq. 2*)[51]:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad \qquad \text{(Eq. 1)}$$

$$H_2O_2 + Fe^{2+} + H^+ \rightarrow Fe^{3+} + \bullet OH + H_2O \qquad \text{(Eq. 2)}$$

These generated hydroxyl radicals then oxidize the organic pollutant (*Eq. 3*)[51]:

$$RH + \bullet OH \rightarrow R\bullet + H_2O \qquad \qquad \text{(Eq. 3)}$$

Also a recombination of radicals and their uncontrolled reactions with other reagents present in the solution might occur including the unwanted ferrous ions

destruction by hydroxyl radicals which means that it is necessary to continuously add Fe^{2+} to the solution to keep the reaction running (*Eq. 4, 5*)[52].

$$R\bullet + Fe^{3+} \rightarrow R^+ + Fe^{2+} \qquad \text{(Eq. 4)}$$

$$Fe^{2+} + \bullet OH \rightarrow Fe^{3+} + OH^- \qquad \text{(Eq. 5)}$$

A crucial stage of the electro-Fenton reaction is the regeneration of Fe^{2+} which is required in order to save externally added Fe^{2+}. These regeneration reactions could occur in different ways. It could be either by reaction with hydrogen peroxide which is present in solution or by generated hydroperoxyl radicals - which in turn may be produced by reaction of hydrogen peroxide with either ferric ions or with hydroxyl radicals (*Eq. 6, 7, 8*)[50].

$$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + HO_2\bullet + H^+ \qquad \text{(Eq. 6)}$$

$$Fe^{3+} + HO_2\bullet \rightarrow Fe^{2+} + O_2 + H^+ \qquad \text{(Eq. 7)}$$

$$H_2O_2 + \bullet OH \rightarrow HO_2\bullet + H_2O \qquad \text{(Eq. 8)}$$

Meanwhile, in the anode compartment various reactions are taking place, some of which are listed below (*Eq. 9, 10, 11*)[53].

$$O_2 + 3H^+ + 3e^- \rightarrow H_2O + \bullet OH \qquad \text{(Eq. 9)}$$

$$H_2O \rightarrow \tfrac{1}{2} O_2 + 2H^+ + 2e^- \qquad \text{(Eq. 10)}$$

$$\tfrac{1}{2} O_2 + H_2O \rightarrow 2\,OH\bullet \qquad \text{(Eq. 11)}$$

2.   Aims of the doctoral dissertation

The aims of this thesis were to investigate methods for the degradation of widely used antibacterial agents chlorophene **A1** and triclosan **C1** which are causing pollution in the aquatic environment. One of the methods chosen for this purpose was reductive dechlorination by Al-Ni Raney alloy (50% Al -50% Ni) in alkaline aqueous solution at ambient temperature and pressure. There were investigated such parameters as amount of alloy, type and amount of base, etc. The above mentioned Al-Ni alloy has been already tested in the past studies for hydrodehalogenation of several halogenated anilines, and 2,4,6-tribromophenol and were suggested as good reduction agent for chlorinated phenols.[31-35]

The other method investigated for degradation of above mentioned pollutant triclosan **C1** was electro-Fenton process using electrolysis cell comprised of titanium electrodes coated with IrO_2 mixed with RuO_2. The whole system was continuous and in this regard, the effect of different reaction parameters (e.g. different starting concentrations of **C1**, Fe^{2+}, different type and concentration of supporting electrolyte, different pH, flow rates and current values) have been investigated. This method has been inspired by studies which were testing electrochemical reaction alone using various electrodes or slightly modified electro-Fenton oxidation (e.g. various electrodes, addition of $Fe^{2+}/Fe^{3+}/H_2O_2$, using of UV radiation etc.)

In studies on electro-Fenton processes presented in this thesis were achieved some degrees of degradation so it could be said that this method might be combined

with using of Raney Al-Ni alloy for decay of analogous halogenated phenols which are often detected in surface and waste waters during analyses.

3.   Experimental

3.1   Materials and methods

3.1.1   Chemicals and reagents used for reductive dechlorination

Chlorophene **A1** and triclosan **C1** of highest available purity (95-97%) were both obtained from Sigma-Aldrich Co. (Czech Republic). All other reagents such as Raney Al-Ni alloy, Devarda's Al-Cu-Zn alloy (45% Al - 50% Cu - 5% Zn), Arnd's Cu-Mg alloy (60% Cu - 40% Mg), CH_2Cl_2, NaOH, KOH, NaF, Na_2CO_3, NH_4OH, CH_3COONH_4, CH_3COONa, Na_3PO_4, H_2SO_4,   and Na_2SO_4 were purchased from commercial suppliers (Penta, Across, Sigma-Aldrich, Merck, Lach-Ner, Fluka) in purity of at least 95% without any further purification.

3.1.2   Experimental procedure of reductive dechlorination

Experiments were carried out in 250 cm^3 round flasks on a magnetic stirrer equipped with StarFish attachment (Radleys Discovery Technologies, UK) which enables to perform five different experiments at the same time and at the same ambient conditions. All experiments were carried out in air at ambient temperature (20 – 25 °C). All used solutions were prepared in distilled water. Stock solutions of **A1** or **C1** were prepared in concentrations 10 $mmol·dm^{-3}$ in aqueous solution of appropriate base (salt respectively). To the 10 $mmol·dm^{-3}$ solution of studied **A1** or **C1** dissolved in 100 $mmol·dm^{-3}$ of base the appropriate amount of tested alloy (Al-Ni, Devarda's, Arnd's) was added. The flask with the reaction mixture was closed with glass tube filled with $CaCl_2$ and the reaction mixtures were stirred at 350 rpm at ambient temperature (20 – 25 °C) for approximately 21 hours, filtered subsequently and taken samples for AOX and dissolved aluminum. Obtained filtrate was acidified using 18% H_2SO_4 to pH around 3, then transferred into the separation funnel, extracted with CH_2Cl_2 (2 x 5 cm^3), dried by Na_2SO_4, filtered and then let evaporate in the fume hood. After evaporation were prepared samples for GC/MS by dissolving the solid or viscous liquid in pure CH_2Cl_2.

3.1.3   Analytical methods used for reductive dechlorination

Mass spectra were measured on a GC-MS configuration comprised of an Agilent Technologies 6890N gas chromatograph equipped with a 5973 NetworkMS detector (EI 70 eV, mass range 33–550 Da). Samples were prepared by dissolving in pure dichloromethane.

AOX determination was conducted according to valid norm ČSN EN ISO 9562.

The content of soluble aluminum in filtered reaction mixture samples was carried out with a sequential, radially viewed inductively coupled plasma (ICP) atomic emission spectrometer INTEGRA XL 2 (GBC, Dandenong Australia), equipped with a ceramic V-groove nebulizer and a glass cyclonic spray chamber (both Glass Expansion, Australia).

