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**Unconventional processes for effective removal of problematic pollutants from
wastewater and solid waste**

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Abstract

This dissertation thesis studied non-conventional techniques of removal of persistent pollutants such as halogenated aromatic compounds (represented by selected drugs, dyes and pesticides) from aqueous solutions. Separation of contaminants (drugs – flufenamic acid and diclofenac and Mordant Blue 9 dye) was tested using adsorption on carbonaceous sorbents such as activated carbon or biochar. The possibility of using commercial ionic liquids to increase biochar sorption capacity was also tested. The next part of this thesis studies the possibilities of chemical degradation of concentrated aqueous solutions of halogenated pollutants using reductive hydrodehalogenation. Hydrodehalogenation using the Raney (Al-Ni) alloy or Devarda's (Al-Cu-Zn) alloy in diluted aqueous sodium or potassium hydroxide was verified to be a very efficient degradation method for the tested halogen aromatic derivatives. The last research part of this thesis was focused on regeneration and recycling of ion pairs produced by action of the above-mentioned ionic liquids on halogenated organic acids or their salts, respectively. Chemical reduction of the ion pairs using $\text{NaBH}_4/\text{NiSO}_4$ and/or the Raney Al-Ni alloy was found to be capable of regenerating the used ionic liquids which can be applied in a subsequent process of ion exchange, even in several cycles. The thesis presents a complex research of linked steps of halogenated organic contaminants removal from aqueous solutions. The results have been published in seven journals and presented at national as well as international conferences in lectures and as posters; additionally, results constitute a chapter in a book and are included in a national patent.

Abstrakt

V této disertační práci byly studovány nekonvenční techniky odstraňování persistentních, biologicky obtížně rozložitelných halogenovaných organických polutantů (zastoupenými vybranými sloučeninami z řad léčiv, barviv a pesticidů) z vodných roztoků. Jako první krok byla testována separace kontaminantů (léčiva Diklofenak a Flufenamová kyselina, barviva Mordant Blue 9) z vod adsorpcí na uhlíkatých sorbentech jako je aktivní uhlí a alternativní levnější sorbent biochar. Byla také ověřena efektivní možnost aplikace komerčně dostupných iontových kapalin pro navýšení sorpčních kapacit biocharu nebo již nasyceného aktivního uhlí. Další část výzkumu této disertační práce byla zaměřena na regeneraci a recyklaci iontových párů vznikajících působením zmíněných iontových kapalin na halogenované organické kyseliny. Bylo zjištěno, že chemickou redukcí iontových párů pomocí NaBH_4 a/nebo Raneyovy slitiny Al-Ni je možné regenerovat iontové kapaliny a využít v dalším procesu iontové výměny, a to až v několika cyklech. Poslední část práce srovnávala účinnosti konvenční metody chemické degradace vybraných halogenovaných polutantů Fentonovou oxidací a inovativní metody jejich reduktivní hydrodehalogenace pro možné zpracování koncentrovaných proudů kontaminantů vznikajících při pyrolytické

desorpci aktivního uhlí. Bylo ověřeno, že reduktivní hydrodehalogenace vybraných polutantů pomocí Raneyovy (Al-Ni) nebo Devardovy slitiny (Al-Cu-Zn) v prostředí hydroxidu sodného nebo draselného je velmi efektivní metodou degradace halogenderivátů. Tato disertační práce prezentuje komplexní výzkum na sebe navazujících kroků odstraňování halogenovaných organických kontaminantů z vodných roztoků. Výsledky zmíněného výzkumu byly publikovány v sedmi impaktovaných zahraničních časopisech, byly prezentovány na třinácti národních a šesti mezinárodních konferencích formou přednášek a plakátových sdělení a jsou součástí kapitoly v knize a národního patentu.

Keywords

halogenated drugs, acid azodyes, pesticides, diclofenac, flufenamic acid, Mordant Blue 9, Bromoxynil, adsorption, biochar, ionic liquid, ion-exchange, chemical degradation, hydrodehalogenation

Klíčová slova

halogenovaná léčiva, kyselá azobarviva, halogenované pesticidy, Diklofenak, Flufenamová kyselina, Mordant Blue 9, Bromoxynil, adsorpce, biochar, iontová kapalina, iontová výměna, chemická degradace, hydrodehalogenace

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Introduction

Aromatic halogen derivatives are widespread and have been used ever more extensively as drugs, pesticides, dyes or pigments and other commercial products [1]. These compounds are often classified as persistent organic contaminants with bioaccumulation in the environment and are highly resistant against degradation [2-4]. The use and sometimes also improper application of aromatic halogen derivatives in the industry or agriculture enable these compounds to enter environmental components, which may cause adverse effects in the environment [5].

However, the biological stage of wastewater treatment plants is not able to fully degrade these mentioned halogenated contaminants, and therefore more efficient methods of their removal from water are being sought [6]. Among many technologies aimed at separation of halogen derivatives from wastewater, adsorption on activated carbon (AC) is commonly used [7,8]. The industrial application of activated carbon to remove of polar acidic contaminants is costly due to the relatively low affinity of polar organic compounds for nonpolar AC surface and also due to the high price of this sorbent. In recent years, inexpensive carbonaceous sorbents produced from waste biomass (e.g. biochar) started to be tested with the aim to reduce the costs of wastewater treatment [9]. On the other hand, the adsorption capacity of biochar is lower compared to activated carbon [10]. Nevertheless, there are impregnation possibilities of carbonaceous sorbents (e.g. using ionic liquids), which lead to an increase of biochar adsorption capacity.

The chemical degradation techniques for treatment of concentrated streams of halogenated contaminants obtained after desorption of depleted activated carbon was often studied as well. Besides conventional methods of studied pollutants degradation (e.g. Advanced Oxidation Processes, AOPs) [11], the innovative reductive hydrodehalogenation (HDH) using aluminium based alloys was verified too [12]. HDH using a Raney Al-Ni alloy [13] or Devarda's Al-Cu-Zn alloy [14] in aqueous alkaline metal hydroxide solutions was verified as promising reductive degradation method for organic halogenderivatives in aqueous solutions. It is a possible way for detoxification of chlorinated/brominated organic compounds without production of toxic by-products [12,15].

This thesis also describes new method available for regeneration of ion pair (produced upon action of the above-mentioned ionic liquids on halogenated organic acids or their salts) using chemical reduction with $\text{NaBH}_4/\text{NiSO}_4$ and/or Raney Al-Ni alloy. Produced ion pairs can be effective and easily recycle in several cycles. This work was the object of our research team patent No. 308220B6, Czech rep. [16].

This Ph.D. thesis presents the effective methods for removal of halogenated organic pollutants (represented by drugs, dyes and pesticides) from model wastewater. This work also deals with a complex research of linked steps of mentioned problematic pollutants removal from aqueous solutions.

1 Theoretical Part

1.1 Problematic contaminants

Aromatic halogen derivatives are widespread and have been used ever more extensively [1]. Fine chemicals with attached halogen group(s) are used as dyes or pigments, pesticides, drugs, flame retardants, etc. These compounds are often persistent, bio-accumulative and highly resistant against (bio)degradation [2-4].

The chlorinated azo dye Mordant Blue 9 (MB9, see Fig.1) is a widely used dye with a worldwide production of hundreds of tons. This dye is applied for dyeing of silk, wool or nylon [17,18]. Another similar acid chlorinated azo dye is Acid Yellow 17 (AY17), see Fig. 2.

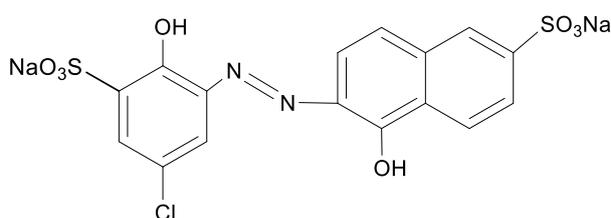


Figure 1 Chemical structure of MB9

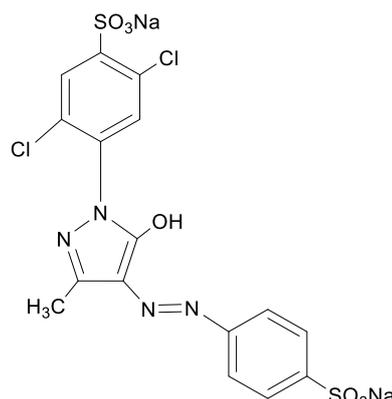


Figure 2 Chemical structure of AY17

Diclofenac (DCF; Fig. 3) is an analgesic-antiflogistic drug (NSAID). DCF is effective in treating of acute inflammations and painful conditions. This medicament belongs to the very frequently used drugs. The global market produces about 1000 tons of diclofenac per year [19]. The almost similar NSAID is flufenamic acid (FFA), see Fig. 4. FFA is polyfluorinated compound and is not widely used for treating of inflammations due to gastrointestinal side effects [20].

Herbicide Bromoxynil (BXN, see Fig. 5) can be applied to control of broadleaf weeds. In the recent years, the consumption of this herbicide increases due to replacement for banned pesticides (e.g. atrazine) [21].

