

UNIVERSITY OF PARDUBICE
FACULTY OF CHEMICAL TECHNOLOGY

Institute of Environmental and Chemical Engineering

Jana Václavíková

**Application of Ionic Liquids for Removal of
Pollutants from Model Waste Waters**

Theses of the Doctoral Dissertation

Pardubice 2018

Study program: Chemical and Process Engineering

Study field: Environmental Engineering

Author: Jana Václavíková

Supervisor: doc. Ing. Tomáš Weidlich, Ph.D.

Year of the defence: 2018

References

VÁCLAVÍKOVÁ, Jana. *Application of Ionic Liquids for Removal of Pollutants from Model Waste Waters*. Pardubice, 2018. 217 pages. Dissertation thesis (Ph.D.). University of Pardubice, Faculty of Chemical Technology, Institute of Environmental and Chemical Engineering. Supervisor doc. Ing. Tomáš Weidlich, Ph.D.

Abstract

This thesis is focused on the study of the effectiveness of the removal of water-soluble dyes, namely acid azo-dyes, especially reactive dyes and from the model wastewater using by tetrasubstituted phosphonium respectively ammonium salts or their combination with inorganic coagulants, which are hydrated forms of aluminum sulphate or ferric sulphate. In addition there was tested verification of possibility of application of the auxiliary filter material (powdered calcium carbonate) for easy separation of ionic pairs produced by reaction of acid dyes with quaternary ammonium or phosphonium salts. The aim of this thesis was to explore simple and cheap method for effective wastewater treatment with potencial utilization of produced sludge.

Abstrakt

Disertační práce je zaměřená na studium účinnosti odstraňování ve vodě rozpustných barviv, konkrétně kyselých azobarviv, se zaměřením na reaktivní barviva z modelových odpadních vod použitím kvartérních fosfoniových resp. amoniových solí, a/nebo jejich kombinacemi s anorganickými koagulanty, jakými jsou hydratované formy síranu hlinitého a železitého. Vedle toho bylo provedeno ověření možnosti aplikace pomocného filtračního materiálu (práškového uhličitanu vápenatého) pro snadné oddělování iontových párů vznikajících reakcí testovaných kyselých barviv s kvartérními amoniovými nebo fosfoniovými solemi. Cílem bylo dosáhnout maximální účinnosti čištění kontaminovaných vod s použitím jednoduché a rychlé metody, která by umožnila potenciální využití separovaného kalu.

Keywords

dye removal, azo dye, reactive dye, hydrolyzed reactive dye, ionic liquid, precipitation

Klíčová slova

odstraňování barviv, azobarvivo, reaktivní barvivo, hydrolyzované barvivo, iontová kapalina, srážení

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1. INTRODUCTION

Environment, the topic we deal with every day. The lifestyle of the 21st century forces us systematically to use non-renewable natural resources, to recycle, to innovate old technologies or to use renewable energy resources efficiently to sustain the development of the economy.

Water is a natural source necessary for life. Waste water is an integral part of the producers who are obliged to take part in recycling and is one of the biggest problems in the world today. Pollution of watercourses and reservoirs deteriorates the quality of aquatic and surrounding ecosystems. Dyes are an important source of environmental pollution. Textile wastewater usually contains a considerable amount of dyes, many of which are azo dyes. Environmental pollution with organic dyes is an ecological problem, as most of these dyes are toxic to micro-organisms. The azo dyes, which represent the largest and most important class of commercial dyes, are hardly biodegradable and their stability is proportional to the complexity of their molecular structure.

Water protection is one of the most important tasks in the field of the environment and the most demanding area in terms of the Czech Republic's accession to the European Union too. The objective is to comply with the requirements of the European Union legislation to improve the state of watercourses, aquatic ecosystems and promote sustainable water use.

1.1 Characteristics of ionic liquids

There has been increased attention on ionic liquids because of their unique properties. They are often associated with “green chemistry” because they possess certain advantageous properties typically linked to environmentally friendly solvents, such as negligible volatility, being nonflammable, thermal and chemical stability, extensive liquid range, the ability to dissolve pollutants/dyes, and a number of possible variations in cationic and anionic features that allow for fine-tuning of their properties [1, 2]. Ionic liquids are organic salts in the liquid state whose melting point is below some arbitrary temperature, such as 100 °C [2]. An ionic liquid consists of a bulky and asymmetric organic cation, such as imidazolium or pyridinium, and an inorganic or sometimes an organic anion [3]. Ionic liquids contain a functional group that is covalently tethered to its cation or anion [4]. They can be used for the removal of dye pollutants from model wastewaters. The ionic bond is usually stronger than the Van der Waals forces between the molecules of an ordinary liquid. The utility of ionic liquids comes from their melting points to their temperatures of decomposition. Ionic liquids have temperatures of decomposition between 250 °C and 350 °C. Interestingly, it was found that precipitates can be formed rapidly when the ammonium and phosphonium based ionic liquids were added to aqueous solutions of anionic dyes [5, 6]. Ionic liquids have been successfully used to remove anionic dyes.

1.2 Characteristics of dyes

Azo-dyes are very important synthetic dyes that are used extensively in industry. Aromatic diazonium salts are important building blocks in the preparation of azo dyes, which are synthesized by the diazotation of aryl amines using nitrous acid [7]. The overwhelming majority of synthetic dyes currently used are the highly water soluble

azo dyes. They are characterized by the existence of nitrogen-nitrogen double bonds and the presence of bright color, which is due to the azo bonds and associated chromophores. The azo dyes also contain auxochromes, such as $-OH$ or $-SO_3H$, which are responsible for the increase of color intensity [8]. Textile dyes are of environmental interest because of their widespread use, potential to form toxic aromatic amines, and their low removal rate during waste treatment [9, 10].

Dye wastewaters stem mainly from dyeing, carpet manufacturing, and textile and papermaking industries. The presence of dyes in wastewater is a major environmental problem since they are generally resistant to degradation by biological treatment methods. They constitute one of the most difficult wastewaters to be treated, not only because of their high chemical oxygen demands and suspended solids, but due to their content of toxic compounds, which may be deadly to some aquatic life since they contain aromatics, metals, chlorides, etc. [11, 12].

2. EXPERIMENTAL

Apparatus

The Hach-Lange DR 2800 Spectrophotometer was used to measure the absorbances of both the stock solutions of dyes and the filtrates obtained after their ionic precipitation. Measurements can be made in the visible range of the electromagnetic spectrum in the wavelength range 340-900 nm.

Following the precipitation of the studied dyes with selected tetrasubstituted phosphonium / ammonium salts, the COD parameters (the chemical oxygen demand) were measured in selected sample of filtrates. For the mineralization of samples measured using the Hach-Lange cuvette test, the Hach-Lange two-block LT 200 mineralizer was used, which contained 2 independently controlled heating blocks with separate protective covers. Temperature setting is possible between $37\text{ }^\circ\text{C}$ and $150\text{ }^\circ\text{C}$ in steps of $1\text{ }^\circ\text{C}$, setting the time between 1 and 480 minutes.

The BOD parameters were measured with a HQ430d table multimeter with the probability measurement of dissolved oxygen equipped with the required probe and necessary accessories (BOD kit) and reagents (BOD nutrients, nitrification inhibitor, BOD inoculum).

AOX parameters were obtained on selected samples with the AOX Multi X 2500 analyzer.

The phosphorus content of the selected quaternary phosphine dye precipitates and the ILS stock solutions were determined by the ICP-OES method.

The NMR spectrums of the individual compounds were measured in deuterated solvents ($CDCl_3$ or $DMSO-d_6$) in 5 mm cuvettes at about 295 K on a Bruker Ascend™ 500 pulse mode Fourier transform. 1H (500.13 MHz) and ^{13}C $\{^1H\}$ (125.76 MHz), NMR spectrums were measured in a 5 mm broadband liquid nitrogen cooled Prodigy crystalline with a Z-gradient.

Reagents and chemicals

Preparation of ionic liquids and reactive dyes

The chemical structures of the anionic dyes and the ionic liquids used in this work were shown in Table 1-8.