3.2.1 Chemicals and reagents used for electro-oxidation experiments

Triclosan **C1** of highest available purity (97%) and potassium permanganate were obtained from Sigma-Aldrich (Denmark). Sulfuric acid, hydrogen peroxide (35%), HPLC grade solvents such as methanol, acetonitrile were obtained from Rathburn Chemicals Ltd. (Scotland). Sodium hydroxide, sodium sulfate, iron(II) sulfate, ammonium iron(II) sulfate, nitrilotriacetic acid (NTA); 1,10-phenanthroline hydrochloride (PHT), glycine (GLY), hydroxylamine hydrochloride were obtained from Merck (Germany). All above mentioned chemicals were obtained of highest available purity without any further purification. For experiments was used deionized water (with conductivity of 5.5×10^{-5} S·m^{-1} at 25°C) obtained from a Millipore Milli-Q system. Triclosan stock solution was prepared in methanol to secure good solubility[54], the concentration was 1 g·dm^{-3} and from this **C1** stock solution were prepared solutions for degradation experiments with **C1** concentration of 10 mg·dm^{-3}.
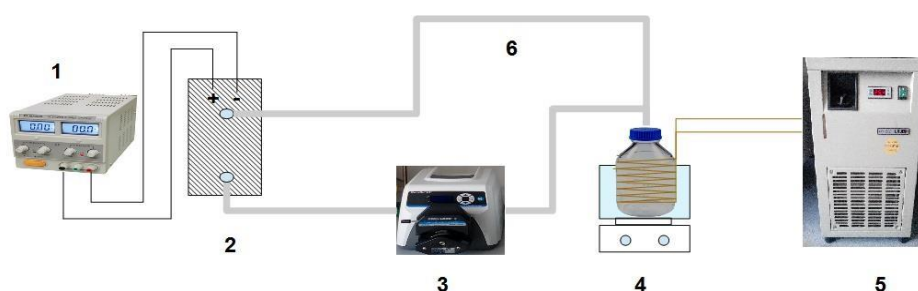

Fig. 2 Experimental setup: 1 – Power supply, 2 - Electrolytic cell: Ti/RuO$_2$-IrO$_2$ as cathode and anode in polypropylene case, 3 - Peristaltic pump, 4 - **C1** aqueous solution (10 mg·dm^{-3}), pH = 3 or 4 (sodium sulfate or sodium chloride, iron(II)), 5 – Thermostat, 6 - PTFE tubing.

3.2.2 Equipment used for electro-oxidation experiments

The experimental setup is illustrated in *Figure 2*. Triclosan **C1** dissolved in Milli-Q water was circulated through an electrochemical cell for 80 minutes at a flow rate 50 or 100 ml·min^{-1}. The electrolytic unit provided by Adept Water Technologies AS, Denmark, consisted of undivided reactor cell of volume about 70 cm^3 with the electrodes covered by a polypropylene (PP) case. Both electrodes were titanium electrodes coated with RuO$_2$ mixed with IrO$_2$ and were used as cathode and anode. The surface area of each electrode was 165 cm^2, with a distance between the electrodes of 1.6 mm. The cell was connected to a 1L glass reservoir (with 10 mg·dm^{-3} **C1** aqueous solution) and a peristaltic pump (Cole-Parmer, Masterflex L/S, Easy load II) with connector tubings made of polytetrafluoroethylene (PTFE) and with Tygon LFL Masterflex tubing as the pump tubing. If not specified otherwise the time of electrolysis process was 80 minutes.

3.2.3 General procedures of electro-oxidation experiments

3.2.3.1 Sorption and degradation of triclosan C1

For quantification of sorption **C1** solutions in presence of different electrolytes was circulated through the electrolytic equipment with the electrolysis unit off. Flow rate was either 50 or 100 ml·min^{-1}. **C1** solutions were prepared by diluting appropriate amount of **C1** stock solution (1 g·dm^{-3} **C1** in methanol) and appropriate amount of

aqueous electrolyte stock solution in Milli-Q water. The pH was adjusted to the required value by adding 1 mol·dm^{-3} sulfuric acid. Samples were taken from the glass reservoir (*Figure 2, entry 4*) every 20 minutes.

Degradation experiments were conducted in the same manner as for the sorption experiments but with the electrolysis unit on. Flow rate was either 50 or 100 ml·min^{-1}. Triclosan solutions were prepared by diluting appropriate amounts of **C1** stock solution (1 g·dm^{-3} **C1** in methanol), aqueous electrolyte stock solution, and aqueous iron(II) sulfate stock solution (pH ≈ 2) in Milli-Q water. The pH was adjusted to the required value by adding 1 mol·dm^{-3} sulfuric acid. Current densities were set to 6, 12, or 24 mA·cm^{-2} by setting the appropriate current value on the electrolysis cell (I = 1, 2 or 4 A) and samples were taken from the glass reservoir (*Figure 2, entry 4*) every 20 minutes.

No oxygen saturation of the solution was provided during experiments, the reservoir was open to atmosphere and there was much headspace.

3.2.4 Analytical methods used for electro-oxidation experiments

Triclosan was quantified by an Agilent Technologies HPLC 1100/1200 series equipped with Zorbax Eclipse XDB - C18 column (4.6 x 150 mm, 5 μm) and a DAD detector. The mobile phase was a mixture of acetonitrile and water (65:35, v/v) at a flow rate 1 ml·min^{-1}. The detection wavelength was 214 and 220 nm. Soluble and total soluble iron were measured by the 1,10-phenantroline method[55] using Perkin Elmer UV-VIS spectrometer Lambda 25 at the wavelength of 512 nm. Samples were mixed with beforehand prepared iron(II) reagents in ratio of GLY:PHT:NTA = 5:5:1. The concentration of total soluble iron was determined by adding reduction agent hydroxylamine to the sample, letting to react for a several minutes with subsequent adding of iron(II) reagents. Samples were taken from the glass reservoir (*Figure 2, entry 4*) every 20 minutes. For measurement of generated hydrogen peroxide two spectrophotometric methods were tested – DMP method using copper(II) ion with 2,9-dimethylphenantroline[56] and also Iodide method using potassium iodide with several reagents[57]. However, both of these methods for H$_2$O$_2$ determination showed significant interferences with either iron present in the solution or even triclosan itself. Because of this H$_2$O$_2$ possibly generated during the electrolytic process was not measured.

4   Results and discussion

4.1   Reductive dechlorination of chlorinated phenols chlorophene and triclosan by using metal alloys

The course of RD of **A1** and **C1** in alkaline solution was examined by using Cu and Ni based alloys, Raney Al-Ni, Devarda's Al-Cu-Zn, and Arnd's Cu-Mg alloys. As mentioned above, this method is highly effective for reductive debromination (hydrodebromination) of 2,4,6-tribromophenol in case of Al-Ni and Al-Cu-Zn application.[33,34] Arnd´s alloy was added to the set of studied alloys without any previous research or any knowledge of its usage for such experiments as reductive dehalogenation of halogenated organic compounds. In *Table 1* in section 1.1.1 could be seen the summarization of similar studies on topic of dehalogenation of aromatic compounds.

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The reductive dechlorination of **A1** and **C1** experimental procedure was described in section 3.1.2.

4.1.1 Effect evaluation of used alloys for reductive dechlorination of chlorophene A1

To 1 mmol of **A1** in aqueous solution were added various amounts of alloys and various excessive amounts of NaOH to cause complete corrosion (and dissolution) of the electropositive metal from used alloy (*Table 2*). Experiments showed that RD completely failed in case of Devarda's and Arnd's alloys (*Table 2, entries 1-4*). Only the Raney Al-Ni alloy was proved as effective reduction agent (*Table 2, entries 5, 6*).

Table 2 Effect of used alloy on the reductive dechlorination of **A1**[a]

Entry	Used alloy	Quantity of alloy (g)	Reductant (mmol)	NaOH (mmol)	Content of unreacted **A1** (%)
1	Devarda's	0.9	Al (15)	35	100
2	Al-Cu-Zn	1.2	Al (20)	35	100
3	Arnd's	0.11	Mg (1.7)	20	100
4	Cu-Mg	1.07	Mg (17.7)	100	100
5	Raney	0.81	Al (15)	35	0
6	Al-Ni	0.27	Al (5)	20	0

[a] **A1** (1 mmol; 0.22 g) was dissolved in 100 cm^3 of 100 $mmol·dm^{-3}$ aqueous NaOH solution, additional base and tested alloy was added at ambient temperature and the reaction suspension was stirred at 350 rpm overnight.