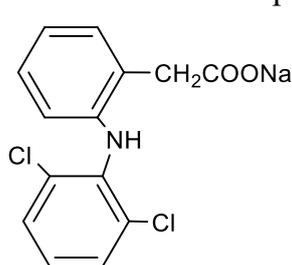


Figure 3 Chemical structure of DCF, sodium salt

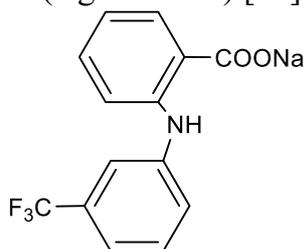


Figure 4 Chemical structure of FFA, sodium salt

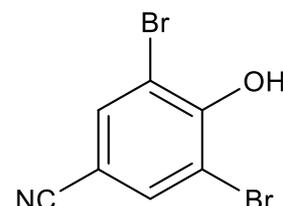


Figure 5 Chemical structure of BXN

1.2 Adsorption

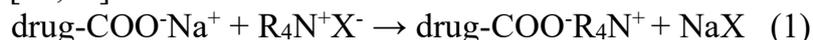
Among many technologies aimed at halogen derivatives separation from wastewater, adsorption on activated carbon (AC) is commonly used [7,8]. Range of scientists [22-25] verified high sorption efficiency of diclofenac using different types of commercially activated carbons. It was also published many works focused on adsorption of (acid) dyes on AC. These publications describe the high adsorption

capacity of AC too [26-30]. Available studies also show that powdered AC is better sorbent than granulated activated carbon [22,23]. High adsorption capacities of powdered AC are in a good agreement with high specific area of this sorbent [25].

However, industrial application of activated carbon is costly due to the relatively low affinity of polar organic compounds to AC and also due to the high price of AC. In addition, the depleted activated carbon has to be combusted at hazardous waste incinerators [5] or recovery using pyrolysis [5,6]. In recent years, inexpensive sorbents produced from waste biomass (e.g. biochar) was tested [10,33]. On average, biochar is cheaper by approx. USD 700 per tonne than the powdered activated carbon [33].

Researchers [34-39] have studied the application of biochar prepared by pyrolysis from sewage or different agricultural waste for removal of selected dyes or pharmaceuticals from model wastewater. Lonnappan et al. [34-37] published several works focused on sorption of anti-inflammatory drug diclofenac on biochar. They described the application of biochar produced from pig manure or pine wood. These biochars reported relatively good results of DCF sorption [35,36]. However, other scientists tested sorption of DCF on biochar too. For example, Solanki and Boyer [38] tested the biochar produced from bamboo or shells or Weidemann et al. [39] tested the biochar produce from agricultural waste. All of these scientists describe relatively good efficiency of DCF removal using sorption on biochar, though the sorption on biochar was performed at low diclofenac concentrations ($\mu\text{g/L}$ or mg/L) and higher dosages of biochar (mg/L or even g/L). Scientific papers [40-44] also presented the sorption of acid dyes on discussed carbonaceous sorbent. Biochar produced from wood or green waste, nuts shells, bamboo waste, even sewage sludge was tested. The findings show almost similar results such as DCF – good efficiency of sorption at low concentration of dyes using relatively high dosages of biochar [40-44].

Thus, the adsorption capacity and removal efficiency of alternative cheaper adsorbent biochar is lower compared to commercially AC [10]. However, as was proved in this work, application of carbonaceous sorbent biochar with co-action of ionic liquids is a possible way to increase the removal efficiency of organic acids and their salts from aqueous solution [45]. Ionic liquids are ionic compounds including large organic cations and inorganic or organic anions (quaternary ammonium salts – R_4NX ; where R_4 is an alkyl chain and X is an anion, typically halide Cl^- , Br^-) [46,47]. These compounds have also found application in an innovative method of separation of acidic contaminants from water [48]. The method is based on addition of R_4NX to the aqueous solution of an organic acid (e.g. DCF or MB9), which results in ion-exchange and subsequent formation of hydrophobic (low soluble) ion pairs [48,49]. Described ion exchange is illustrated by chemical equations (1) and (2). Our research group tested the possibilities of co-action of mentioned ionic liquids (R_4NX) with biochar (*in situ* biochar impregnation) [50,70].



1.3 Chemical degradation

Significant efforts have been made to develop new and efficient chemical degradation processes of drugs, dyes or pesticides removal from water. Advanced oxidation processes (AOPs) were tested as one of the promising methods due to successful removal of organic pollutants. For example, oxidative degradation of

problematic pollutants using O₃, O₃/H₂O₂, UV/H₂O₂, photo/Fenton processes or sonolysis were studied [11,51-56]. However, these treatment processes can be limited by high operational costs, technologically complex equipment and relatively long time of degradation [52]. Several toxic by-products including highly toxic PCDD/Fs can be also produced via some described processes [52,53].

Due to above-mentioned reasons, the reductive methods – such as hydrodehalogenation (HDH) – which are less reagents consuming, technologically easier and more selective, were developed [12,13]. HDH allows the substitution of halogen bound in the organic molecule by hydrogen using moderate conditions (laboratory temperature and atmospheric pressure). This reaction produces more easily biodegradable non-halogenated compounds [57].

The scientists tested different metals systems (for example iron plated with Pt or Pd) for efficient hydrodehalogenation [58,59]. However, the HDH of halogenated organic derivatives using non-plated iron is very slow [58]. This suggests that for complete hydrodehalogenation is necessary to use a large amount of iron in role of reducing agent [60]. It was proved that the application of bimetallic HDH systems especially containing platinum-group metals allows effective hydrodehalogenation of mentioned pollutants. The electropositive zero-valent metal *in situ* generates H₂ by reaction with water which allows hydrodehalogenation of halogen derivatives in co-action of catalyst (e.g. platinum group metal) [12-15].

For example, Ghaush et al. tested bimetallic system – Fe plated with valuable metals (Co, Pd, Pt) [58] or trimetallic system – Fe plated with Pd/Cu/Ni [59] for HDC of DCF. The efficient hydrodechlorination of drug diclofenac was observed using this trimetallic system. Nieto-Sandoval et al. [62] applied commercially catalyst Pd/Al₂O₃ and gaseous hydrogen for HDC of DCF. The scientists observed complete hydrodehalogenation of tested drug and they also detected decreasing of ecotoxicity of treated aqueous solution.

Some papers [63-66] also describe reductive hydrodehalogenation of azo dyes using metal iron or nano-iron. The hydrodebromination of pesticide Bromoxynil using hydrogenation with Pd/Au catalytic system was tested too [67]. It was observed complete conversion of BXN to 4-hydroxybenzoxynitrile after 30 minutes using 100 mg Pd/Au per one liter of 5 mg/L BXN.

However, mentioned platinum group metals (serve as hydrodehalogenation catalysts) are rare, highly toxic, costly, and susceptible to poisoning [61]. Therefore, cheaper reduction agents of aluminium alloys with Ni or Cu were tested [61,62]. Our Chemical technology research group tested application of Al-based alloys for hydrodechlorination (HDC) or hydrodebromination (HDB) [12-15]. Aluminium alloys with Ni or Cu are very efficient agents for hydrodehalogenation of chlorinated or brominated organic fine chemicals [12,13] because of high content of catalytically active Ni or Cu catalysts compared to plated electropositive metal (e.g. Fe) with a narrow layer of catalyst [12-15].

The one example of described aluminium alloy is Raney Al-Ni alloy (50% Al and 50% Ni). We observed [12-14] that mentioned alloy is very efficient HDH agent in aqueous solution of NaOH/KOH. The mechanism of HDC of chlorinated organic derivatives using Raney Al-Ni alloy/NaOH describes Fig 6. As we published earlier [68], other very effective aluminium alloy for hydrodehalogenation (hydrodebromination, respectively) is Devarda's Al-Cu-Zn alloy. HDB of 2,4,6-tribromophenol using

Devarda's Al-Cu-Zn alloy (45% of Al, 50% of Cu and 5% Zn) in aqueous NaOH solution was verified [14]. The mechanism of HDB is very similar to HDC mechanism presented in Fig. 6.

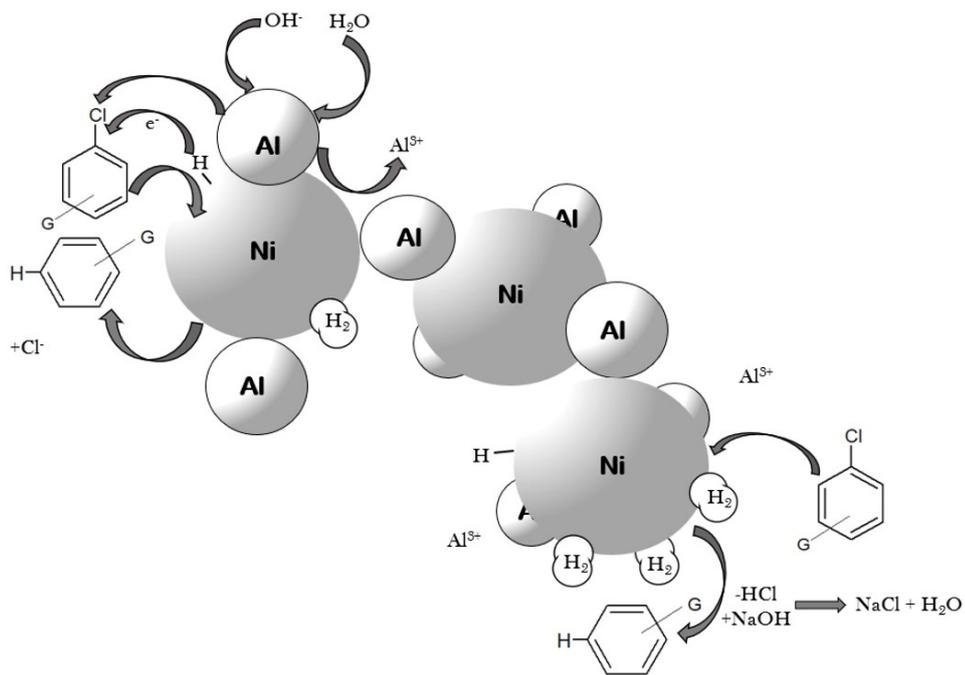


Figure 6 HDC mechanism using Raney Al-Ni [13]