Table 1 Chemical structures of phosphonium ionic liquids

$R_4P^+X^-$ (Supplier)	CAS	Mr	Formula
0.1M EtPh ₃ PBr (Sigma- Aldrich)	1530-32-1	371,26	
0.1M Bu ₄ PCl (Fluka)	2304-30-5	294,89	$\begin{array}{c} (CH_2)_3CH_3 \\ \\ H_3C(H_2C)_3 - P^+ - (CH_2)_3CH_3 \\ \\ (CH_2)_3CH_3 \end{array} Cl^-$
0.01M Bu ₃ C ₁₄ PCl (Fluka)	81741-28-8	432,15	$\begin{array}{c} (CH_2)_3CH_3 \\ \\ H_3C(H_2C)_3 - P^+ - (CH_2)_{13}CH_3 \\ \\ H_3C(H_2C)_3 \end{array} Cl^-$
0.01M Ph ₄ PBr (Merck)	2751-90-8	419,29	
0.01M Bu ₃ C ₁₆ PBr (Merck)	14937-45-2	507,67	$\begin{array}{c} (CH_2)_3CH_3 \\ \\ H_3C(H_2C)_3 - P^+ - (CH_2)_{15}CH_3 \\ \\ H_3C(H_2C)_3 \end{array} Br^-$
Hex ₃ C ₁₄ PCl (Fluka)	258864-54-9	519,31	$\begin{array}{c} (CH_2)_5CH_3 \\ \\ H_3C(H_2C)_5 - P^+ - (CH_2)_{13}CH_3 \\ \\ (CH_2)_5CH_3 \end{array} Cl^-$
Okt ₄ PBr (Merck)	23906-97-0	563,78	$\begin{array}{c} (CH_2)_7CH_3 \\ \\ H_3C(H_2C)_7 - P^+ - (CH_2)_7CH_3 \\ \\ (CH_2)_7CH_3 \end{array} Br^-$

Table 2 Chemical structures of ammonium ionic liquids

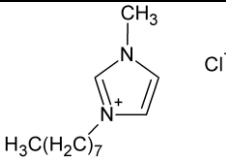
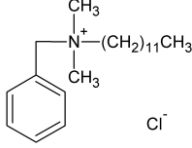
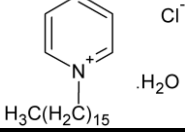
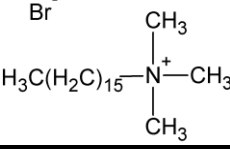
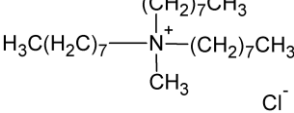
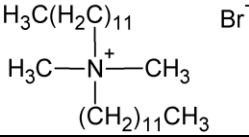
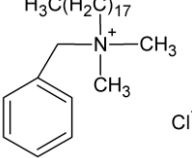
R₄N⁺X⁻ (Supplier)	CAS	Mr	Formula
OMIMCl (Fluka)	64697-40-1	230,78	
0.1M AlkdiMeBzNCl (Merck)	85409-22-9	339,45	
0.1M C ₁₆ PyCl (Merck)	6004-24-6	358	
0.01M C ₁₆ Me ₃ NBr (Acrós)	57-09-0	364	
Aliquat 336 (Sigma-Aldrich)	63393-96-4	404,17	
0.05M DiDDiMeABr (Sigma-Aldrich)	3282-73-3	406,54	
0.1M BdMeSACl (Sigma-Aldrich)	206752-43-4	442,16	

Table 3 Chemical structures of 0.01M azo-dyes without bound reactive groups

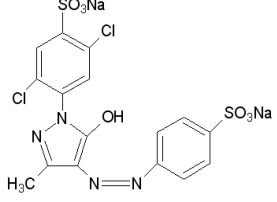
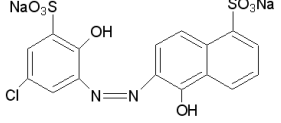
Dye (abbreviation) Supplier	CAS	C.I.No.	Mr	Formula
2xSO ₃ Na Acid Yellow 17 (AY17) Sigma Aldrich	6359-98-4	18965	551,3	
2xSO ₃ Na Mordant Blue 9 (MB9) Sigma-Aldrich	3624-68-8	14855	502,82	

Table 4 Chemical structures of 0.01M monochlorotriazine reactive azo-dyes

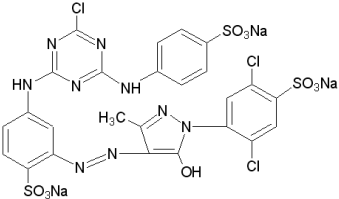
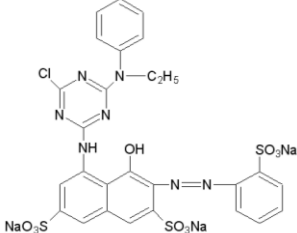
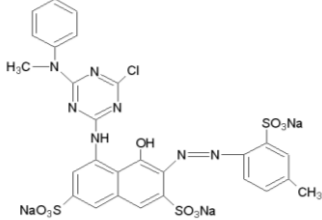
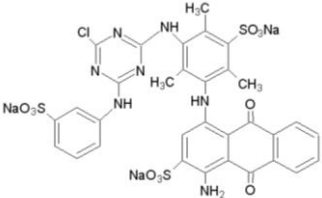
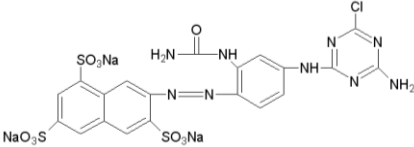
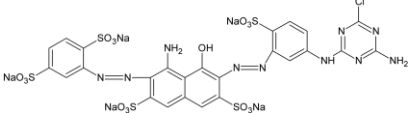
Dye (abbreviation) Supplier	CAS	C.I., C.I.No.	Mr	Formula
3xSO ₃ Na Cibacron Brilliant Yellow 3G-P (CBY) Sigma-Aldrich	50662-99-2	18972	872,97	
3xSO₃Na Reactive Red 24:1 (RR 24:1) Synthesia	72829-25-5	18208:1	804,45	
3xSO₃Na Reactive Red 45:1 (RR 45:1) Synthesia	73816-74-7	18209:1	771,5	
3xSO₃Na Reactive Blue 49 (RB 49) Synthesia	72214-18-7	621526	884,45	
3xSO₃Na Reactive Orange 12 (RO12) Synthesia	70161-14-7	13248	742	
5xSO₃Na Reactive Black 39 (RB 39) Synthesia	68259-02-9	20507	1025,5	

Table 5 Chemical structures of 0.01M monochlorotriazine vinylsulphonic reactive azo-dyes

Dye (abbreviation) Supplier	CAS	Mr	Formula
2xSO₃Na Reactive Yellow 186 (RY 186) Synthesia	84000-63-5	833,45	

Table 6 Chemical structures of 0.01M dichlorotriazine reactive dyes

Dye (abbreviation) Supplier	CAS	C.I., C.I.No.	Mr	Formula
2xSO₃Na Procion Red MX-5B (PR MX-5B) Sigma-Aldrich	17804-49-8	20195	615,34	
2xSO₃Na Reactive Blue 4 resp. Procion Blue MX-R (RB4) Sigma-Aldrich	13324-20-4	61205	637,43	
6xSO₃Na Reactive Red 120 (RR120) Sigma-Aldrich	61951-82-4	292775	1469	

Table 7 Chemical structures of 0.01M vinylsulphonic reactive dyes

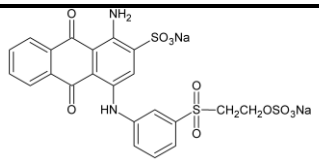
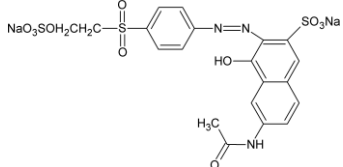
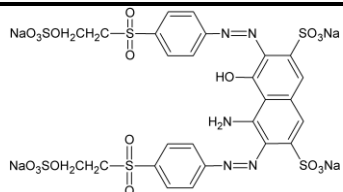
Dye (abbreviation) Supplier	CAS	C.I., C.I.No.	Mr	Formula
2xSO ₃ Na Remazol Brilliant Blue R (RBBR) Sigma-Aldrich	2580-78-1	61200	626,54	
2xSO ₃ Na Reactive Orange 16 (RO16) Sigma-Aldrich	12225-83-1	17757	617,54	