4.1.2 Effect evaluation of Al-Ni alloy amount on reductive dechlorination of chlorophene A1 in aqueous NaOH solution

At first, the optimal amount of Al-Ni alloy was examined generating the product of total RD, then the optimal amount of NaOH was tested. The obtained results are illustrated in *Table 3*. Total RD was found to be completed when 2.5 equivalents of aluminum in the form of Al-Ni alloy (i.e. 0.07 g; 2.5 mmol of Al) against **A1** and 10 equivalents of NaOH (i.e. 0.4 g; 10 mmol) against aluminum were used and the reaction was performed at ambient temperature for approximately 21 hours, see *Table 3, entry 8*. Using a high excess of the Al-Ni alloy against **A1**, substituted cyclohexanol **A1b** is produced and subsequent hydrogenation of **A1a** occurred. A time course of the RD of **A1** is shown in *Fig. 3* − the lowest amount of alloy (0.14 g of Al-Ni, i.e. 0.07 g; 2.5 mmol of Al as mentioned few lines earlier) was used when the reaction was completed. However the reactions did not result in 100 % of **A1a**, still around 5% in average was present in the reaction mixture. This could be the experimental error, which is included in the standard deviation of this value. However, about 75 % of dechlorinated product present in the reaction mixture after 240 minutes is a good result under mild conditions. The results show that the metal:base:substrate ratios are very low in contrary to similar studies.[24-30] The ratios are close to those reported by Tundo et al.[21] and Rodríguez and Lafuente[22], however, they did not achieve those results under mild conditions as aqueous solution at ambient temperature and pressure, see *Table 1* in section 1.1.1.
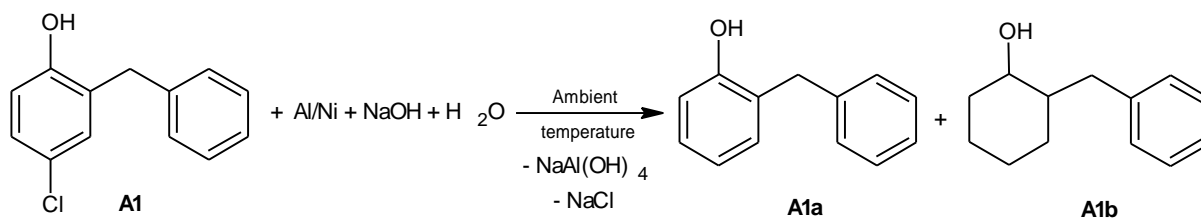
Scheme 1 Reductive dechlorination of **A1** using Raney Al-Ni alloy in the presence of NaOH.

Table 3 Reductive dechlorination of **A1** using Al-Ni alloy.[a]

Entry	Mmol of aluminum (amount of Al-Ni)	NaOH (mmol)	GC-MS (%)		
			A1	**A1a**	**A1b**
1	30 (1.62 g)	20	0	80.5	19.5
2	20 (1.08 g)	20	0	86.7	13.3
3	15 (0.80 g)	20	0	92.7	7.3
4	10 (0.54 g)	20	0	97.4	2.6
5	5 (0.27 g)	20	0	100	0
6	5 (0.27 g)	5	0	100	0
7	2.5 (0.14 g)	20	0	100	0
8	2.5 (0.14 g)	10	0	100	0
9	1.3 (0.07 g)	35	24.6	75.4	0
10	1.3 (0.07 g)	10	61.2	38.8	0
11	0.74 (0.04 g)	20	83.7	16.3	0

[a] To **A1** (1 mmol, 0.22 g) dissolved in 100 cm^3 of aq. NaOH solution Al-Ni was added and stirred at 350 rpm overnight at room temperature.
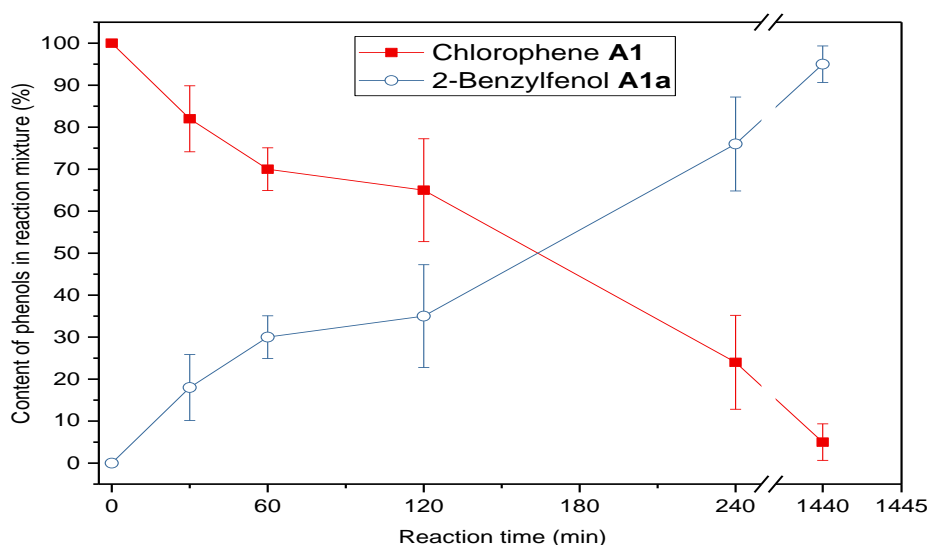
Fig. 3 Time course of RD of **A1** by Al-Ni/NaOH. Reaction conditions: room temperature (20 - 25°C) and ambient pressure, stirring at 350 rpm; 1 mmol (0.22 g) of **A1**, 0.14 g Al-Ni (2.5 mmol aluminum), 0.8 g NaOH (20 mmol).

4.1.3 Reductive dechlorination of chlorophene A1 in aqueous solution – effect evaluation of base

The effect of different bases on the RD of **A1** using Al-Ni alloy in aqueous solutions was investigated (*Table 4*). A stock solution of **A1** was prepared by dissolving an appropriate amount of **A1** (10 mmol·dm^{-3}) and an appropriate amount of

15

base (100 mmol·dm^{-3}) in distilled water. Apart from the above mentioned way of dissolving (adding small portion of NaOH) the studied compound, in this case to achieve dissolving total amount of **A1**, the stock solution was heated at around 70 °C. Although in cases of Na_2CO_3 and NaF only heating was not sufficient and a small portion of NaOH (one pellet, ca 0.2 g) was added to the stock solution. The lowest effective amount of Al-Ni alloy for the complete RD of **A1** was 0.27 g (0.135 g; 5 mmol of aluminum) or 0.14 g (0.07 g; 2.5 mmol of aluminum) mainly these amounts had been weighed to the reactions, only the amounts of base differed. Effective amounts of bases needed for the total RD varied a lot, for example in case of Na_3PO_4 only the quantity present in the stock solution (10 mmol in 100 cm^3 of solution with which was made experiment) was sufficient to provide as much as 100% of totally dechlorinated product, however, with a higher amount of Al-Ni alloy, which was probably the main reason for the complete RD of **A1** (see *Table 4, entries 7, 9*). In *Table 4* can be also seen that with higher amounts of base/salt the RD completion percentage increases (*entries 2–6*), but in the case of Na_2CO_3 with increasing amount the percentage of dechlorinated **A1a** is actually decreasing (*entries 16-21*). This phenomenon is in agreement with the fact that the excess of base/salt prevent the dissolution of aluminum from Al-Ni alloy. The reaction mechanism is very complex but from the information we obtained from publications reporting on the same topic[27,28,31] we assume the main steps are as follows: first, the dissolution of the passivated aluminum (Al_2O_3 layer on the surface of Al-Ni alloy) is taking place; subsequently, hydrogen is generated by a reaction of aluminum with water; hydrogen is reacting in assistance by Ni catalyst (probably on Ni surface) with the organic substrate to promote RD and give products (in case of **A1** it is **A1a, A1b** respectively; in case of **C1** it is **C1a**, **C1b**, **C1c** respectively). The basic aqueous solution also helps to secure total dissolution of **A1** and **C1**. As can be seen below in *Table 5*, the higher amounts of dissolved aluminum in the reaction mixture were analyzed the higher conversion to products of total RD. Also the possibility of direct reduction of the substrate by Al-Ni alloy might be taken into account, yet it is a hypothesis which needs to be secured by more information obtained from data as well as from the literature.