2 Experimental Part

2.1 Chemicals and materials

- Diclofenac, sodium salt (NaDCF), 97%, Sigma Aldrich, Prague, CZ
- Flufenamic acid, sodium salt (NaFFA), p.a., Sigma Aldrich, Prague, CZ
- Mordant Blue 9 (MB9), 50%, Sigma Aldrich, Prague, CZ
- Acid Yellow 17 (AY17), 60%, Sigma Aldrich, Prague, CZ
- Bromoxynil (BXN), 95%, abcr chemicals, Germany
- cetyltrimethylammonium chloride (AlkMe3NBr), Alfa Aesar inc., USA
- Luviquat Mono LS, 30% aq. solution, Sigma Aldrich, Prague, CZ
- poly(diallyldimethylammonium) chloride (poly(Allyl2Me2N)Cl), 20% aq. solution, Sigma Aldrich, Prague, CZ
- Benzalkonium chloride (AlkBzMe2NCl), 50% aq. solution, Sigma Aldrich, Prague, CZ
- Aliquat 336 (A336), Merck Schuchardt OHG, Germany
- Mixture (ratio 3:2) of Aliquat 336 and 50% AlkBzMe2NCl
- Biochar, UCHP, specification in publication [50]
- Powdered activated carbon, SilCarbon CW20, Brenntag Co.
- Granulated activated carbon, Hydriffin CC8x30, Donau Carbon GmbH & Co.
- *Ex situ* impregnated biochar with poly(allyl2Me2N)Cl or AlkMe3NBr
- Raney Al-Ni alloy, Sigma Aldrich, Prague, CZ
- Devarda's alloy, Merck, Germany
- NaBH₄, Tokyo Chemical Industry Co.
- NaBH₄, 12% solution in 14M NaOH, Sigma Aldrich, Praha, CZ
- NiSO₄·7H₂O, Penta s.r.o., Prague
- Na₂S₂O₅, Sigma Aldrich, Prague, CZ
- H₂O₂, 30%, Sigma Aldrich, Prague, CZ
- FeSO₄, Penta s.r.o., Prague
- Ullmann Cu, VUOS a.s.
- Arnd's alloy, Sigma Aldrich, Prague
- Cu-Zn alloy, powder, Sigma Aldrich, Prague, CZ
- Cu-Sn alloy, powder – 200 mesh, Sigma-Aldrich, USA
- Cu, powder <425 μm, Sigma Aldrich, Prague, CZ
- Cu, nanopowder, 60-80 nm, Sigma Aldrich, Prague, CZ
- Cu₂O, Sigma-Aldrich, USA
- CuO, powder < 10 μm, Sigma Aldrich, Prague, CZ
- CuO nanopowder <50 nm, Sigma Aldrich, Prague, CZ

The other chemicals were purchased from local suppliers (Penta; Lachner; Sigma-Aldrich – Prag; Czech Republic): NaOH, KOH, H₂SO₄, dichloromethane, deuterated chloroform, methylalcohol and oktan-1-ol.

2.2 Methods

2.2.1 Determination of partition coefficient octal-1-ol/water

An aqueous solution of DCF (sodium salt) was added to the flask (in case of P_{OW} of ion pairs: subsequently addition of 1 mmol of R₄NX per 1 mmol of -COONa group bound in DCF). The equivalent volume of octan-1-ol was added to aqueous phase. These phases were stirred two days, then the phases were separated and a concentration of

NaDCF or R₄N.DCF in the aqueous phase was analysed. The log P_{ow} was calculated using equal (1):

$$\log P_{ow} = \frac{c_{octanol}}{c_{water\ phase}} \quad (1)$$

2.2.2 Sorption experiments

The quantity of sorbents was added to aqueous solutions of contaminants (possibly after the addition of R₄NX) in flasks equipped with electromagnetic stirring. The adsorption of flufenamic acid and diclofenac drugs and Mordant Blue 9 dye were tested. After appropriate time period, suspensions were filtered and analysed. The sorption capacity was calculated according equation (2). The adsorption isotherms were evaluated according Freundlich (physical multilayer adsorption) and Langmuir (chemical adsorption in one layer) isotherms, see equals (3) and (4).

$$q = \frac{(c_0 - c) \cdot V}{m} \quad (2) \quad q = k_F c^{1/n} \quad (3) \quad q = q_{max} \frac{k_L c}{1 + k_L c} \quad (4)$$

(*c*₀) is initial concentration [mg/L]; (*c*) is equilibrium concentration [mg/L]; (*V*) is volume of contaminants solution [L]; (*m*) is dosage of sorbent [g]; (*q*) is amount of sorbed contaminants per 1 g of sorbent [mg/g]. (*K_L*) is Langmuir constant, (*K_F*) is Freundlich constant and (*q_{max}*) is maximum amount of adsorbate [mg/g].

2.2.3 Degradation experiments

The appropriate quantity of oxidation (H₂O₂/Fe²⁺) or reduction (Raney or Devarda's alloy, Cu-based materials etc.) agents was added to different contaminants solutions (e.g. MB9, DCF, BXN) in flasks equipped with electromagnetic stirring. After an appropriate time period, reaction mixtures were filtered and analysed.

2.2.4 Regeneration and recycling of quaternary ammonium salts of halogenated organic acids

The first step was ion pair production – the reaction of R₄NX with dyes MB9 or AY17 in flasks equipped with electromagnetic stirring. The dosage of R₄NX was adjusted according to the number of dyes -SO₃⁻ groups. Produced ion pair was separated and dissolved in methanol. The reduction of ion pair dissolved in methanol was carried out using Raney Al-Ni alloy with the addition of NaOH aqueous solution and/or using NaBH₄ with co-action of NiSO₄. After chemical reduction and/or hydrodehalogenation, methanol was distilled and ion pair agents obtained by reduction was applied for next step of ion exchange.

2.3 Analysis

Concentration of dyes was analysed using determination of absorbance at maximum absorbance wavelength (VIS spectrophotometer Hach Lange). Concentration of NaDCF and NaFFA was determined using square wave voltammetry (Metrohm) at surfactant-modified carbon paste electrode [69]. Voltammetric measurements were carried out at instrumental conditions: 0.1 M PBS at pH = 7 with 1.10⁻⁴ M Alk3MeNBr, potential scan 0.2-1.2 V vs. ref., scan rate 50 mV/s. Chemical oxidation demand in contaminated water was determined using Hach Lange cuvette test. The other analysis (AOX, NMR, ICP-OES, XRD and LC-MS) were outsourced at University of Pardubice or VUOS a.s. (Research Institute of Organic Syntheses, Rybitví).

3 Results and Discussion

3.1 Removal of halogenated organic acids using ionic liquids

The ion exchange between selected quaternary ammonium salts (R_4NX) and halogenated organic acids (e.g. Mordant Blue 9, diclofenac, etc.) is an effective method of halogenated organic acids separation from contaminated water [49,50,70]. A more detailed description of the method is provided in the theoretical part, page 8. We found earlier [49,70] that the effectiveness of ion exchange increases with the number of long alkyl chains bound to the quaternary ammonium cation of the tested ionic liquids (e.g. for MB9 and sodium salt of DCF – NaDCF, see Fig. 7). This is due to low solubility of the produced ion pairs in water.

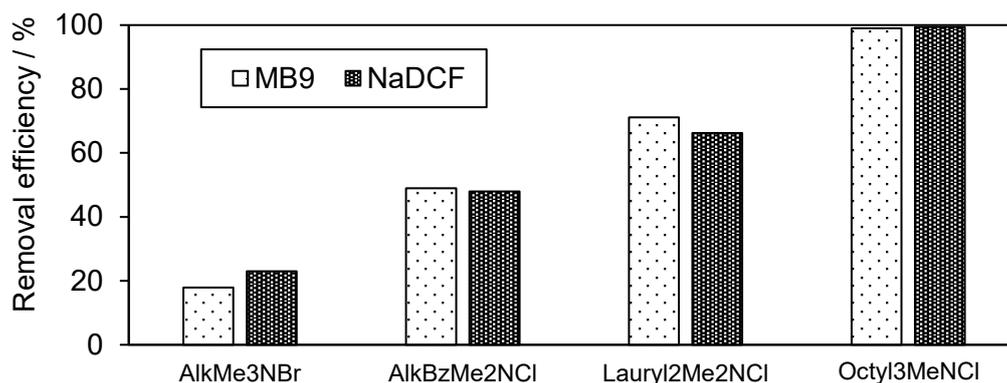


Figure 7 Comparison of removal efficiency of MB9 and DCF using R_4NX [72] ¹

Table 1 Results of octan-1-ol/water partition coefficients for DCF and MB9 and ion pairs $R_4N.DCF$ and $2(R_4N).MB9$

Contaminant	Ion pair ($R_4N.DCF$ / $2(R_4N).MB9$)	log P_{ow}
diclofenac	-	1.34
diclofenac	AlkMe3N.DCF	1.57
	AlkBzMe2N.DCF	1.73
	Allyl2Me2N.DCF	1.87
	Oktyl3MeN.DCF	2.89
Mordant Blue 9	-	-0.20
Mordant Blue 9	(AlkMe3N) ₂ .MB9	0.61
	(Allyl2Me2N) ₂ .MB9	0.76
	(AlkBzMe2N) ₂ .MB9	0.78
	(Oktyl3MeN) ₂ .MB9	2.90

Quaternary ammonium salts with three methyl groups and one larger alkyl group shows relatively high solubility in water. However, trialkylmethylammonium salts with the highest removal efficiency for studied halogenated organic acids provide only very limited solubility in water. It was proved that the formed ion pairs show lower solubility in water compared to R_4NX . This fact is supported by the results of the octan-1-ol / water partition coefficient (P_{ow}) for ion pairs with the chlorinated acidic dye MB9 [50,70] and the drug diclofenac [50], see Table 1. Higher solubility of the ion pairs $2(R_4N).MB9$ or $R_4N.DCF$ in octan-1-ol can be achieved by using an R_4NX containing

¹ AlkMe3NBr – cetyltrimethylammonium bromide; AlkBzMe2NCl – Benzalkonium chloride; Lauryl2Me2NCl – dilauryldimethylammonium chloride; Octyl3MeNCl – trioctylmethylammonium chloride

two and more long alkyl chains. These new results confirm a previously found fact [50,70] that the most effective R_4NX s used for halogenated acidic contaminants removal show low solubility in water. On the other hand, this low solubility in water together with their high viscosity cause problems with their application. Nevertheless, a commercial 50% aqueous solution of benzalkonium chloride (AlkBzMe₂NCl) offers a satisfactory compromise between solubility in water and separation efficiency for organic acidic contaminants from water [50,70]. Most effective hydrophobic Aliquat 336 (R_4NX with three long alkyl chains and one methyl group) is extremely viscous and its accurate application is troublesome. Therefore, less viscous solution of Aliquat 336 in 50% aqueous solution of benzalkonium chloride was effectively tested [50,70].