Table 8 Chemical structures of 0.01M divinylsulfonic reactive dyes

Dye (abbreviation) Supplier	CAS	C.I., C.I.No.	Mr	Formula
4xSO ₃ Na Reactive Black 5 (RB5) Sigma-Aldrich	17095-24-8	20505	991,82	

Precipitation process

A solution of reactive dye with concentration of a 0.01 M was placed in a beaker. Individual dyes contain a definite number of SO₃⁻ groups in their structure. A calculated volume of ionic liquid was added to the solution of reactive dye. Reactive dyes were coagulated by the addition of an ionic liquid. The solution was brought to a total volume of 100 mL with distilled water. Next, the mixture was stirred overnight at approximately 300 rpm at room temperature. After the reaction time, the mixture was filtered through a Buchner funnel or filter paper. The organic oily layer, which had usually captured on the walls of the beaker, was washed with distilled water and dissolved in dichloromethane. Decolorization was determined spectrophotometrically by monitoring the decrease in absorbance at λ_{max} of the dye, and then calculated according to the following formulation:

$$\text{Concentration of sample} \left(\frac{\text{mol}}{\text{L}} \right) = \frac{\text{Absorbance of sample} * \text{Concentration of stock solution}}{\text{Absorbance of stock solution}}$$

It was necessary to integrate the dilution factor to the formulation above. Finally, the exact concentration of dye was calculated and the COD, BOD, and AOX values were determined.

General procedure

After the reaction time was a mixture filtered through a Buchner funnel. It was measured absorbance of the filtrate to determine the effectiveness of the removal of dye. Finally was calculated the exact concentration of dye.

A model calculation 1: (Precipitation of 50 mL of 0.01M Reactive Blue 39 of 0.1M Bu₄PCl)

$$n_{dye} = c_{dye} \cdot V_{dye} = 0,01 \cdot 0,05 = 0,0005 \text{ mol} = \underline{0,5 \text{ mmol}} \quad (1)$$

$$n = n_{dye} \cdot n_{number.SO_3skup.} = 0,5 \cdot 5 = \underline{2,5 \text{ mmol}} \quad (2)$$

$$V_{Bu_4P^+Cl^-} = \frac{n}{c} = \frac{2,5}{0,1} = \underline{25 \text{ mL}} \quad (3)$$

A model calculation 2:

$$c_x = \frac{A_x \cdot \frac{c_{st}}{\text{dilution}}}{A_{st}} \cdot \text{dilution} \quad (4)$$

c_x dye concentration after precipitation cationic agent

A_x absorbance of dye after precipitation

c_{st} concentration of the stock solution of the dye

A_{st} absorbance of the dye stock solution

Table 9 Absorbance of the dye solutions at a concentration of 0.01 M in their absorption maximum in the visible range at DR 2800 Spectrophotometer

Dye	λ _{max} [nm]	Absorbance	Dilution
Reactive Orange 12	415	0,494	1000x
Reactive Yellow 186	427	0,646	250x
Cibacron Brilliant Yellow 3G-P	403	0,272	500x
Acid Yellow 17	400	0,289	1000x
Reactive Orange 16	492	0,417	1000x
Reactive Red 45:1	544;520	0,294;0,290	1000x
Reactive Red 24:1	532	0,813	250x
Procion Red MX-5B	513; 537	0,403; 0,405	1000x
Reactive Red 120	511	0,704	1000x
Reactive Black 39	610	0,371	1000x
Reactive Blue 49	587; 625	0,289; 0,286	500x
Mordant Blue 9	516	0,250	1000x
Procion Blue MX-R/Reactive Blue 4	597	0,483	100x
Remazol Brilliant Blue R	592	0,825	100x
Reactive Black 5	596	0,491	1000x

Table 10 Absorbance of the solutions of hydrolyzed dyes at a concentration of 0.01 M in their absorption maximum in the visible range at DR 2800 Spectrophotometer

Hydrolyzed form of dye	λ_{\max} [nm]	Absorbance	Dilution
Reactive Orange 12	425	0,427	1000x
Acid Yellow 17	389	0,262	1000x
Reactive Orange 16	492	0,252	1000x
Reactive Black 39	610	0,390	1000x
Remazol Brilliant Blue R	600	0,294	100x
Reactive Black 5	597	0,459	1000x

Chapter 1

Precipitation of dyes by $R_4P^+X^-/R_4N^+X^-$

General procedure

In the following experiments, the dyes were removed by precipitation using by ionic liquids (tetrasubstituted ammonium and phosphonium salts) from aqueous solutions. Solution of azo-dye with a concentration of 0.01 M was inserted into a beaker. There were used following reactive dyes: Reactive Orange 12, Reactive Orange 16, Reactive Red 45:1, Procion Red MX-5B, Reactive Red 120, Reactive Black 39 and Reactive Black 5. Beside these reactive dyes there were selected two acidic azo-dyes: Acid Yellow 17 and Mordant Blue 9.

Individual dyes contain definite number of SO_3^- groups in their molecules. Calculated volume of tetrasubstituted ammonium or phosphonium salt was added to solution of dye according to A model calculation 1.

There were selected tetrasubstituted phosphonium and ammonium salts (via table 1-2): tetrabutylphosphonium-chloride (0.1M $Bu_4P^+Cl^-$), tributyltetradecylphosphonium-chloride (0.01M $Bu_3C_{14}P^+Cl^-$), tributylhexadecylphosphonium-bromide (0.01M $Bu_3C_{16}P^+Br^-$), tetraphenylphosphonium-bromide (0.01M $Ph_4P^+Br^-$), ethyltriphenylphosphonium-bromide (0.1M $EtPh_3P^+Br^-$), tetraoctylphosphonium-bromide ($Okt_4P^+Br^-$), trihexyltetradecylphosphonium-chloride ($Hex_3C_{14}P^+Cl^-$), Aliquat 336, hexadecyltrimethylammonium-bromide (0.01M $C_{16}Me_3N^+Br^-$), *N*-alkyl-*N,N*-dimethyl-*N*-benzylammonium-chloride (0.1M $AlkdiMeBzN^+Cl^-$), 1-cetylpyridinium-chloride (0.1M $C_{16}Py^+Cl^-$) and 1-methyl-3-oktylimidazolium-chloride ($OMIM^+Cl^-$).

The solution was refilled by distilled water to a total volume of 100 mL. The solution was mixed in a covered beaker with a watch glass overnight at a rate of 300 rpm. After the reaction time was a mixture filtered through a Buchner funnel. It was measured absorbance of the filtrate to determine the effectiveness of the removal of dye. Finally was calculated the exact concentration of dye, according to A model calculation 2.

Chapter 2

Precipitation of selected dyes of hydrolysed form by $R_4P^+X^-/R_4N^+X^-$ with addition of auxiliary filtering material

General procedure

In next part of the experiments, it was verificated the possibility of application of the auxiliary filter material, which was powdered calcium carbonate for easy separation of ionic liquids produced by reaction of acid dyes tested with quaternary ammonium or phosphonium salts. Hydrolysis was performed in five selected dyes:

Reactive Orange 16, Remazol Brilliant Blue R, Reactive Red 45:1, Reactive Black 39 and Reactive Black 5. To a 1L Erlenmeyer flask, immersed in a water bath and equipped with magnetic stirrer and thermometer, it was presented 600 mL of 0.01M aqueous solution of dye. In that order it was added 12.72 g Na₂CO₃ and 30 g NaCl during stirring at 900 rpm at 30 °C. After that the mixture was stirring for 60 minutes at 90 °C.

After cooling, an aqueous solution of hydrolysed dye was verified by selected hydrolysed dyes with quaternary ammonium or phosphonium salts. There were selected: tributyltetradecylphosphonium-chloride (0.01M Bu₃C₁₄PCl), tributylhexadecylphosphonium-bromide (0.01M Bu₃C₁₆PBr), trihexyltetradecylphosphonium-chloride (Hex₃C₁₄PCl), 1-methyl-3-oktylimidazolium-chloride (OMIMCl), *N*-alkyl-*N,N*-dimethyl-*N*-benzylammonium-chloride (0.1M AlkdiMeBzNCl), 1-cetylpyridinium-chloride (0.1M C₁₆PyCl) and Aliquat 336.