Table 4   Effect of used base on the reductive dechlorination of **A1** using Al-Ni alloy.[a]

Entry	Mmol of aluminum (amount of Al-Ni)	Used base (mmol)	NaOH[b] (mmol)	GC-MS (%)		
				A1	**A1a**	**A1b**
1	10 (0.54 g)	NaOH (10)	-	0	83.6	16.4
2	10 (0.54 g)	NaF (10)	1	7.2	92.8	0
3	5 (0.27 g)	NaF (10)	1	36.2	63.8	0
4	5 (0.27 g)	NaF (35)	1	2.9	96.3	0.8
5	2.5 (0.14 g)	NaF (22.5)	1	15.1	84.9	0
6	2.5 (0.14 g)	NaF (35)	1	3.3	96.7	0
7	10 (0.54 g)	Na_3PO_4 (10)	-	0	99.5	0.5
8	10 (0.54 g)	Na_3PO_4 (20)	-	0	100	0
9	7.5 (0.4 g)	Na_3PO_4 (10)	-	0	100	0
10	7.5 (0.4 g)	Na_3PO_4 (17.5)	-	0	100	0
11	5 (0.27 g)	Na_3PO_4 (15)	-	0	100	0
12	5 (0.27 g)	Na_3PO_4 (35)	-	0	100	0
13	5 (0.27 g)	Na_3PO_4 (60)	-	1.5	98	0.5
14	2.5 (0.14 g)	Na_3PO_4 (20)	-	4	96	0

Continuation of Table 4   Effect of used base on the reductive dechlorination of **A1** using Al-Ni alloy.[a]

Entry	Mmol of aluminum (amount of Al-Ni)	Used base (mmol)	NaOH[b] (mmol)	A1	A1a	A1b
9	7.5 (0.4 g)	Na_3PO_4 (10)	-	0	100	0
10	7.5 (0.4 g)	Na_3PO_4 (17.5)	-	0	100	0
11	5 (0.27 g)	Na_3PO_4 (15)	-	0	100	0
12	5 (0.27 g)	Na_3PO_4 (35)	-	0	100	0
13	5 (0.27 g)	Na_3PO_4 (60)	-	1.5	98	0.5
14	2.5 (0.14 g)	Na_3PO_4 (20)	-	4	96	0
15	2.5 (0.14 g)	Na_3PO_4 (35)	-	4	96	0
16	10 (0.54 g)	Na_2CO_3 (10)	1	0	100	0
17	5 (0.27 g)	Na_2CO_3 (10)	1	0	100	0
18	5 (0.27 g)	Na_2CO_3 (35)	1	10	90	0
19	5 (0.27 g)	Na_2CO_3 (110)	1	28.7	71.3	0
20	2.5 (0.14 g)	Na_2CO_3 (22.5)	1	37	63	0
21	2.5 (0.14 g)	Na_2CO_3 (47.5)	1	47.9	52.1	0

[a] **A1** (1 mmol, 0.22 g) in 100 cm^3 aqueous solution of mentioned base (salt respectively) with Al in the form of Al-Ni alloy, ambient temperature (20 – 25 °C) and pressure, stirred at 350 rpm overnight.
[b] Given amount of NaOH is in 100 cm^3 of solution with which was made the experiment. NaOH was added to secure total dissolution of **A1**.

4.1.4 Effect evaluation of reductive dechlorination of chlorophene A1 using Al-Ni alloy in aqueous solution on amount of dissolved aluminum

The content of dissolved aluminum in the reaction mixture was measured by inductively coupled plasma optical emission spectroscopy. The higher the percentage of dechlorinated products (**A1a**, **A1b** respectively) in the reaction mixture, the higher content of dissolved aluminum. In other words the higher content of aluminum in the reaction mixture the more aluminum is available for reduction of chlorinated derivative. Usually in cases when high excess of alloy was used the higher content of dechlorinated product **A1a** was present in the reaction mixture or even the hydrogenation of one aromatic ring was taking place to give the product **A1b**.

Table 5   Effect evaluation of dissolved aluminum on reductive dechlorination of **A1** using Al-Ni alloy in the presence of aqueous NaOH as a base.[a]

Entry	Mmol of aluminum (Al-Ni amount)	NaOH (mmol)	A1	A1a	A1b	Dissolved aluminum ($mg.dm^{-3}$)
1	30 (1.62 g)	35	0	82.5	17.5	4857
2	4 (0.22 g)	10	0	97.8	2.2	891.8
3	4 (0.22 g)	20	0	99.3	0.7	969.1
4	3 (0.16 g)	10	0.4	99.1	0.5	701.2
5	2.5 (0.14 g)	12.5	0	100	0	724.4
6	2.5 (0.14 g)	10	0	100	0	680.8
7	1.3 (0.07 g)	35	24.6	75.4	0	527.8
8	1.3 (0.07 g)	15	45	55	0	415
9	1.3 (0.07 g)	12.5	68.3	31.7	0	160
10	1.3 (0.07 g)	10	61.2	38.8	0	187.7

Continuation of Table 5 Effect evaluation of dissolved aluminum on reductive dechlorination of **A1** using Al-Ni alloy in the presence of aqueous NaOH as a base.[a]

Entry	Mmol of aluminum (Al-Ni amount)	NaOH (mmol)	GC-MS (%)			Dissolved aluminum (mg.dm^{-3})
			A1	**A1a**	**A1b**	
11	0.74 (0.04 g)	35	77.6	22.4	0	125
12	0.74 (0.04 g)	20	83.7	16.3	0	96.8

[a] **A1** (1 mmol, 0.22 g) in 100 cm^3 aqueous solution of NaOH, aluminum in the form of Raney Al-Ni, room temperature, stirred vigorously overnight. In the table are listed total amounts of NaOH (including the amount in the stock solution).

4.1.5 Effect evaluation of used alloys for reductive dechlorionation of triclosan C1

The experimental procedure was the same as mentioned in section 4.1.1. Only in this case was also tested the elevated temperature of the reaction mixture. The effect of elevated temperature on the reaction was tested in case of Devarda's and Arnd's alloys by heating of the reaction mixture at reflux for tens of minutes (30 – 120 minutes, *Table 6, entries 3, 5*). Nevertheless, none of these actions were leading to any products of RD whatsoever using both Cu based alloys. One of the reasons for the failure in the case of Devarda's and Arnd's alloys could be the higher stability of the C_{aryl}-Cl bond compared with the C_{aryl}-Br bond.[33]

Table 6 Effect of used alloy on the reductive dechlorination of **C1**[a]

Entry	Used alloy	Quantity of alloy (g)	Reductant (mmol)	NaOH (mmol)	Reflux time (min)	Content of unreacted **C1** (%)
1	Devarda's Al-Cu-Zn	0.96	Al (16)	20	-	100
2		1.92	Al (32)	20	-	100
3		0.6	Al (10)	25	120	100
4	Arnd's Cu-Mg	0.55	Mg (10)	35	-	100
5		0.53	Mg (9)	55	60	100
6	Raney Al-Ni	1.08	Al (20)	35	-	0
7		0.56	Al (10)	35	-	0

[a] **C1** (1 mmol, 0.29 g) dissolved in NaOH, alloy and NaOH were added (heated) and stirred at 350 rpm overnight without heating.