3.2 Comparison of adsorption of halogenated contaminants on carbonaceous sorbents

Sorption experiments were used to test possible adsorption of the drugs flufenamic acid and diclofenac and of the dye Mordant Blue 9 on biochar. Additionally, the possibility of *in situ* impregnation of biochar using ionic liquids (co-action of R_4NX with biochar) was tested. The verified [70] 50% aqueous solution of benzalkonium chloride and a mixture of the hydrophobic Aliquat 336 dissolved in 50% benzalkonium chloride were chosen as the impregnation agents. The aqueous 20% solution of poly(diallyldimethylammonium) chloride and cetyltrimethylammonium bromide was tested for impregnation of biochar, too.

Initial sorption was carried out in aqueous solutions of tested contaminants at concentration of 0.25-8 g/L. These model solutions simulated industrial wastewater from the production of mentioned organic compounds (e.g. drugs and dyes) [70,71,72]. The sorption of DCF and MB9 on biochar (20 g/l) and *in situ* impregnated biochar (R_4NX 1 g/L) was compared with sorption of tested contaminants on commercially available powdered activated carbon (PAC, 20 g/L), see Fig. 8 and Fig. 9.

As illustrated by Fig. 8 and Fig. 9, the highest sorption capacity for DCF and MB9 is shown using activated carbon, followed by *in situ* impregnated biochar using solution of Aliquat 336 in 50% AlkBzMe₂NCl, then by *in situ* impregnated biochar using AlkBzMe₂NCl, and finally the least efficiency is shown by biochar alone. Efficiency of sorption of these contaminants on the tested biochar are relatively low also when a large amount of this sorbent is applied. This fact agrees with the polarity of dissociable contaminants and to low affinity of these contaminants to the low polar sorbent biochar [50,70]. Only the sorption capacity of biochar combined with mixture of Aliquat 336 in 50% aqueous benzalkonium chloride (*in situ* impregnation using 1 g/L of R_4NX) approached values of sorption capacities of powdered AC, see Fig. 8 and Fig. 9.

Additionally, the number of long alkyl chains R in the used ionic liquids R_4NX and water solubility of the produced ion pairs play an important role in terms of efficiency of removal of the studied contaminants. The determined efficiency of DCF or MB9 removal (see Fig. 8 and 9) using combinations of various R_4NX with biochar corresponds very well to the measured P_{ow} values for DCF or MB9 [50,70] and their ion pairs (see Table 1, page 13).

We published the above-described results of adsorption in book chapter focused on application of biochar [50]. Then, this research was extended by additional

adsorption experiments testing lower concentration NaDCF representing potential contaminant of real polluted water.

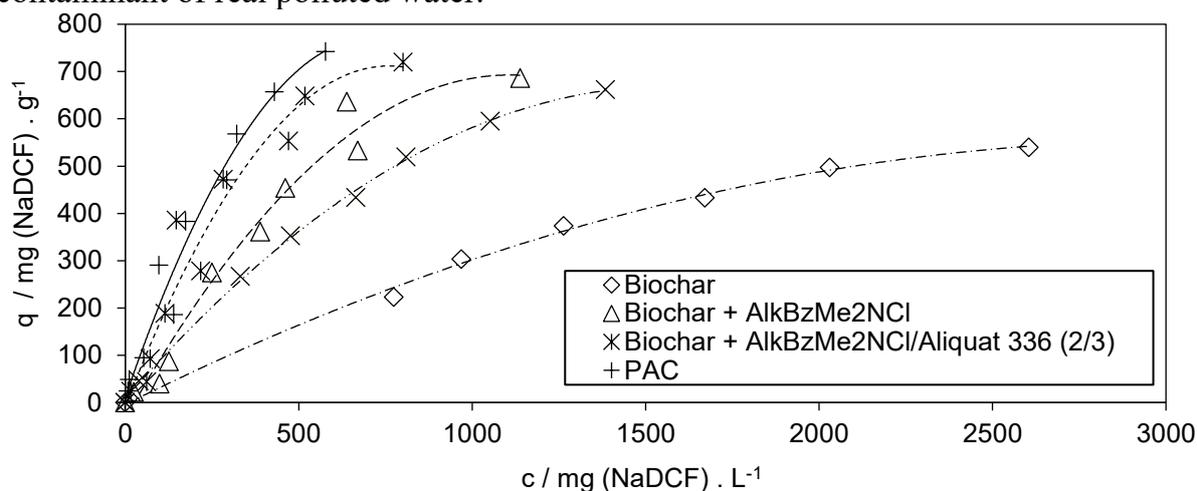


Figure 8 The differences in sorption capacities – adsorption of NaDCF (0.25-8 g/L) on carbonaceous sorbents (20 g/L) or on *in situ* impregnated biochar (20 g/L) with R₄NX (1 g/L)

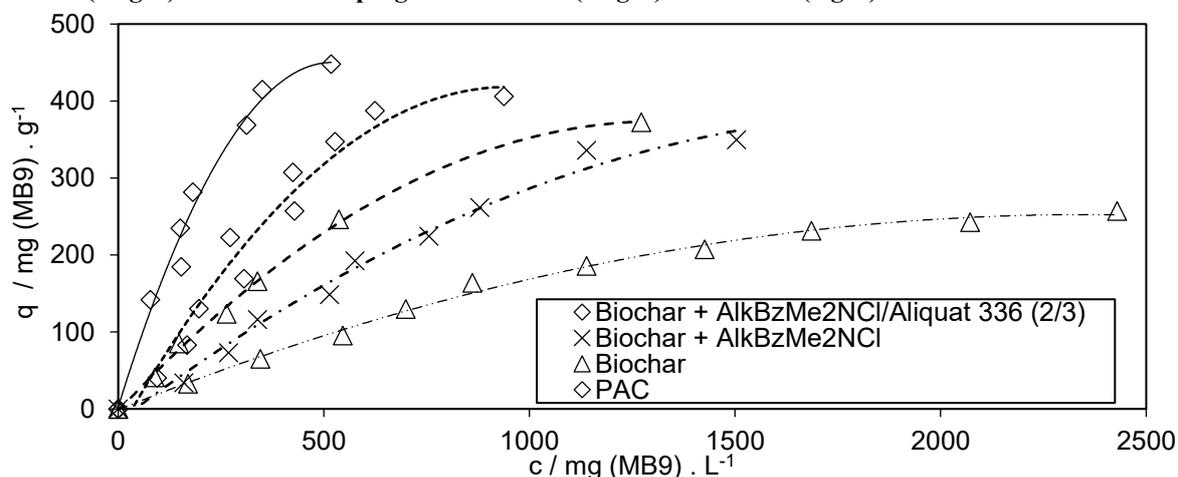


Figure 9 The differences in sorption capacities – adsorption of MB9 (0.5-5 g/L) on carbonaceous sorbents (20 g/L) or on *in situ* impregnated biochar (20 g/L) with R₄NX (1 g/L)

The differences in sorption capacity of biochar and *in situ* impregnated biochar with the selected R₄NX (poly(allyl2Me2N)Cl and AlkMe3NBr) for NaDCF (initial concentration 10–100 mg/l) are illustrated by the adsorption isotherms, see Fig. 10. Furthermore, sorption on biochar and impregnated biochar was compared to adsorption on powdered AC. Clearly, the sorption capacity decreases in the order: PAC > *in situ* impregnated biochar with AlkMe3NBr ~ *in situ* impregnated biochar with poly(allyl2Me2N)Cl > biochar. Biochar alone (0.4 g/l) showed the maximum sorption capacity of 113.7 mg/g. The sorption capacity of PAC (0.4 g/l) was up to approx. 40% higher compared to biochar alone. On the other hand, in the case of *in situ* impregnation of biochar with R₄NX (0.2 g/l), the sorption capacity of PAC is higher only by approx. 10%. As follows from the results, the combination of biochar and e.g. poly(diallyldimethylammonium) chloride provides a sorption capacity almost comparable to activated carbon. According to the equals (3) and (4), the experimental data can be evaluated better using Langmuir isotherms than Freundlich isotherms. It means, that possible mechanism of adsorption should be the sorption in one layer.

Results very similar to those obtained after application of poly(allyl2Me2N)Cl were also obtained after NaDCF sorption on the *in situ* impregnated biochar using AlkMe3NBr, see Fig. 10. In this case, the removal efficiency of contaminants was also increased by approx. 20% compared to biochar alone. Nevertheless, poly(allyl2Me2N)Cl is relatively well soluble in water, it is economically affordable and it is commercially available as a 20% aqueous solution (that is easy to apply) [73]. For these reasons above, poly(allyl2Me2N)Cl provides a good compromise to increase the sorption capacity of the tested biochar.