Individual dyes contain definite number of SO₃⁻ groups in their molecules (via Table 3-8). Calculated volume of tetrasubstituted ammonium or phosphonium salt was added to solution of dye according to A model calculation 1.

After equilibration (2 hours stirring time) was a mixture filtered through a Buchner funnel. It was measured absorbance of the filtrate to determine the effectiveness of the removal of dye. Finally was calculated the exact concentration of dye, according to A model calculation 2.

The collected filtrates were compared, and absorbance determination of phosphorus and COD. To the residue mixture hydrolysed dye/ionic liquid was added powdered auxiliary filtering material (1 g / 100 mL of the reaction mixture, CaCO₃). After equilibration (usually 2-20 hours) the reaction mixture was filtered through a Buchner funnel - defined size and weight, the filtration time was observed and described amount of undissolved material sticking to the sides of the beaker. The resulting graphs of the efficiency of removal of selected dyes by their precipitation with aqueous solutions of tetrasubstituted ammonium and phosphonium salts and auxiliary filter material are mentioned in chapter Results and discussions.

Chapter 3

Precipitation and flocculation of dilute aqueous solutions of salts selected reactive dyes in solutions of mixtures R₄P⁺X⁻/R₄N⁺X⁻, and with 0.1M Al₂(SO₄)₃/Fe₂(SO₄)₃

General procedure

In the third set of experiments, attention was focused on the precipitation of salts of selected reactive dyes and comparison of precipitation of their hydrolyzed forms with some of the aforementioned phosphoniums, ammonium ion liquids and subsequently with aluminum sulphate or ferric sulphate solution.

The following dyes were used: Reactive Red 45:1, Reactive Orange 12, Cibacron Brilliant Yellow 3G-P, Reactive Black 39 and Reactive Red 120.

The individual dyes have a corresponding number of SO₃ groups in their molecules according to the structures. To a 50 mL of a 0.01M aqueous dye solution was added the calculated volume of the ionic liquid according to the models of calculations 1 and 2. For these experiments the following ILs were selected: tributyltetradecylphosphonium-chloride (0.01M Bu₃C₁₄PCl), tributylhexadecylphosphonium-bromide (0.01M Bu₃C₁₆PBr),

hexadecyltrimethylammonium-bromide (0.01M C₁₆Me₃NBr) and 1-cetylpyridinium-chloride (0.1M C₁₆PyCl). Subsequently, a given volume of 0.1M aluminum or ferric sulphate was added to the mixed solution according to the pre-selected molar ratio of dye: IL:Al³⁺. Aqueous solutions of selected dyes, ionic liquids, and aluminum sulphate were added in various molar ratios.

The volume of the solution was always supplemented with distilled water to a total volume of 100 mL. Subsequently, these solutions were adjusted to a pH of 6, due to the flocculation of the mixed solution in Al³⁺/Fe³⁺ medium at a pH of about 6. The mixture thus formed was left in a beaker covered with a clock glass freely stirred for 1 hour at a rate of 300 rpm.

To determine the efficiency of the removal process, the exact concentration of the dye after precipitation was obtained by measuring the absorbance at the absorption maximum of the separated dye in the visible spectrum on the DR 2800 spectrophotometer. The resulting graphs of the efficiency of removal of selected dyes by their precipitation with aqueous solutions of tetrasubstituted ammonium and phosphonium salts and aluminum sulphate are mentioned in chapter Results and discussions.

Chapter 4

Precipitation and flocculation of selected dye solutions and with aqueous solutions of R₄N⁺X⁻ + Al³⁺/Fe³⁺

General procedure

In the last row, selected experiments involved the precipitation of selected reactive dyes with aqueous solutions with a mixture of tetrasubstituted ammonium salts and aluminum or ferric sulphate. The following selected reactive dyes were used: Reactive Yellow 186, Procion Blue MX-R, Cibacron Brilliant Yellow 3G-P, Reactive Red 24:1 and Reactive Blue 49. To 50 mL of a 0.01 M dye solution was added a given volume of an aqueous solution of tetrasubstituted ammonium salt and aluminum or ferric sulphate. These were mixed solutions: 0.1 M *N*-alkyl-*N,N*-dimethyl-*N*-benzylammonium-chloride (AlkdiMeBzNCl) with 0.1M Al₂(SO₄)₃; 0.05M Di-*n*-decyl(dimethyl)ammonium-bromide (DiDDiMeABr) with 0.1M Al₂(SO₄)₃; 0.1M benzyl(dimethyl)stearylammonium-chloride (BdMeSACl) with 0.1M Al₂(SO₄)₃; 0.1 M Al₂(SO₄)₃; 0.1M *N*-alkyl-*N,N*-dimethyl-*N*-benzylammonium-chloride (AlkdiMeBzNCl) with 0.4M Fe₂(SO₄)₃; 0.1M benzyl(dimethyl)stearylammonium-chloride (BdMeSACl) with 0.4M Fe₂(SO₄)₃; 0.4M Fe₂(SO₄)₃.

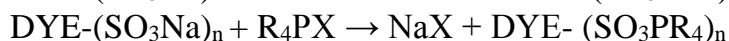
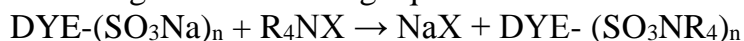
The volume of the solution was always supplemented with distilled water to a total volume of 100 mL. Subsequently, these solutions were adjusted to a pH of 6, due to the flocculation of the mixed solution in Al³⁺/Fe³⁺ medium at a pH of about 6. The mixture thus formed was left in a beaker covered with a clock glass freely stirred for 1 hour at a rate of 300 rpm.

To determine the efficiency of the removal process, the exact concentration of the dye after precipitation was obtained by measuring the absorbance at the absorption maximum of the separated dye in the visible spectrum on the DR 2800 spectrophotometer. The resulting graphs of the efficiency of removal of selected dyes by their precipitation with aqueous solutions of tetrasubstituted ammonium and

phosphonium salts and aluminum sulphate are mentioned in chapter Results and discussions.

3. RESULTS AND DISCUSSION

In the dissertation thesis the methods of precipitation of water-soluble acid dyes, especially reactive dyes and products of their hydrolysis from model wastewater, based on the use of ionic exchange induced by the addition of liquid ion exchanger, such as low melting tetrasubstituted phosphonium and ammonium salts (ionic liquids, IL) were verified. The process of separating dyes from aqueous solutions using the quaternary ammonium or phosphonium salts mentioned is based on the use of ion exchange in the course of forming a water soluble DYE-(IL)_n ion pair of water according to the following equations:



The formation of ion pairs of DYE-(IL)_n was confirmed by NMR spectroscopy; NMR-characterized ion pairs, unlike starting acid dyes, are well soluble in the perfluorodithio-dimethylsulfoxide and chloroform.

In order to facilitate the separation of the resulting ion pairs, the possibility of applying the auxiliary filtering material, powdered calcium carbonate, was carried out in order to absorb the resulting ionic vapors to absorb the inorganic material and to obtain a dye-saturated powder material potentially usable, for example, for dyeing the polymers. For comparison, the possibility of separating the DYE-(IL)_n ion pairs with the addition of inorganic coagulants was verified.

The dye removal efficiency of model wastewater was evaluated by comparing the absorbance of the starting dye solutions and the obtained filtrates measured at the absorption maximum of the dye using the Lambert-Beer law. As an additional method for evaluating the efficiency of removing the dyes from the solutions, the AOX, COD, BOD or ICP-OES assays were used in selected experiments.

The results found in the study of precipitation of studied dyes from aqueous solutions only with tetrasubstituted phosphonium or ammonium salts are summarized in tables 1-2 and charts 1-11.

The results obtained by studying the precipitation of studied hydrolysed dyes from aqueous solutions with ionic liquids followed by the addition of auxiliary filtering material (CaCO₃) are summarized in charts 12-18.

A further series of experiments was carried out using ionic liquids with the addition of inorganic coagulants. The results found in the study of the sorption of studied dyes from aqueous solutions using ionic liquids and flocculants are summarized in graphs 19-31.