4.1.6 Effect evaluation of Al-Ni alloy amount on reductive dechlorination of triclosan C1 in aqueous NaOH solution

In preliminary experiments a high excess of reduction agent over **C1** was used. Amounts of alloy were gradually lowered and amounts of NaOH were adjusted to optimize the process. The results can be seen in *Table 7*. It was found that optimal conditions for complete RD were when using at least 0.22 g of Al-Ni alloy (i.e. 4 mmol of aluminum) and 0.8 g NaOH (20 mmol), see *Table 7, entry 7*. These ratios (substrate:metal:base) are far lower than reported.[24-28]
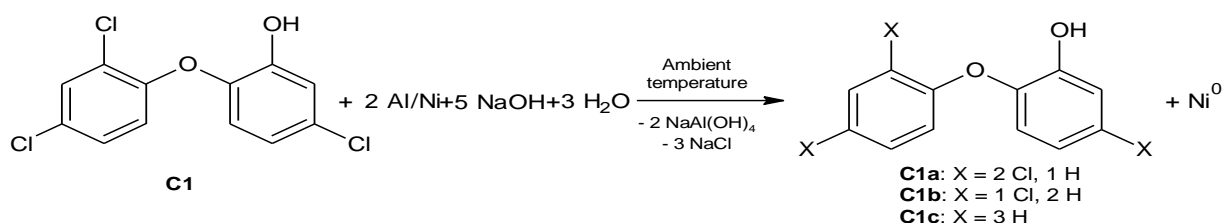
Scheme 2 Reductive dechlorination of **C1** using Raney Al-Ni alloy in the presence of NaOH.

Table 7   Reductive dechlorination of **C1** using Al-Ni alloy.[a]

Entry	Mmol of aluminum (Al-Ni amount)	NaOH (mmol)	GC-MS (%)			
			1	**1a**	**1b**	**1c**
1	20 (1.08 g)	35	0	0	0	100
2	10 (0.54 g)	35	0	0	0	100
3	10 (0.54 g)	20	0	0	0	100
4	7.5 (0.4 g)	20	0	0	0	100
5	5 (0.27 g)	20	0	0	0	100
6	5 (0.27 g)	35	0	0	0	100
7	4 (0.22 g)	20	0	0	0	100
8	3 (0.16 g)	30	7.7	8.9	9.4	74
9	3 (0.16 g)	20	20.3	11	17.7	51
10	5 (0.27 g)	30	0	0	0	100
11	3 (0.16 g of Al foil[b])	30	99	1	0	0
12	3 (0.16 g of Al foil[c])	30	100	0	0	0

[a] **C1** (1 mmol, 0.29 g) in aqueous NaOH, stirred at 350 rpm overnight at ambient temperature.
[b] Decanted Ni slurry produced in entry 10 was used together with Al foil.
[c] Decanted Ni slurry produced in entry 11 was used together with Al foil.

In order to see the RD of **C1** (1 mmol) profile in time the experiments were conducted (*Fig. 4*) using 0.27 g of Al-Ni alloy (i.e. 5 mmol of aluminum) and 0.8 g NaOH (20 mmol). As it can be seen in *Fig. 2*, after 480 minutes there was about 90% of totally dechlorinated 2-phenoxyphenol **C1c** and there were only traces of **C1** in the reaction mixture. After approximately 24 hours, **C1c** was the only product present in the reaction mixture.

The observed time consumption goes against the results of other scientists who were able to reduce the reaction times to several minutes or several hours, however, those experiments were conducted either at increased temperature or by using way higher substrate:metal:base ratios.[21,22,24-30] Surprisingly, in case of Choi and Kim[24] the reaction times are in days though the metal is in high excess against the organic substrate – RD of 2,4,6-TCP by zinc or zinc bimetals (Zn/Pt, Zn/Pd, Zn/Ni, Zn/Cu). The results are not satisfactory, after 20 days the total degradation was achieved only with Zn/Pd. Yang et al.[27,28] reports RD of 2-chlorophenol (2-CP) by Al-Ni alloy at ambient temperature and pressure in times around 45 – 120 minutes. However, the excess of reducing metal was 24:1 (aluminum:2-CP). It is worth mentioning that this kind of excess was used for a molecule containing only one chlorine atom whereas in case of **C1** there are three chlorine atoms in the molecule.
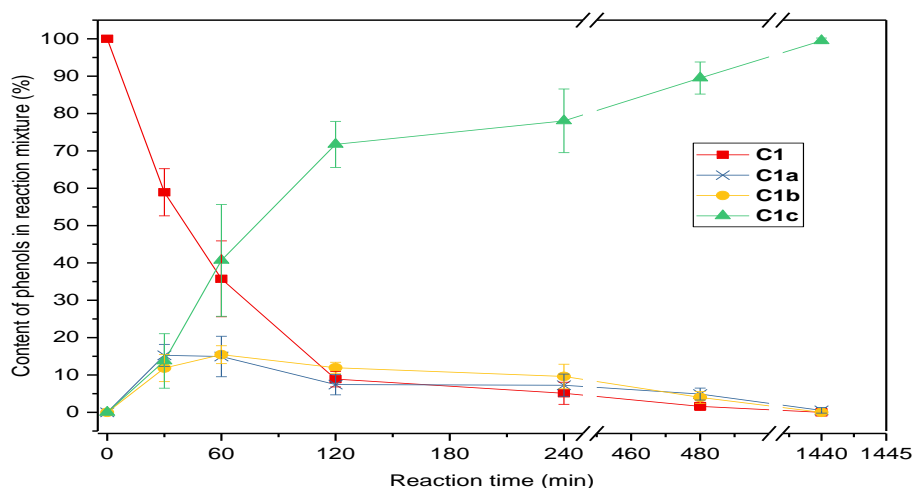
Fig. 4 Time course of RD of **C1** by Al-Ni/NaOH. Reaction conditions: room temperature (20 °C), ambient pressure, stirred at 350 rpm; 1 mmol (0.29 g) of **C1** and 0.8 g NaOH (20 mmol) dissolved in H_2O (100 cm^3) + 0.27 g Al-Ni (5 mmol of aluminum). (■) **C1**, (×) dichloro isomers **C1a**, (●) monochloro isomers **C1b**, (▲) 2-phenoxyphenol **C1c**.

An economic aspect of the reaction and possible multiple re-using of the alloy used in high excess is an important part in considering the practical application of the alloy for RD.[27,28] However, the experiments on recyclability of the Al-Ni alloy were conducted with co-action of Al-foil as possible source of Al reductant with unsatisfactory results (*Table 7, entries 10-12*).

4.1.7 Reductive dechlorination of triclosan C1 in aqueous solution – effect evaluation of base

The effect of different bases on the RD of **C1** using Al-Ni alloy in aqueous solutions was investigated (*Tables 8, 9*). A stock solution of **C1** was prepared by dissolving an appropriate amount of **C1** and an appropriate amount of base in distilled water. An important fact to mention is that in some cases (*Table 8, entries 3 – 7, 14 – 18, Table 5*) the basicity of the bases (or alkaline salts) was not sufficient to deprotonate and dissolve **C1** (pKa of **C1** is 7.9)[58] Thus a low quantity of stronger base, such as NaOH had to be used to prepare the aqueous stock solution. Amounts of base/salt needed for the complete RD varied a lot, e.g. in case of Na_3PO_4 the quantity present in the stock solution was sufficient to provide as much as 96% of totally dechlorinated product **C1c** (*Table 8, entry 8*).