In situ and *ex situ* impregnation methods were also compared (*in situ* impregnation – biochar with addition of R₄NX vs. *ex situ* impregnated biochar – biochar impregnated with R₄NX prepared before sorption), see Fig. 10. The differences in the action of biochar and impregnated biochar are expressed according to the increasing ratio of the maximum sorption capacity of *ex/in situ* impregnated biochar (q_{max}) and biochar alone (q_{max}^*), see Table 2. The results indicate that *in situ* impregnation provides higher sorption capacities compared to *ex situ* impregnation. The lower efficiency of *ex situ* impregnation could be caused by the low concentration of R₄N⁺ cations immobilised on the biochar surface. Alternatively, it may be due to the specific biochar surface being clogged with the ionic liquid (R₄NX) [50].

The high sorption capacities of *in situ* impregnated biochar can be explained by the parallel effect of the ion exchange reaction between the added R₄NX and acidic drugs [49,50,70,74]; the high affinity of biochar to the *in situ* formed ion pairs [70,75,76]; and effect of multivalent metal cations from inorganic components of biochar on precipitation of insoluble salts of drugs (see biochar description in our book chapter) [50,70].

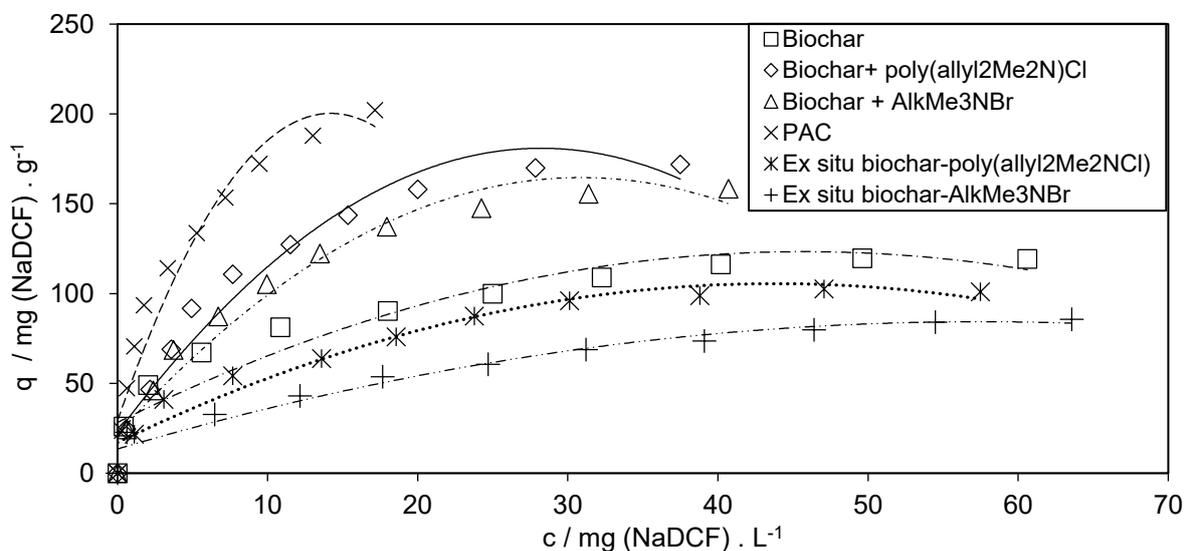


Figure 10 Sorption isotherms – adsorption of NaDCF (10-100 mg/L) on carbonaceous sorbents (0.4 g/L) or *in situ* impregnated biochar (0.4 g/L) with R₄NX (0.2 g/L)

It should be noted that above-mentioned experiments have been studied with another NSAID – flufenamic acid (FFA; sodium salt; initial concentration 0.25-7 g/L [50] and 10-100 mg/l see Fig. 11). The results [50] of sorption of FFA on biochar, PAC and *in situ* impregnated biochar were very similar to results of sorption of diclofenac. It could be caused the similar chemical structure of both medicaments – NaDCF and NaFFA, see Fig. 3 and Fig. 4 [19,20]. On the other hand, NaDCF and NaFFA sorption experiments were carried out under various pH values because of the low solubility of

NaFFA in water at pH < 10. However, when a separation method based on the formation of ion pairs is used, the pH value has no considerable effect on sorption of the tested contaminants [50,70,76].

Table 2 The comparison of impregnation techniques of biochar applied for DCF adsorption

Adsorbent	Sorption capacity q_{\max} (mg/g)	Ratio of sorption capacities (q_{\max}/q_{\max}^*)
Biochar	113.69 *	-
Biochar + poly(allyl2Me2N)Cl	217.62	1.91
Biochar + AlkMe3NBr	188.32	1.69
<i>ex situ</i> biochar-poly(allyl2Me2N)Cl	102.23	0.89
<i>ex situ</i> biochar-AlkMe3NBr	99.13	0.87

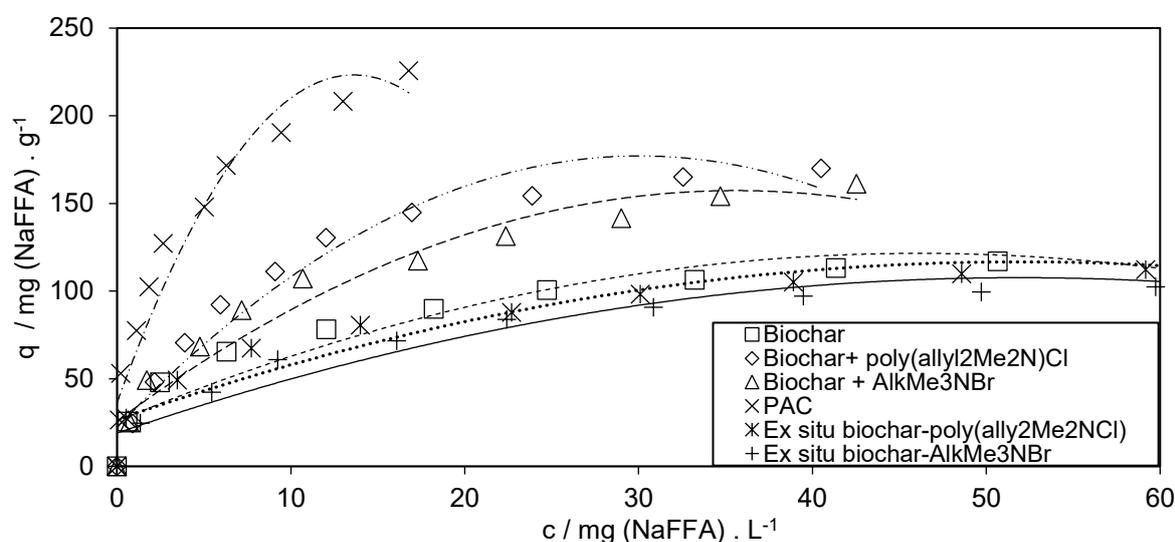


Figure 11 Sorption isotherms – adsorption of NaFFA (10-100 mg/L) on carbonaceous sorbents (0.4 g/L) or *in situ* impregnated biochar (0.4 g/L) with R₄NX (0.2 g/L)

3.1 Chemical degradation of halogenated organic compounds in aqueous solutions

The next part of the thesis compares conventional chemical degradation methods (oxidation processes) of aqueous concentrates of halogenated pollutants and innovative methods of reductive hydrodehalogenation (HDH). Mentioned aqueous concentrates can be produced upon application of membrane separation as well as regeneration of depleted sorbents by thermal desorption. Our research group verified earlier [12-15] a method of hydrodechlorination (HDC) of aromatic chloro-derivatives using the Raney Al-Ni alloy [12,13, 15] or debromination (HDB) of bromo-derivatives using Devarda's Al-Cu-Zn alloy [14]. Hydrodehalogenation using the Al alloys is based on dissolving aluminium in the sodium hydroxide solution. Hydrogen is thus produced, acting on the nickel or copper surface as a catalyst to convert chlorinated organic compounds to non-halogenated products, which are easily biodegradable [61]. Above-described reaction occurs under laboratory temperature and atmospheric pressure. In addition, HDH consumes only a small quantity of the reactants compared with chemical oxidation of

halogenated organic compounds and is much more selective compared to conventional oxidation processes [3,12-15,61,62].

Hydrodechlorination of MB9 dye with the Raney Al-Ni alloy was verified using 0.27 grams of the Al-Ni alloy (Al 5 mmol) per 0.05 mmol of MB9 (in 1mM aqueous solution) with the addition of NaOH (5 mmol). After 18 hours of intensive stirring, almost 97% efficiency of decolorization and almost 95% efficiency of the AOX (Adsorbable Organically bound Halogens) parameter removal were observed. An increase of the Raney Al-Ni alloy quantity did not allow any considerable enhancement of MB9 removal (see Fig. 12 for the results). Moreover, LC-MS analyses verified that the action of the Raney Al-Ni alloy leads to complete hydrodechlorination of MB9 according to the scheme in Fig. 13. MB9 was also found to partially adsorb on the Raney Al-Ni alloy. The addition of 1 gram of Al-Ni alloy to aqueous solution contaminated with 0.05 mmol MB9 without subsequent addition of NaOH caused 60% decolorization efficiency. Thus, sorption of this dye on the Raney Al-Ni alloy may be a parallel mechanism of MB9 removal from aqueous solutions.