3.1 Effect of the structure of R₄P⁺X⁻/ R₄N⁺X⁻ on the efficiency of precipitation of selected dyes

In these experiments, acidic azo dyes (MB9, AY17) and acid reactive dyes (PR MX-5B, RO16, RR 45:1, RO12, CBY, RB5, RB39, RR120) were removed from aqueous solutions by precipitation tetrasubstituted ammonium and phosphonium salts. For the precipitation, relatively cheap, commercially available quaternary ammonium and phosphonium salts with one, two, three or four long alkyl chains (or phenyl

groups) attached to the central quaternized nitrogen or phosphorus forming the cation base of the ionic liquid was used. Specifically, there were used following phosphonium salts: tetrabutylphosphonium-chloride ($\text{Bu}_4\text{P}\text{Cl}$) tetraoctylphosphonium-bromide ($\text{Okt}_4\text{P}\text{Br}$), tetraphenylphosphonium-bromide ($\text{Ph}_4\text{P}\text{Br}$) ethyltriphenylphosphonium-bromide ($\text{EtPh}_3\text{P}\text{Br}$) tributyltetradecylphosphonium-chloride ($\text{Bu}_3\text{C}_{14}\text{P}\text{Cl}$) tributylhexadecylphosphonium-bromide ($\text{Bu}_3\text{C}_{16}\text{P}\text{Br}$) trihexyltetradecylphosphonium-chloride ($\text{Hex}_3\text{C}_{14}\text{P}\text{Cl}$), where the removal efficiency of the dyes studied when adding an equimolar amount of the quaternary phosphonium salt to the amount of sulpho groups bound in the dye molecules is shown in charts 1-8.

To assess the efficiency of removing acidic dyes by treatment with quaternary ammonium salts there were tested: 1-methyl-3-octylimidazolium-chloride (OMIMCl), *N*-alkyl-*N,N*-dimethyl-*N*-benzylammonium-chloride (AlkdiMeBzNCl), 1-cetylpyridinium-chloride (C_{16}PyCl), hexadecyltrimethylammonium-bromide ($\text{C}_{16}\text{Me}_3\text{NBr}$) and methyltrioctylammonium-chloride (Aliquat 336) added in an equimolar ratio to the amount of sulpho groups bound in dye molecules, the results are shown in charts 9-11.

The formation of an ionic pair between the cationic quaternary phosphonium or ammonium part of R_4PX , respectively R_4NX and acidic dyes causes a significant increase in molecular weight and a decrease in polarity of the resulting $\text{DYE}-(\text{IL})_n$ ion pair.

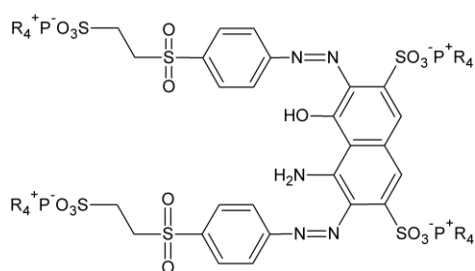


Figure 1 Structure of $4\text{R}_4\text{P.RB5}$ salt prepared by Reactive Black 5 precipitation with - $4.\text{R}_4\text{PX}$

The aim was to test the effect of the structure of phosphonium and ammonium IL_s on dye removal efficiency of the structurally often very different acid dyes from aqueous solutions. All experiments presented in this chapter were performed under conditions of effective agitation for a minimum of 20 hours.

3.1.1 Influence of the structure of phosphonium IL_s used on removal of acid dyes

During comparison of the chain length effect in the homologous quaternary phosphonium salt series with four identical substituents attached to the central phosphorus atom ($\text{Bu}_4\text{P}\text{Cl}$, $\text{Ph}_4\text{P}\text{Cl}$ and $\text{Okt}_4\text{P}\text{Br}$) for efficiency of removal of dye, there is apparent decrease of solubility of the respective ion pairs with a significantly greater molar mass than the molar mass of the starting of the acidic dye, the least soluble are in almost all cases ionic vapors $\text{DYE}-(\text{Okt}_4\text{P})_n$, via chart 2. The difference in the efficiency of separation of ion pairs of dyes using tetraoctylphosphonium-bromide is also affected by its insolubility in water, to the contaminated water was

dosed undiluted unlike the other two R₄PX dosed in the form of an aqueous solution), which, when dosed with an equimolar amount, sometimes resulted in the coating of the particles of Okt₄PBr forming with the insoluble precipitate DYE-(Okt₄P)_n, which could be accompanied by low conversion of ion exchange reaction, whose kinetics depend on the rate of diffusion of water-soluble dye through the layer of insoluble ion-pair dye:(Okt₄P)_n to water insoluble Okt₄PBr. It has been observed that the isolated ion pairs DYE-(Okt₄P)_n are water insoluble to the extent that the addition of water to the isolated tar pitch ion pair DYE-(Okt₄P)_n is not accompanied, even after a long mixing time, by the coloration of the aqueous phase. Selective reactive dyes were subjected to their alkaline hydrolysis and the effectiveness of the removal of the hydrolysed dyes from aqueous solutions with the most effective water-soluble Ph₄PCl quaternary phosphonium salt was tested.

Chart 1 Comparison of the effect of the R size on the efficiency of dye removal using the equimolar amount of R₄PX relative to the number of the sulpho groups bound in the dye structure