Table 8 Effect of used base on the reductive dechlorination of **C1** using Al-Ni alloy.[a]

Entry	Mmol of aluminum (amount of Al-Ni)	Used base (mmol)	NaOH[b] (mmol)	GC-MS (%)			
				1	**1a**	**1b**	**1c**
1	10 (0.54 g)	KOH (2)	-	0	0	0	100
2	10 (0.54 g)	NaOH (10)	-	0	0	0	100
3	10 (0.54 g)	NaF (10)	1	28.8	45.8	11.5	13.9
4	10 (0.54 g)	NaF (35)	1	1.8	3.3	0.8	94.1
5	5 (0.27 g)	NaF (35)	1	12.4	23.6	8.5	55.5
6	5 (0.27 g)	NaF (85)	1	81.4	9,5	2.1	7
7	2.5 (0.14 g)	NaF (35)	1	47.6	34	5.6	12.8
8	10 (0.54 g)	Na_3PO_4 (10)	-	0	0	4	96
9	5 (0.27 g)	Na_3PO_4 (11)	-	9.2	23.5	13.8	53.5

Continuation of Table 8   Effect of used base on the reductive dechlorination of **C1** using Al-Ni alloy.[a]

Entry	Mmol of aluminum (amount of Al-Ni)	Used base (mmol)	NaOH[b] (mmol)	GC-MS (%)			
				1	**1a**	**1b**	**1c**
10	5 (0.27 g)	Na_3PO_4 (15)	-	10.4	25.4	16.2	48
11	10 (0.54 g)	Na_2CO_3 (10)	-	68	24.2	5.7	2.1
12	5 (0.27 g)	Na_2CO_3 (10)	-	68	24.7	4.6	2.7
13	5 (0.27 g)	Na_2CO_3 (35)	-	70.3	24.9	4.3	0.5
14	10 (0.54 g)	CH_3COONa (10)	1	54	28.9	8.3	8.8
15	5 (0.27 g)	CH_3COONa (35)	1	73	18.5	5.5	3.0
16	10 (0.54 g)	CH_3COONH_4 (10)	5	4.1	24.5	21.4	50
17	5 (0.27 g)	CH_3COONH_4 (10)	5	11.2	29.8	13.6	45.4
18	5 (0.27 g)	CH_3COONH_4 (35)	5	100	0	0	0

[a] To **C1** (1 mmol, 0.29 g) dissolved in 100 cm^3 of aqueous solution of mentioned base (or salt) Al-Ni alloy was added and stirred at 350 rpm overnight at ambient temperature.
[b] Given amount of NaOH is in 100 cm^3 of solution with which was made the experiment. NaOH was added to secure total dissolution of **C1**.

In most cases, a high excess of added salts tested as bases negatively influenced the RD of **C1**, see *Table 8*. This fact corresponds with observations published earlier.[31,33] For effective RD using Al-Ni alloy formation of soluble Al^{3+} salts ($NaAl(OH)_4$) is crucial. Most of the tested salts used instead of NaOH retards oxidation of aluminum added as Al-Ni alloy and/or prevent subsequent dissolution of oxidized Al^{3+} from the Al-Ni alloy surface into the alkaline aqueous solution, which is accompanied by failure of RD.

4.2   Electro-oxidative removal of triclosan C1 from aqueous solutions

4.2.1   Sorption evaluation of triclosan C1 to the experimental equipment

At first initial sorption experiments were conducted to see if **C1** is adsorbing to surfaces of tubings, cell and reservoirs of the experimental equipment. Results were surprising – **C1** was heavily adsorbed to the surface of almost all plastic tubing used. This has led to a need to avoid working with plastics during the manipulation with **C1** solutions. When dissolved in methanol, there was no sorption to any surfaces of the equipment however a strong sorption was observed while working with low concentrations of **C1**. After 60 minutes of **C1** solution circulating through off electrolysis cell with different types of tubing the sorption was between 55-80 %.

Many different types of tubing were tested. Teflon tubing was the final choice as it showed no signs of **C1** sorption. However, there was still difficulty with the pump tubing which was plastic and PTFE tubing could not be used in the pump because of its rigid properties and special requirements. For this setup sorption tests were carried out to quantify the sorption alone in presence of different electrolytes; results are shown in *Figure 5*. When the plastic parts of the equipment were reduced as much as possible, the sorption after 80 minutes of circulating was around 20%. Percentage of **C1** sorption was increasing with increasing electrolyte concentration. Although many studies of **C1** has been carried out, the sorption has only been taken into account in a few studies, and it is likely that sorption may have contributed significantly to more than 50 % of the **C1** dissipation observed and misleadingly has been attributed to true

degradation. Our study confirm that **C1** bind strongly to plastics nevertheless the sorption to glassware is almost none.[59,60]

Since **C1** is not adsorbing to glass, using glass reactors and tubing could be a good solution to the sorption problem but in our case it was not possible to avoid the usage of plastic. However by use of PTFE tubing the sorption problem could be minimized. It was also found, that PTFE syringe filters could not be used for filtration probably because of **C1** sorption to the plastic parts of the filter. However PTFE filters were far better than glucose or nylon syringe filters where the recovery was close to zero and almost whole content of **C1** was adsorbed to the filters. Due to the filter sorption problem it was decided not to filter solutions from the reactor, and HPLC analysis was done without any further filtration. In the solution wasn´t any precipitation and the HPLC pressure was constantly about 56 bar (± 2 bar) which did not implicate any column clogging.
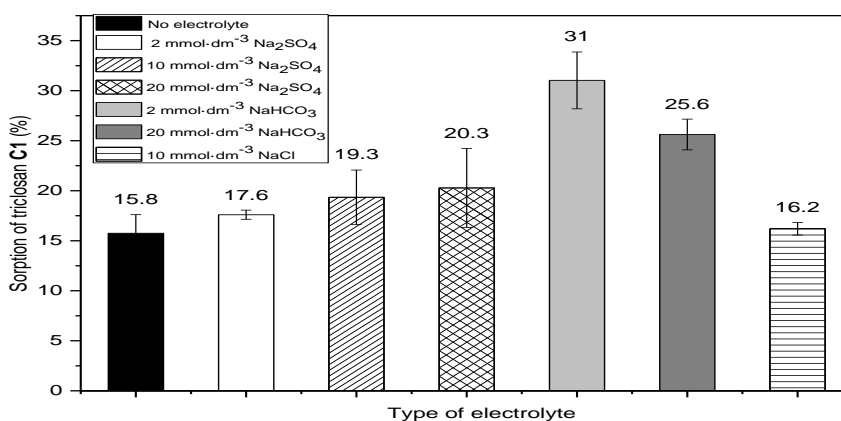

Fig. 5 Sorption of **C1** (electrolysis cell off) in the presence of various supporting electrolytes. Initial reaction conditions: 10 mg·dm^{-3} **C1**, flow rate 50 ml·min^{-1}, no iron(II), I = 0 A. Duration of experiment was 80 minutes. Error bars represent standard deviation of duplicates.

4.2.2 Electro-Fenton degradation of triclosan C1

In the degradation experiments the sorption was deducted from the overall decrease of **C1** during the process. The possible effect of added iron(II) on sorption was not investigated.