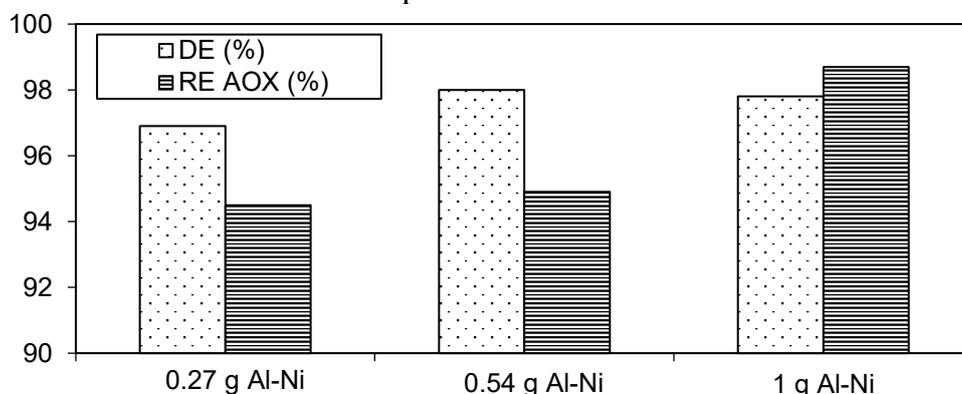


Figure 12 Results of HDC of MB9 using Raney Al-Ni alloy
(Raney Al-Ni alloy added to 0,05 mmol MB9 + 5 mmol NaOH in 100 mL H₂O)²

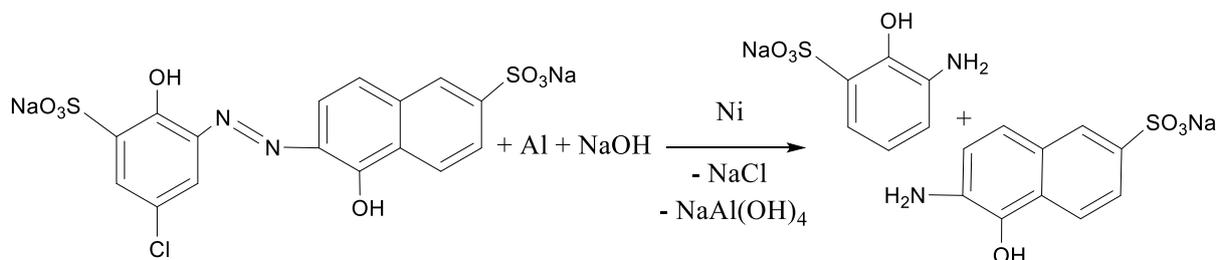


Figure 13 Hydrodehalogenation of Mordant Blue 9 dye using Raney Al-Ni alloy/NaOH

Unlike HDC, a considerable excess amount of $[Fe^{2+}]/[H_2O_2]$ compared to stoichiometry needs to be applied to accomplish efficient Fenton oxidation of MB9 dye. An optimum molar ratio for MB9 oxidation after 3 hours is $[Fe^{2+}]/[H_2O_2]/[MB9] = 1:98:1$.

The HDC method using the Raney Al-Ni alloy was also verified for the chlorinated drug diclofenac (sodium salt – NaDCF) [77]. For HDC of diclofenac (1 mmol), 15 mmol of aluminium (in the form of the Raney Al-Ni alloy) is necessary applied in KOH solution (75 mmol). Under these conditions, NaDCF is converted to 2-anilinophenylacetate (see Fig. 14 for the reaction scheme) almost after one hour, see Fig. 15. Sorption of this drug on the Raney Al-Ni alloy may also be a possible parallel

² DE – decolorization efficiency; RE AOX – removal efficiency of Adsorbable Organically bound Halogens

final product 4-HBN (4-hydroxybenzaldehyde) according to the reaction scheme illustrated in Fig. 17.

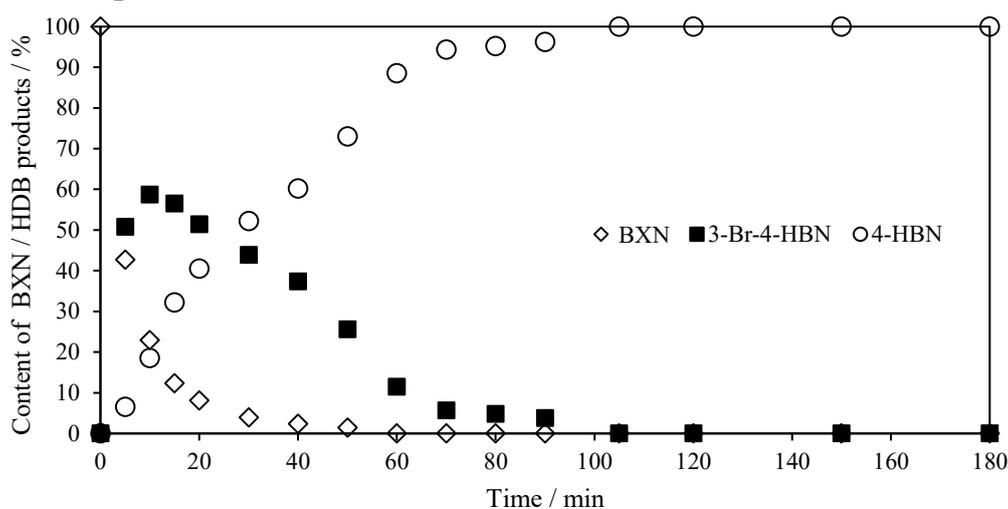


Figure 16 Kinetics of hydrodebromination of BXN using Devarda's alloy (3 g/L of D. alloy added to 5mM BXN in 100mM NaOH)

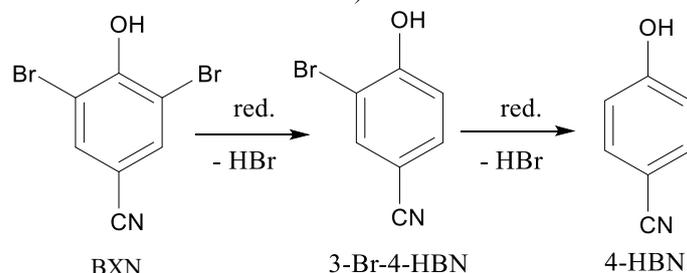


Figure 17 Mechanism of HDB of BXN

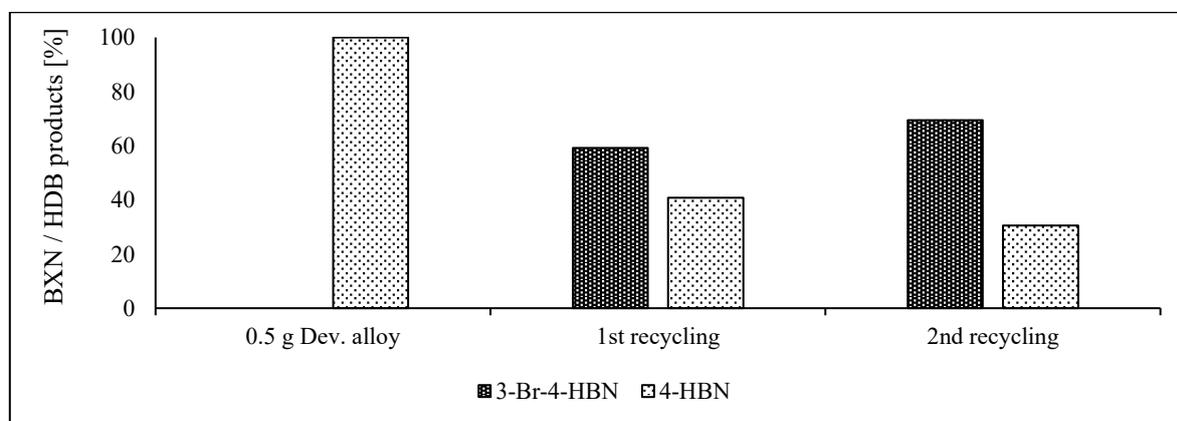


Figure 18 Recycling of Devarda's alloy using NaBH₄

(D. alloy added to 2.5 mmol BXN + 50 mmol NaOH in 100 mL H₂O + addition of 10.5 mmol NaBH₄ in recycling steps)

The possibility of recycling mentioned D. alloy was also verified to establish economic aspects of the process [14]. Effective alloy recycling results were achieved upon addition of sodium borohydride to the already used alloy. It allowed a partial conversion of BXN to 4-HBN via the intermediate product also in the case of a non-dissolved portion of D. alloy, used in 3 cycles, see Fig. 18 above. Nevertheless, none of the experiments [14] aimed to test D. alloy recycling achieved 100% conversion of BXN to 4-HBN according to reaction scheme in Fig. 17.

Other reducing agents such as Arnd's Mg-Cu alloy, Cu-Sn or C-Zn alloys, nano-copper powder, Ullmann-type copper or copper oxides (CuO and Cu₂O) were also tested

to compare them to D. alloy [14]. As indicated by the results, nano-copper showed negligible efficiency on hydrodebromination of BXN. However, application of nanopowder copper enabled at least partial HDB in case of co-action of sodium borohydride. Similar results were observed also for Arnd's Mg-Cu alloy. Compared to D. alloy, the Cu-Sn, Cu-Zn or Ullmann-type copper showed to be much less efficiency. In this cases, total conversion of BXN to debromination product was not achieved even with an addition of NaBH₄, see Fig. 19.