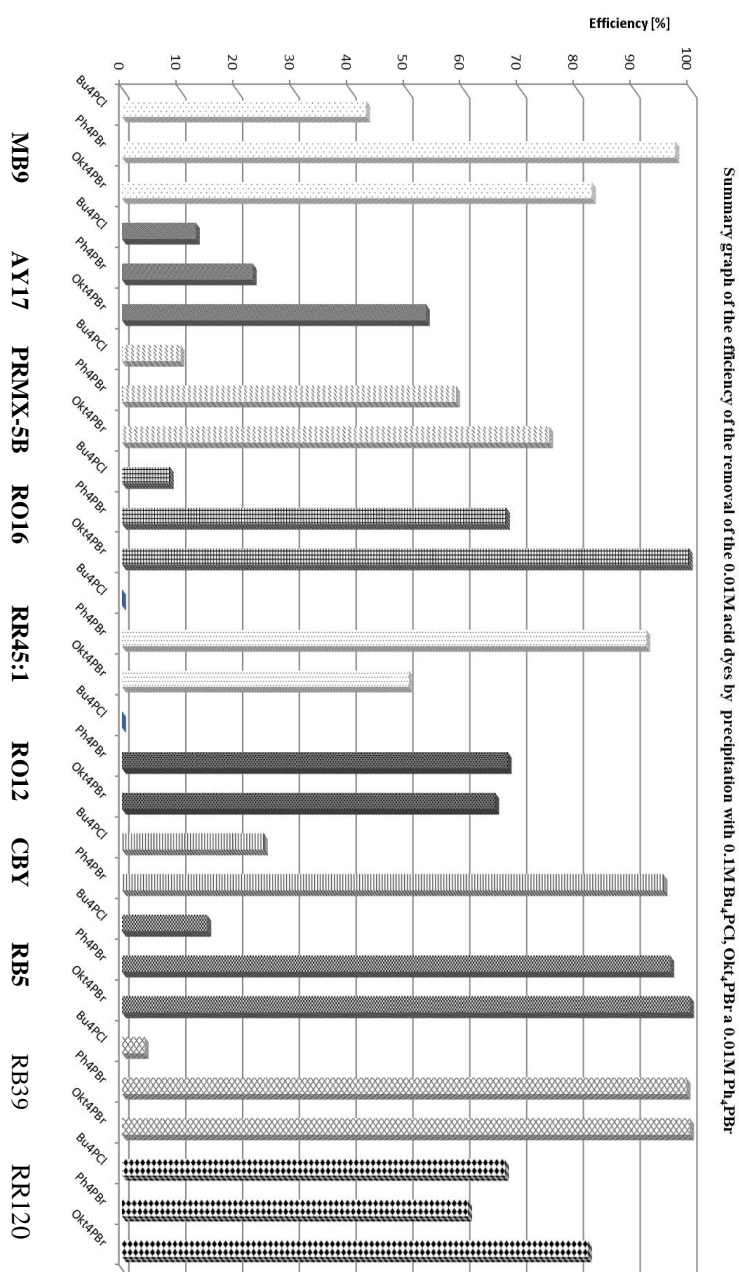
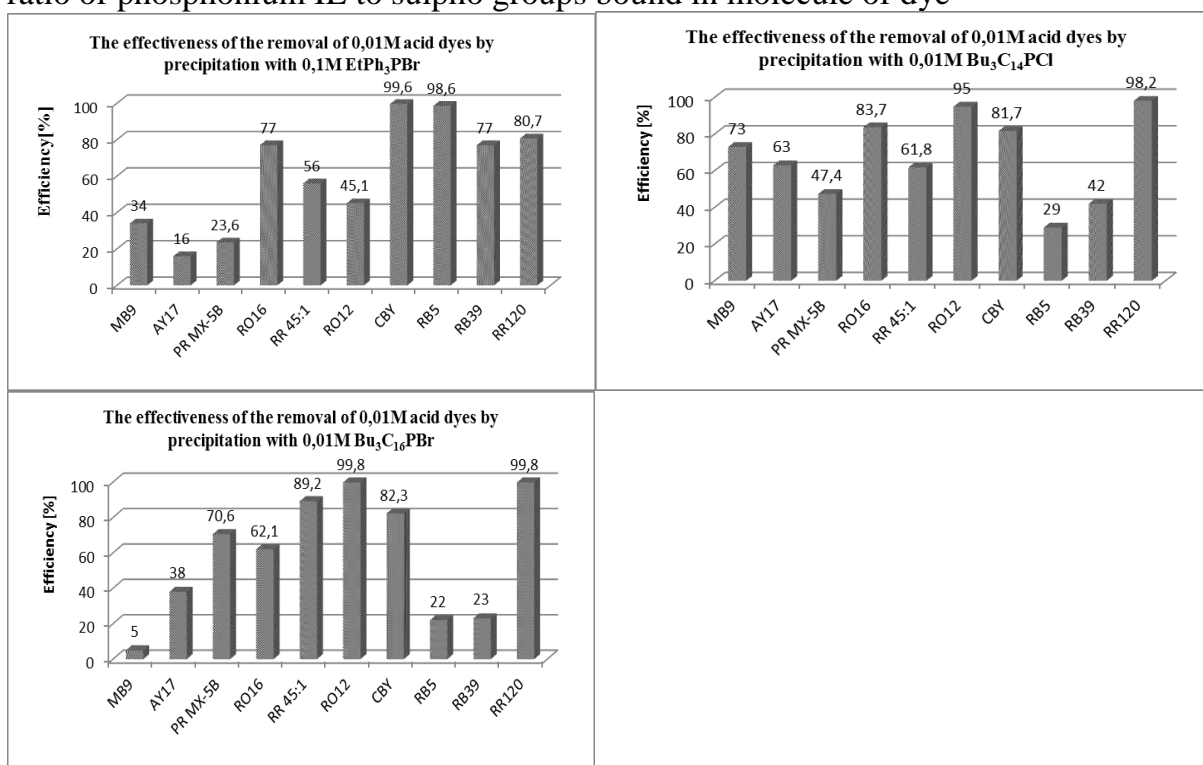


Chart 2, 3, 4 Influence of the addition of 0.1M EtPh₃PBr, 0.01M Bu₃C₁₄PCl and 0.01M Bu₃C₁₆PBr on the efficiency of removal of 0.01M acid dyes at the equimolar ratio of phosphonium IL to sulpho groups bound in molecule of dye



From the above graphs, it is evident that the most effective removal of reactive dyes from water was achieved using Bu₃C₁₄PCl, where Bu₃C₁₄PCl is significantly better water soluble than Bu₃C₁₆PCl, favoring the use of Bu₃C₁₄PCl for the separation of dyes from water when in case of Bu₃C₁₄PCl it is not necessary to add large volumes of an aqueous solution of such precipitating agent.

Chart 5 Influence of the addition of Hex₃C₁₄PCl on the efficiency of the removal of 0.01M acid dyes at the equimolar ratio of IL to the -SO₃Na in molecule of dye

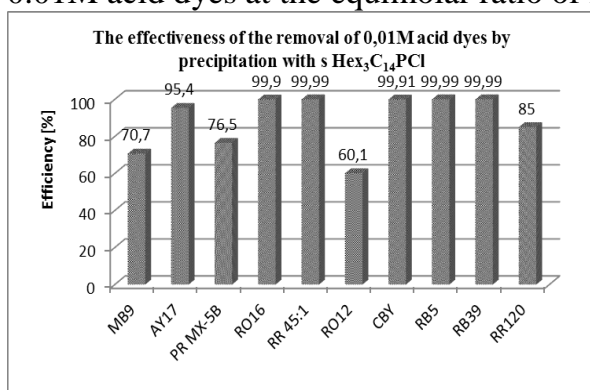


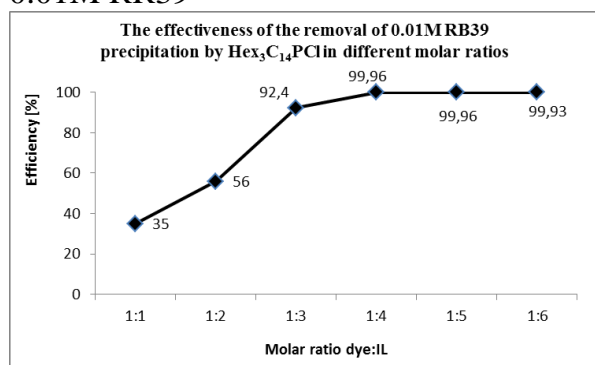
Table 11 Efficiency of removal of COD and AOX in filtrates from precipitation of 0.01M dyes with Hex₃C₁₄PCl

Dye	Efficiency of removal of COD (%)	Efficiency of removal of AOX (%)	Efficiency of removal of absorbance (%)
0.01M RB 39	99,7	99,42	99,99
0.01M RR 45:1	96,3	93,75	99,99
0.01M RR120	90	70	85

Using phosphonium ionic liquid Hex₃C₁₄PCl there was achieved nearly complete removal of other quaternary phosphonium salts hardly separable dye RR 45:1, RB39, next to them also for RR120, whose removal efficiency of the aqueous solution was in use Hex₃C₁₄PCl insufficient. The obtained aqueous filtrates were besides the evaluation of the efficiency of separation of dye based on the measurement of absorbance at wavelength of maximum absorption for the colorant with the subsequent use of the Lambert-Beer law measured and aggregated parameters COD and AOX, whereby the measured values correlate well with the results obtained by evaluating the efficiency calculated on the basis absorbance measurement.

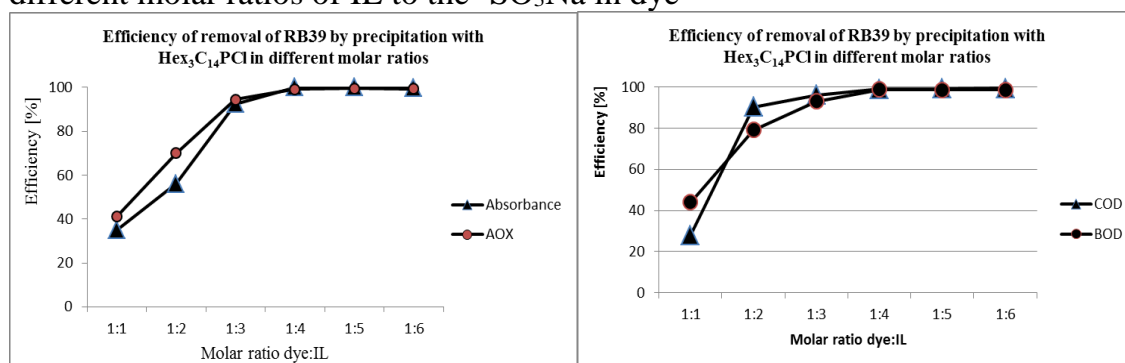
A study of the influence of the amount of quaternary phosphonium salt added on Hex₃C₁₄PCl on the separation efficiency, specifically for the RB39 dye, was performed. As the chart 6 shows the high efficiency separation is already achieved at a ratio of more than 3 moles used Hex₃C₁₄PCl to 1 mol of dye, the optimum ratio is 5, corresponding to the representation Hex₃C₁₄P⁺ cations in the resulting water-insoluble ionic pair RB39-(Hex₃C₁₄P)₅.