Figure 6a depicts the effect of flow rate on sorption and degradation. It is evident that the sorption at a flow of 100 ml·min^{-1} is almost double that at a flow of 50 ml·min^{-1}. The degradation rate is similar for both flow rates but since the sorption at 50 ml·min^{-1} is lower than at 100 ml·min^{-1} it was decided to carry out further experiments at a flow rate of 50 ml·min^{-1} to secure enough time of contact of the solution with the electrodes.
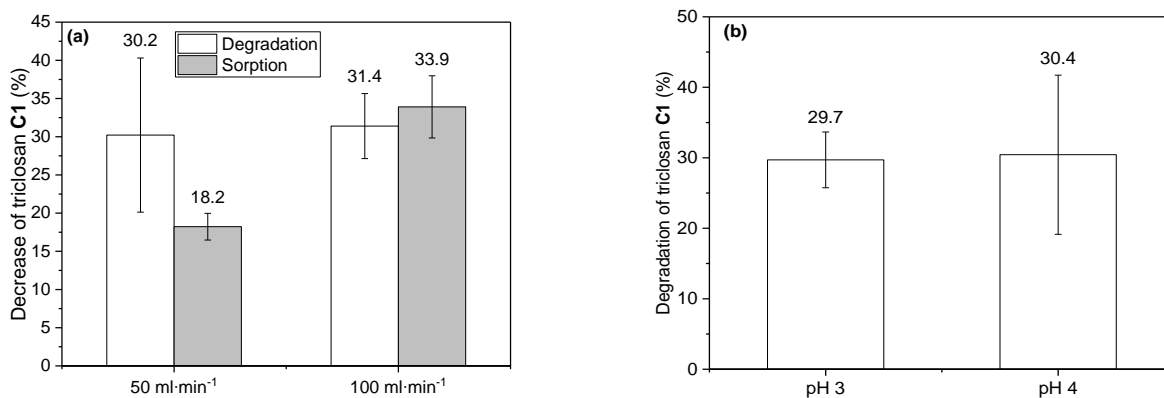
Fig. 6 Electro-Fenton degradation of **C1** depending on flow rate and pH. (**a**) Effect of flow rate on degradation and sorption of **C1**, (**b**) effect of pH on **C1** degradation. Initial reaction conditions: (**a**) and (**b**) 10 mg·dm^{-3} **C1**, 5 or 50 mg·dm^{-3} iron(II), 2 or 20 mmol·dm^{-3} sodium sulfate. Duration of experiments was 80 minutes. For (**a**) the data sets are averages of 24 conducted experiments, for (**b**) the data sets are averages of 17 conducted experiments. Error bars represent standard deviation. In (**b**) the degradation values are shown with already deducted sorption.

Experiments with different initial pH were also conducted (see *Figure 6b*). Since the classical Fenton process was conducted in acidic medium[44] and most of the studies reported that the optimum pH of Fenton process is around 3[61-64], pH values of 3 and 4 were compared. Acidic pH was adjusted by adding 1 mol·dm^{-3} sulfuric acid until the desired pH value. As can be seen no significant difference in degradation could be observed between those two pH values during our studies but pH 4 was preferred since there was a decrease of pH during the process in contrast with other electro-Fenton studies where the pH was increasing and leading to a decrease of iron(II) ions (which are at higher pH oxidized to iron(III) causing precipitation as ferric hydroxide particles[52]) lowering the speed of the electrolytic process.[61,63] On the other hand lower pH might affect the *in situ* generation of H_2O_2 because of the competing hydrogen evolution at the electrode and also because iron species form stable complexes with H_2O_2 at lower pH values, leading to deactivation of iron catalysts.[63,65]
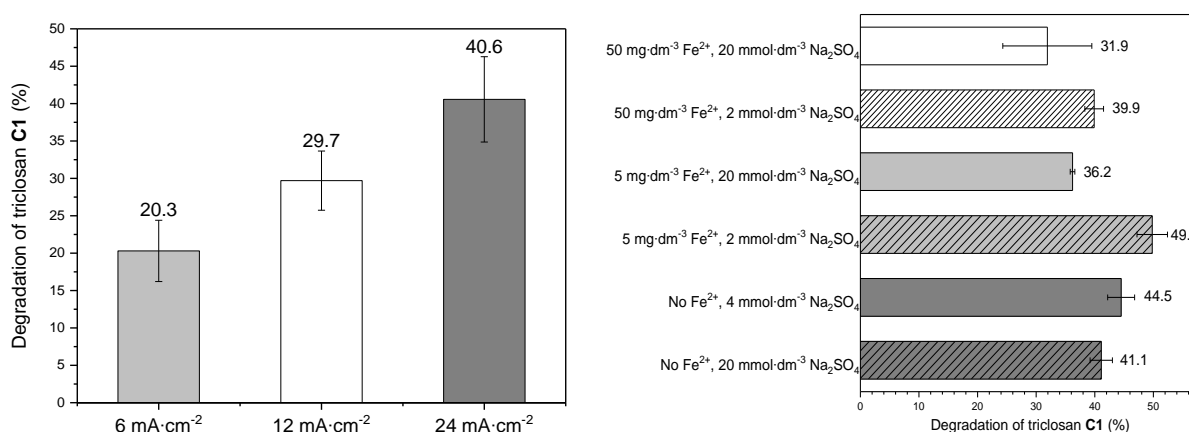

Fig. 7 Electro-Fenton degradation of **C1** as a function of current density and iron(II). (**a**) Effect of current density on **C1** degradation, (**b**) effect of iron(II) and supporting electrolyte concentrations at current density 24 mA·cm^{-2} on **C1** degradation. Initial reaction conditions: (**a**) 10 mg·dm^{-3} **C1**, 5 or 50 mg·dm^{-3} iron(II), 2 or 20 mmol·dm^{-3} sodium sulfate, data sets are averages of 17 conducted experiments. (**b**) 10 mg·dm^{-3} **C1**,

current density 24 mA·cm^{-2}, pH 4, flow rate at 50 ml·min^{-1}. Duration of experiments was 80 minutes. Error bars represent standard deviation of duplicates.

Different current densities had been tested for the purpose of **C1** degradation (*Figure 7* above). The best results were obtained by using the current density of 24 mA·cm^{-2} even though the differences between various current densities are only around 10 percent. There is a clear trend of increasing **C1** degradation rate with increasing current density.

When the optimal current density of the degradation process was determined, various concentration of iron(II) sulfate and also various concentration of sodium sulfate as supporting electrolyte were studied with set current density of 24 mA·cm^{-2}. The best results were obtained (almost 50% of **C1** degradation) with 5 mg·dm^{-3} of iron(II) sulfate concentration and 2 mmol·dm^{-3} of sodium sulfate. It could be seen that increasing the concentrations of iron(II) did lead to decrease in the degradation rate while the sodium sulfate concentrations stayed at 2 mmol·dm^{-3}. However when sodium sulfate concentration increased to 20 mmol·dm^{-3} (with iron(II) concentration at 50 mg·dm^{-3}), another decrease of degradation rate of **C1** followed. It seems that shift in sodium sulfate concentration makes larger impact on the degradation rate than that of iron(II) concentration but in the end the differences are not very significant.

4.2.3 Iron(II) content progression during electro-oxidation of triclosan C1

Progression of iron(II) concentration throughout the process was analyzed by the 1,10-phenantroline method[55] using UV-VIS spectroscopy. Concentrations of both iron(II) and iron(III) were decreasing during the process, and after 80 minutes of electrolysis there was almost no iron(II) present in the solution but instead total soluble iron was still detected. We are assuming that most of the iron precipitated according to the results of soluble iron analysis. No significant difference was observed between 2 mmol·dm^{-3} and 20 mmol·dm^{-3} sodium sulfate electrolyte concentration in experiments with a current density of 24 mA·cm^{-2} nor between different initial concentrations of iron(II) (*Figure 8a, 8b*). Same conclusions apply for *Figures 9a* and *9b* with current density of 6 mA·cm^{-2}. No significant differences could be seen between current densities of 24 and 6 mA·cm^{-2} (compare *Figures 8a, 8b* with *Figures 9a, 9b*).