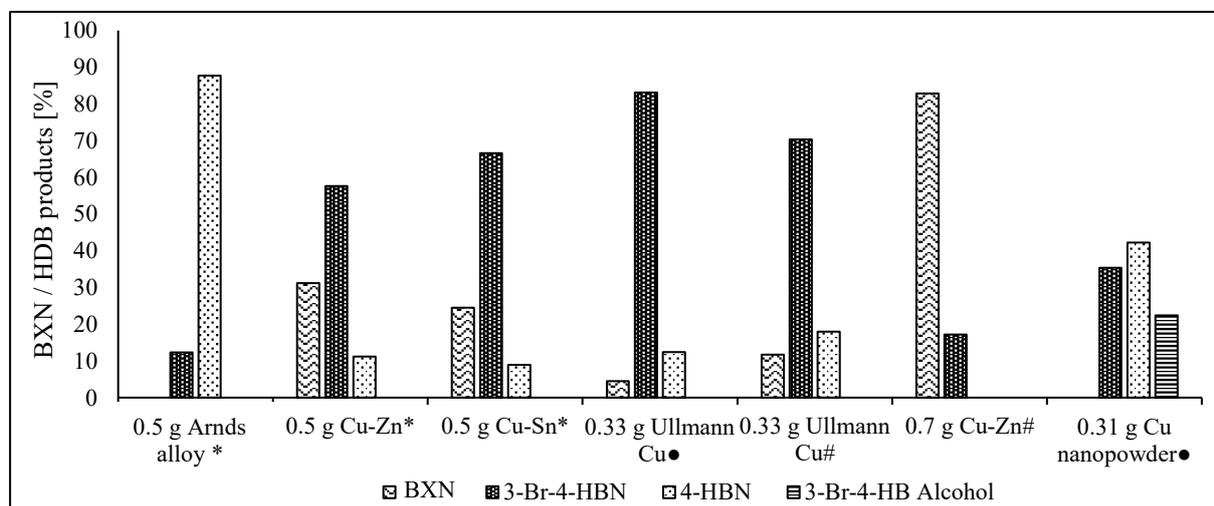


Figure 19 HDB of BXN using different copper forms with co-action of NaBH₄

(18 h stirring. HDB agents added to solution of: *0.5 mmol BXN + 10 mmol NaOH in 100 ml H₂O + 5 mmol NaBH₄; •0.5 mmol BXN + 2 mmol NaOH in 100 ml H₂O + 21 mmol NaBH₄; #0.5 mmol BXN in 100 ml CH₃OH + 21 mmol NaBH₄)

The use of Cu₂O as a catalyst with an addition of NaBH₄ offer 100% conversion of BXN to 4-HBN after intensive stirring overnight (Fig. 20). The combination of CuO nanopowder and sodium borohydride is a considerably worse reductant compared to powdered CuO/NaBH₄. No beneficial effect of the high specific surface area of copper(II) oxide nanopowder on BXN hydrodebromination was thus observed, see Fig. 20. An innovative method of *in situ* generation of Cu/Cu₂O by adding aqueous solution of copper sulphate to an alkaline BXN solution with sodium borohydride was tested too. This method proved beneficial rapid hydrodebromination of BXN (see Fig. 20 for the results).

The described method of reductive hydrodehalogenation using aluminium-based alloys (Raney Al-Ni or Devarda's Al-Cu-Zn alloys) has been verified by our research group in several scientific journals [12-15,77]. It should be noted that in our hand tested HDH method is very efficient, selective, less reagents consuming and simple for performance (laboratory temperature and atmospheric pressure) method.

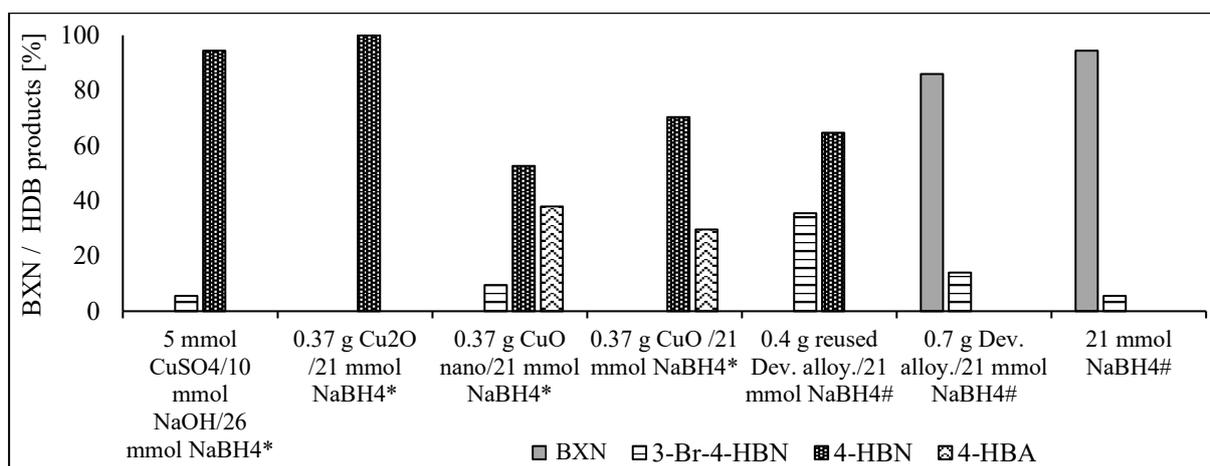


Figure 20 HDB of BXN using Cu-based catalysts and/or NaBH₄

(18 h stirring. HDB agents added to solution of: *0.5 mmol BXN + 2 mmol NaOH in 100 ml H₂O; #0.5 mmol BXN in 100 ml CH₃OH)

3.2 Regeneration and recycling of quaternary ammonium salts of halogenated organic acids

The last part of this research verified that the quaternary ammonium salts of halogenated organic acids, obtained using e.g. ion exchange methods, can be reductively dehalogenated using NaBH₄ and Raney Al-Ni alloy. This research was the subject of a patent [16] of our research group in cooperation with the research team of VUOS a.s. (Research Institute of Organic Syntheses, Rybitví) [16].

Reductive dehalogenation using Raney Al-Ni alloy takes place at pH values over 12. Therefore, the commercially available alkaline 12% aqueous solution of sodium borohydride in 14M NaOH can be used for the reduction. However, sodium hydroxide can also be used to adjust the pH value. The molar ratio of 8:1 of the NaOH and aluminium provide the highest effectiveness. Reductive dehalogenation can take place at 20–35°C. An optimum time period of the reaction ranges between 4 and 16 hours [16]. After the reaction, the produced nickel sludge (from Raney Al-Ni alloy) can be removed by sedimentation and/or filtration. Moreover, the deactivated Ni catalyst can also be regenerated and recycled [78]. This mentioned regeneration was described previously by our research group [78].

Before dehalogenation, ion pairs with low solubility in water need to be dissolved in an alcohol, e.g. methanol. The alcohol has to be distilled from the solution before recycling the regenerated quaternary ammonium salt (ion-pair agent). This separated alcohol can be recycled. Furthermore, the possibility of decreasing the Raney Al-Ni alloy consumption was verified. A chemical degradation step using NaBH₄ together with additives such as sodium metabisulfite (production of a reducing agent – dithionite) [66] or nickel(II) sulphate (reduction of Ni⁰ – hydrogenation catalyst) [78] can be inserted before the reductive dehalogenation step.

The cycle of an effective ion exchange using a commercial product (30% Luviquat Mono LS) with subsequent reduction of produced ion pairs (as described above) and recycling of the obtained ion-pair agent was tested, for example, with the MB9 dye. This separation/regeneration technique was also verified using trioctylmethylammonium chloride. This cycle is described in Fig. 21. The LC-MS analyses demonstrated (VUOS a.s.) that the ion pairs 2(R₄N).MB9 were reduced and even hydrodechlorinated using NaBH₄/Al-Ni alloy according reaction scheme in

Fig. 22. As follows from subsequent recycling of the regenerated ion-pair agent, this agent can be reused in subsequent cycles for an efficient removal of MB9 from aqueous solutions, see Fig. 23. In the third cycle, the separation of MB9 using regenerated ion-pair agent allows almost 40% removal efficiency of tested dye. These findings were also verified, for example, with Acid Yellow 17 or Versal Yellow 2RLP and an intermediate product of its production, the 3,4-dichloroaniline-6-sulfonic acid [16].

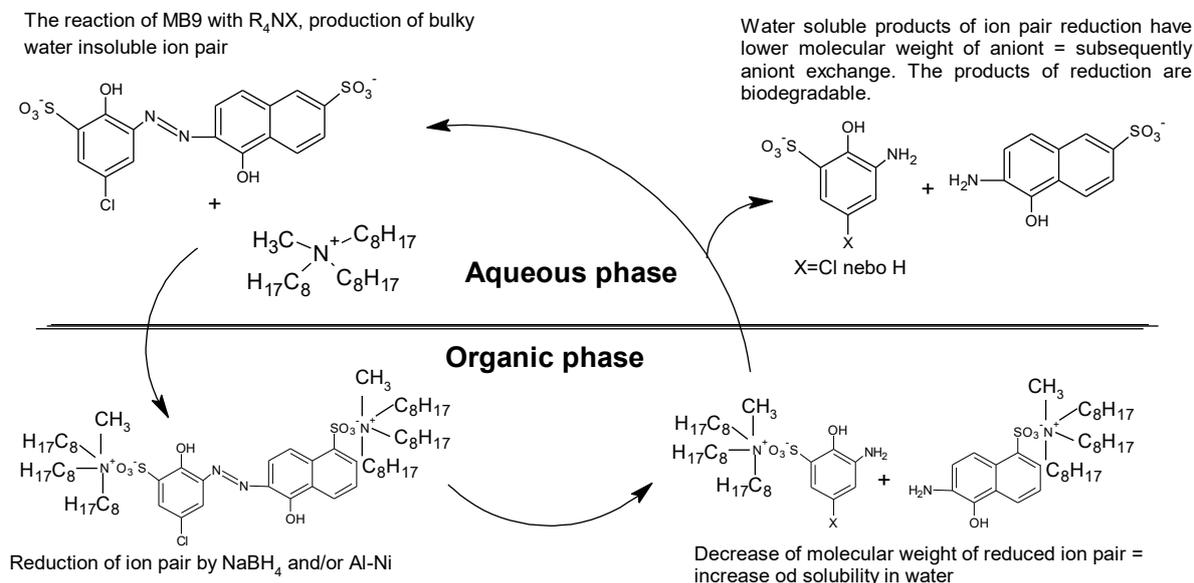


Figure 21 The cycle of recycling of ion pairs 2(R_4N).MB9 [70]

In addition, regenerated ion pairs 2(Luviquat Mono LS).MB9 (Fig. 22) can be effectively applied for desorption of MB9 dye from saturated granulated AC. The desorption of MB9 from GAC using mentioned regenerated ion-pair agent is comparable to efficient desorption using commercially Luviquat Mono LS, see Fig. 24.