Chart 6 Influence of added amount of Hex₃C₁₄PCl on the efficiency of removal of 0.01M RR39



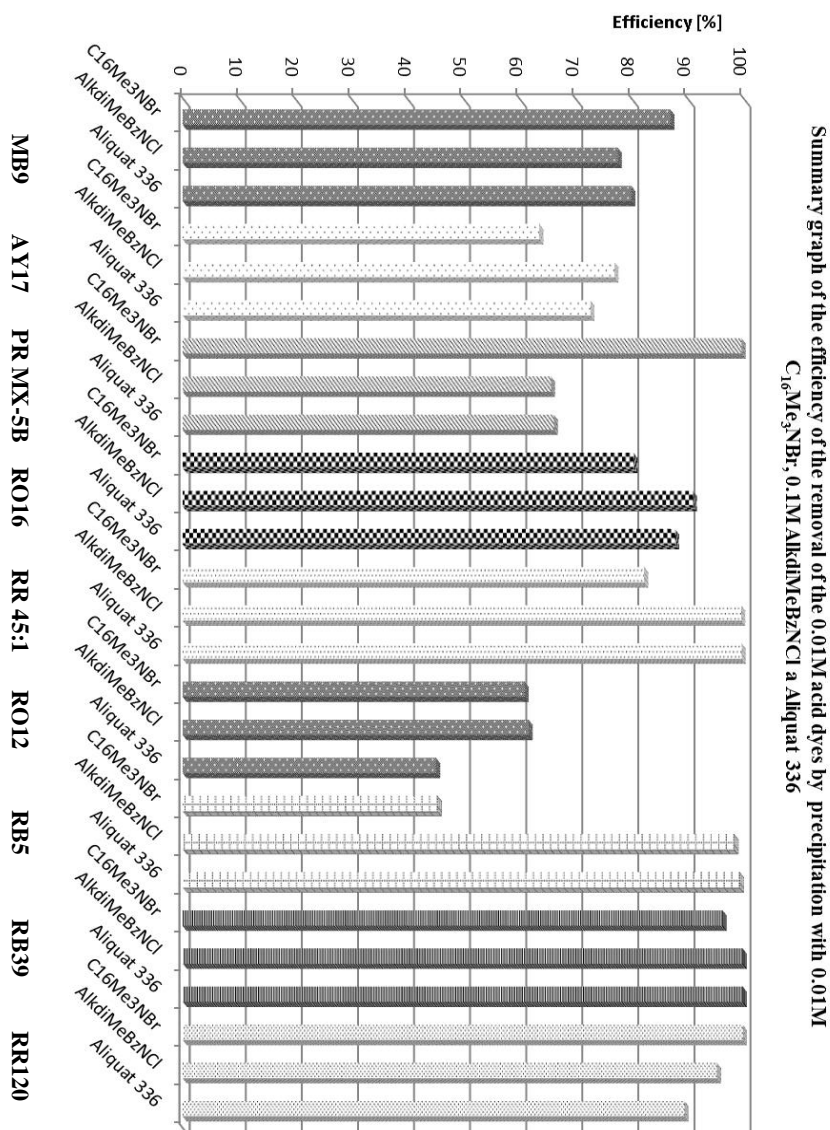
In addition to evaluating the separation efficiency according to the measured absorbance, the aggregate parameters AOX, COD and BOD were determined, with the measured values well correlated with the efficiency of the dye removal as assessed by the Lambert-Beer law, via charts 7, 8.

Chart 7, 8 Comparison of efficiency of removal of RB39 by the COD, BOD and AOX parameters in the filtrates after precipitation of the reactive dye with Hex₃C₁₄PCI at different molar ratios of IL to the -SO₃Na in dye



3.1.2 Influence of the structure of ammonium ILs used on removal of acid dyes

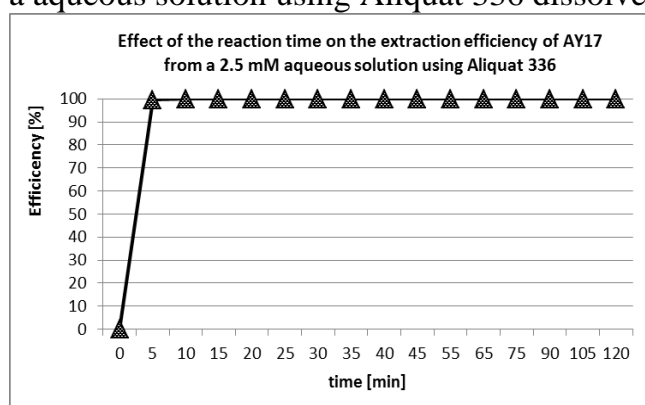
Chart 9 Comparison of the effect of the number of long alkyl chains in the R₄N⁺ cation



An experimental comparison of the effect of the size of quaternary ammonium cations on the formation of water-poorly soluble ion pairs of DYE-(R₄N)_n was performed analogously to testing the influence of phosphonium cation size on the solubility of the resulting ion pairs. The results of this comparison for several commercially readily available quaternary ammonium salts of the formula MeR₃NX differing in the size and type of alkyl R. In the case of a three-length long ionic liquid (R¹-R³ =octyl, commercial product Aliquat 336), this compound is almost insoluble in water, was therefore dispensed without dilution directly into the dye solution. The other two quaternary ammonium salts tested, namely AlkdiMeBzNCl and C₁₆Me₃NBr, bound with one long alkyl group, were added to the dye solutions as an aqueous solution.

As can be seen from Chart 9, the most reliable quaternary ammonium salts for the effective removal of the acidic dyes tested were AlkdiMeBzNCl with two bulky alkyl groups and Aliquat 336, an ionic liquid in organic ion cation, bound to three long alkyls. The use of C₁₆Me₃NBr with a single long-chain bond provided very different results. The fluctuations in the effectiveness of the Aliquat 336 application could again be related to the low solubility of both the ionic liquid and the resulting ionic pairs DYE-(Aliquat336)_n which at an Aliquat 336 feed in an amount equimolar to the amount of sulpho groups bound in the dissolved dye could lead to incomplete conversion in water of the dissolved dye to the desired insoluble ion pair DYE-(Aliquat336)_n due to the slow diffusion of the dye from the aqueous solution to the insoluble organic layer Aliquat 336/DYE-(Aliquat336)_n. To verify the diffusion effect on dye separation efficiency which was not quantitatively eliminated from the aqueous solution by addition of an equimolar amount of Aliquat 336, the possibility of forming an ion pair of AY17 dye with Aliquat 336 using a low polar water-miscible solvent such as octan-1-ol, which dissolves well the Aliquat 336. As can be seen from chart 10, the vigorous mixing of the aqueous solution of AY17 with Aliquate 336 dissolved in octan-1-ol results in a quantitative extraction of the resulting ion pair AY17-(Aliquat336)₂, which confirms the above-mentioned hypothesis the effect of diffusion on the separation efficiency of dyes when using water-insoluble ionic liquids.