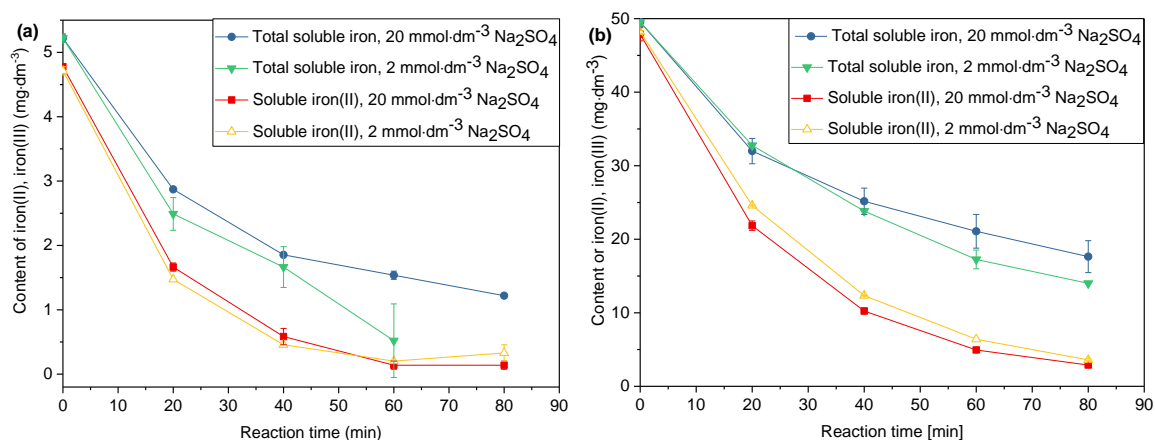**Fig. 8** Time course of iron(II) concentration and total soluble iron throughout **C1** degradation experiments with current density 24 mA·cm^{-2} and with various initial iron(II) concentration.

Initial reaction conditions: (**a**) 5 mg·dm^{-3} iron(II), 2 or 20 mmol·dm^{-3} sodium sulfate, 10 mg·dm^{-3} **C1**, current density 24 mA·cm^{-2}, pH 4, flow rate 50 ml·min^{-1}. For (**b**), 50 mg·dm^{-3} initial iron(II), 2 or 20 mmol·dm^{-3} sodium sulfate, 10 mg·dm^{-3} initial **C1**, current density 24 mA·cm^{-2}), pH 4, flow rate 50 ml·min^{-1}. Duration of experiments was 80 minutes. Error bars in (**a**) and (**b**) represent standard deviation of duplicates.

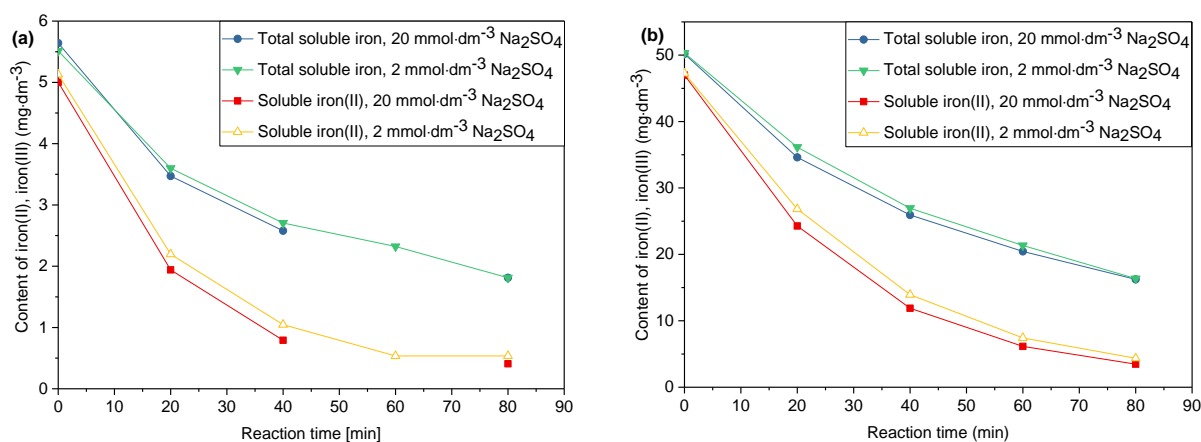**Fig. 9** Time course of iron(II) and total soluble iron concentration throughout **C1** degradation experiments with current density of 6 mA·cm^{-2} and with various initial iron(II) concentration. Initial reaction conditions: (**a**) 5 mg·dm^{-3} iron(II), 2 or 20 mmol·dm^{-3} sodium sulfate, 10 mg·dm^{-3} **C1**, current density 6 mA·cm^{-2}, pH 4, flow rate 50 ml·min^{-1}. (**b**) 50 mg·dm^{-3} iron(II), 2 or 20 mmol·dm^{-3} sodium sulfate, 10 mg·dm^{-3} **C1**, current density 6 mA·cm^{-2}, pH 4, flow rate 50 ml·min^{-1}. Duration of experiments was 80 minutes. Error bars in (**a**) and (**b**) represent standard deviations of duplicates.

As a main conclusion we have found out that **C1** degradation using electrolytic procedure described above is between 30–50 % after 80 minutes of experiment. If we take a look to other studies on similar topic, results vary widely according to the type of electrodes used. Sirés et al.[66] reports total disappearance of **C1** after 8–120 minutes with many different setups, such as different electrodes (Pt/carbon felt cell; Boron-dopped electrode (BDD)/carbon felt cell; Pt/O$_2$ diffusion cell; BDD/ O$_2$ diffusion cell), adding iron(III) as a Fenton reagent, different initial **C1** concentrations etc. Nevertheless our method gives lower degradation percentage in comparison with Sirés et al.[66]. Another study with comparable results as ours reports about **C1** degradation between 42–62% when using electrolytic cell made of titanium coated with RuO$_2$/IrO$_2$ as anode and stainless steel as cathode with iron(II) and hydrogen peroxide as Fenton reagents[67]. Both of those studies were conducted in batch electrolytic systems and did not take into account possibility of **C1** sorption so the results may not reflect the true degradation.

Conclusion

The main aim of this thesis was to study different ways of degradation of chlorinated aromatic compounds in aqueous solutions. Chlorinated phenols, frequent wastewater contaminants, are characterized by their high toxicity to living organisms, especially because of their carcinogenic, mutagenic and cytotoxic properties. Therefore the effective way of remediation was necessary.

In terms of practical research two main substances were studied - chlorophene and triclosan. Reductive dehalogenation and electro-Fenton oxidation were among the two main degradation methods used in this work. Reductive dehalogenation proceeds in comparison with other described methods of degradation under relatively mild conditions using cheap and non-toxic substances (metal alloys, common bases), it was successfully used in the Institute of Environmental and Chemical Engineering to remove various types of aromatic halogen derivatives. Other method of degradation was electrochemical, so-called electro-Fenton oxidation using a special electrochemical cell. This method of degradation was used only to remove triclosan from aqueous solutions, chlorophene was not studied this way.

For the purposes of the reductive dehalogenation study, three metal alloys were tested, the best results were obtained with Raney Al-Ni alloy, reductive dechlorination did not take place with other tested alloys (Devarda´s Al-Cu-Zn, Arnd´s Cu-Mg alloy). Furthermore various types of bases and their influence on the removal of studied chlorinated phenols by reductive dehalogenation were tested. The results have shown that this method of removal is effective and unlike today's popular halogenated pollutant degradation techniques, there are no toxic by-products such as PCBs or PCDDs/PCDFs but dehalogenated phenols that are better biodegradable after dehalogenation without bound chlorine atoms.

Another method of degrading chlorinated phenols (in this case only triclosan) was electro-Fenton oxidation. It was tested in cooperation with a Danish company that deals with sanitation of domestic water resources using electrochemistry and which lent a special electrolytic cell for research. Again, various reaction conditions have been tested, such as the type of electrolyte and its concentration, different current density, pH, different flow rates, etc. This degradation method has also shown that it may be an alternative to the techniques currently used to remove halogenated pollutants from surface water.

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