The described process (reductive hydrodehalogenation of quaternary ammonium salts of halogenated organic acids) provides an effective method of efficient removal of contaminants from water. Subsequently, the produced ion pairs can be recycled with an economic benefit. Based on the achieved results of ion-pair agents regeneration and recycling, it can be noted that:

- 1) application of the 30% commercial solution, Luviquat Mono LS [79] (commercial, easy to apply) for the separation of dyes (e.g. MB9 and AY17) is effective;
- 2) solid $NaBH_4$ combined with $NiSO_4$ can be innovatively used to reduce the produced ion pairs [16];
- 3) in the next step, the Raney Al-Ni alloy [12-16] combined with commercial 12% $NaBH_4$ in 14M $NaOH$ can be used as a dehalogenation agent that allows repeated reduction of the ion pairs and increasing the pH value to the alkaline range for HDC;
- 4) recycling of the regenerated ion-pair agents is effective up to the third cycle of repeated application [16];
- 5) regenerated ion-pair agent is also effective for desorption of dyes from GAC;
- 6) a beneficial possibility of recycling methanol removed by distillation [16] and reusing the Ni catalyst from the used Raney Al-Ni alloy [78] can be utilized; these steps potentially decrease the amount of produced waste and economic costs of materials.

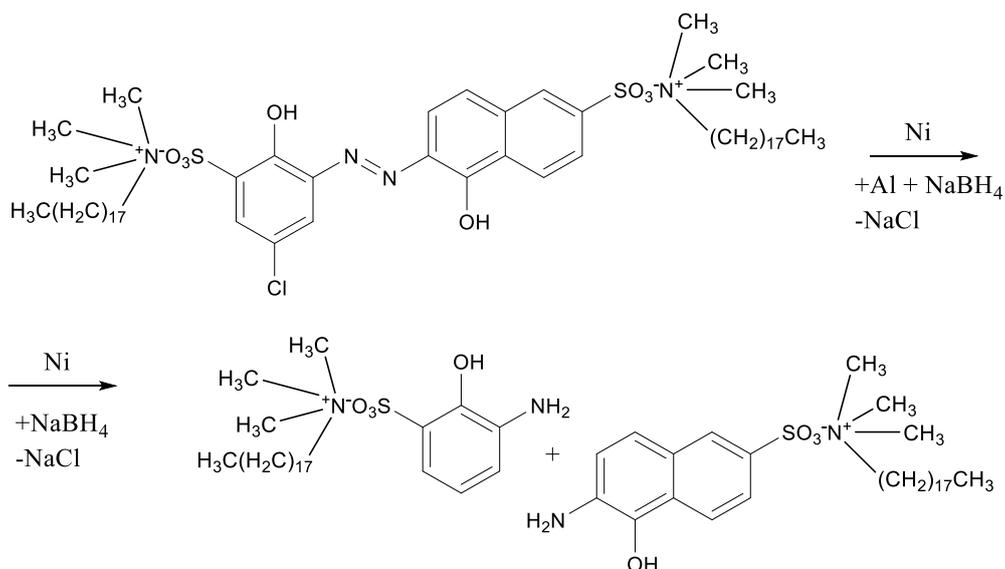


Figure 22 The reduction and hydrodehalogenation of ion pair 2(Luviquat Mono LS).MB9

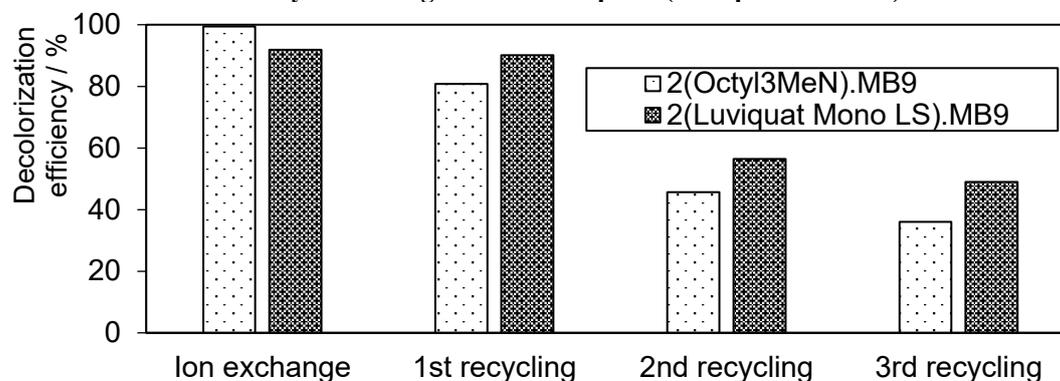


Figure 23 The results of recycling of ion pairs 2(R₄N).MB9

(Ion pair formation: 1 mmol of R₄NX + 0.5 mmol of MB9 / Reduction and dehalogenation: addition of 25 mmol NaBH₄, possibly 5 mmol NiSO₄ and/or 10 mmol of Al in Al-Ni alloy to methanolic solution of ion pair / Recycling of ion pairs agents: ion pairs agents + 0.5 mmol of MB9)

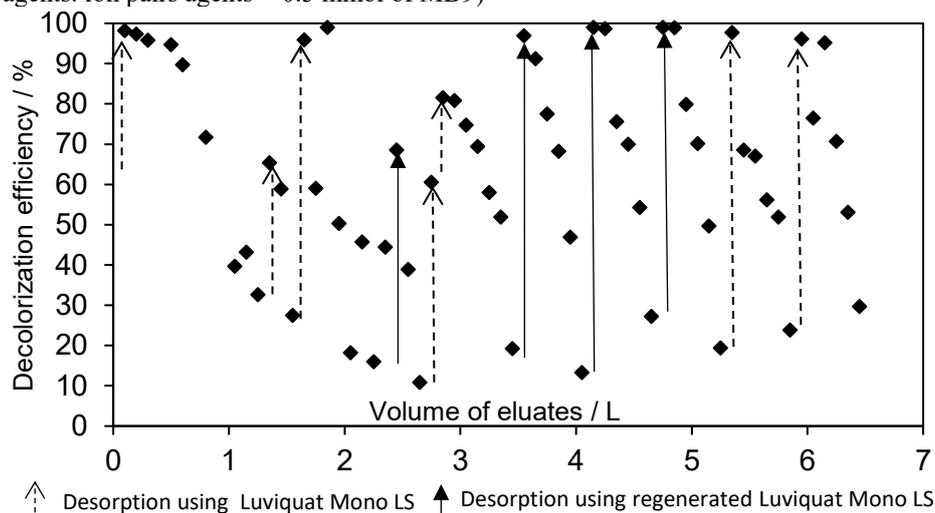


Figure 24 The sorption and desorption of dye MB9 in laboratory column filled with granulated activated carbon [16]

4 Conclusion

This dissertation thesis studied innovative methods for separation and simple degradation of problematic halogenated aromatic contaminants such as drugs, dyes and pesticides from model wastewater. Adsorption of selected contaminants (DCF, FFA, MB9) on carbonaceous sorbents with the possibility of their impregnation using quaternary ammonium salts was compared in the scope of the research. Based on the adsorption study results, it can be noted that *in situ* impregnation of biochar with selected, commercially available ionic liquids (R_4NX) is a suitable method of increasing the sorption capacity of this sorbent. Additionally, it offers a good compromise compared to the relatively expensive, commercially available activated carbon.

In the next part of thesis, it was tested a method of reductive hydrodehalogenation of halogenated aromatic compounds using alloys such as the Raney Al-Ni alloy and Devarda's Al-Cu-Zn alloy. The tested method of reductive hydrodehalogenation is very efficient, selective and simple, and it does not require any significant excessive amounts of the reaction agents. This work verified that the tested aluminium-based alloys can be used for catalytic hydrodehalogenation of halogenated drugs, dyes and herbicides represented by DCF, MB9, BXN.

As shown by the last part of the research, aqueous concentrates of ammonium salts of halogenated organic acids can be chemically degraded and dehalogenated using the $NaBH_4/NiSO_4/Al-Ni$ system. One of the produced flows is represented by the regenerated quaternary ammonium salt which can be recycled. Wastewater containing easily biodegradable organic compounds is another flow available for standard biological treatment. This process allows regeneration of R_4NX with the benefit of subsequent multiple recycling steps.

The complex research undertaken in this thesis and published in several scientific journals studied possible ways of problematic contaminants removal using adsorption and/or ion exchange utilizing alternative sorbents and innovative methods of chemical degradation (reductive hydrodehalogenation). The tested methods of halogenated organic compound separation and degradation are effective and economically acceptable. It should be noted that these processes emphasize regeneration and recycling of reagents and raw materials. The described cycle of problematic pollutants removal from water could potentially reduce economic costs of effective removal of halogenated organic pollutants from (technological) wastewater.

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International traineeship

Organisation: Slovak University of Technology in Bratislava

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Topic: Problematics of halogenated pesticides removal by oxidation and hydrodehalogenation