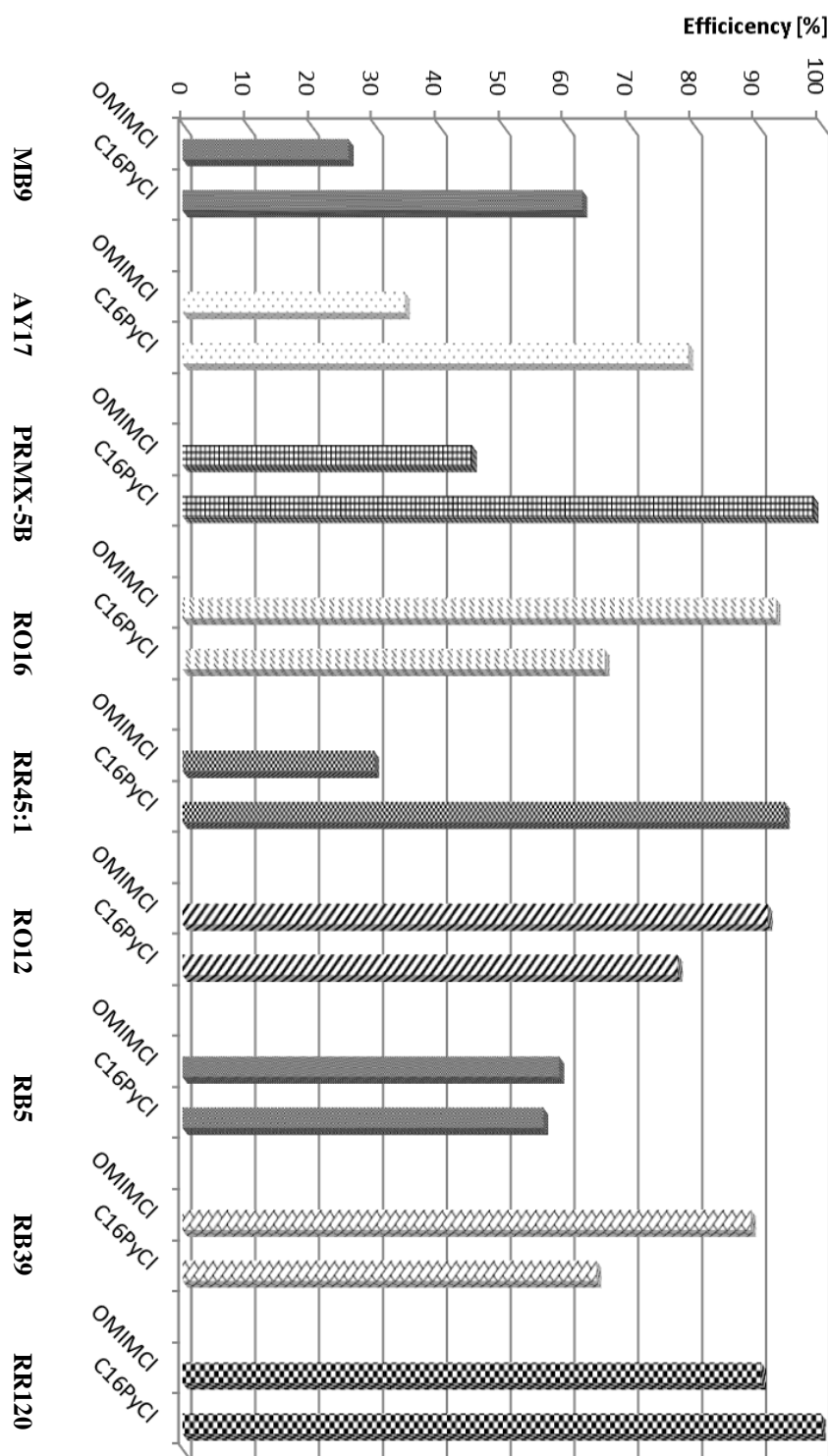
Chart 10 Effect of reaction time on the efficiency of extraction of 2.5 mM AY17 from a aqueous solution using Aliquat 336 dissolved in octan-1-ol at 480 rpm



Quaternary phosphonium salts proved to be well soluble in water with Bu₃C₁₄PCl. All of the water-insoluble quaternary ammonium (Aliquat 336, OMIMCl)

or phosphonium (Okt₄PCl, Hex₃C₁₄PCl) salts provide a large scattering effect, as demonstrated by at least Aliquat 336 and OMIMCl, causing a slow diffusion of the dye from the aqueous solution to a strongly viscous water insoluble ionic liquid coated with a layer of insoluble ion pairs.

Chart 11 Comparison of the effect of R₄NX based on nitrogen-containing heterocycles on the efficiency of removal of acid dyes



Summary graph of the efficiency of the removal of the 0.01M acid dyes by precipitation with OMIMCl a 0.1M C₁₆PyCl

3.2 Verification of the effect of addition of auxiliary filter material on the effectiveness of removing $R_4P^+X^-/R_4N^+X^-$ ionic pairs with acidic dyes and their hydrolysis products from contaminated water

In this part of the experiments, the effectiveness of addition of auxiliary filtration material to dyestuff-contaminated water was added after the addition of ionic liquids. Powdered calcium carbonate was tested as an auxiliary filter material. The efficiency of separation of the resulting ion pairs was tested using ionic liquids, the organic cation of which contains at least one long alkyl chain and at least one alkyl chain with a number of four or more carbon atoms. The main disadvantage of these bulky cationic ionic liquids is the formation of colloidal dispersions that negatively affect the separability of the resulting DYE-(IL)_n ion pairs. The efficiency of separation of reactive dyes was studied after hydrolysis too, and the separability of hydrolyzed dyes in the form of hydrolyzedDYE-(IL)_n was better in all cases than in case non-hydrolyzedDYE-(IL)_n.

Chart 12, 13 Comparison of the efficiency of separation of 0.01M hydrolyzed dyes RO16, RB39, RBBR and RB5 with phosphonium IL added in an equimolar ratio to the number of sulpho groups bound in the dye after addition of 1 and 2 g of CaCO₃ / 100 mL of contaminated water

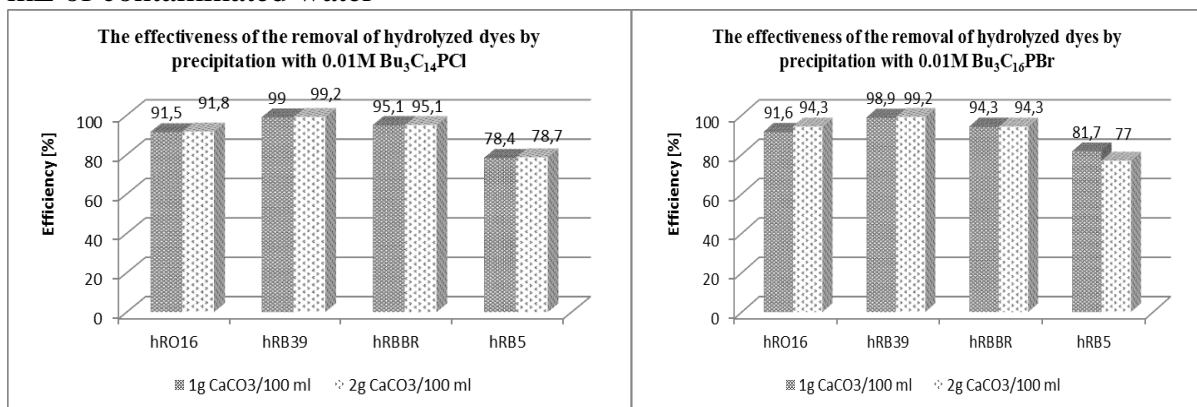
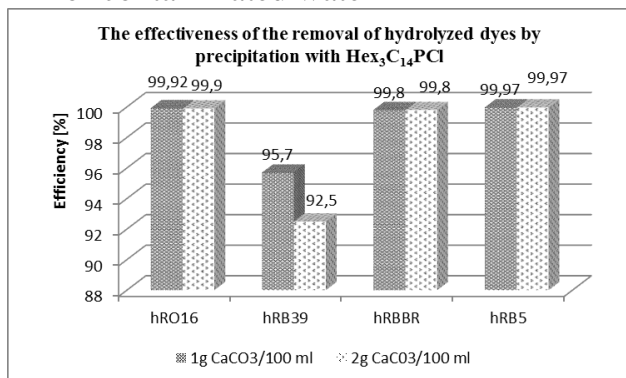


Chart 14 Comparison of the efficiency of separation of 0.01M hydrolyzed dyes RO16, RB39, RBBR and RB5 with phosphonium IL added in an equimolar ratio to the number of sulpho groups bound in the dye after addition of 1 and 2 g of CaCO₃ / 100 mL of contaminated water



For testing, quaternary ammonium salts, which are effective, have been selected but, on the other hand, they tend to interact with dyes to form colloidal dispersions. A comparison of the achieved results is given in the following bar charts 15-18. Again, it is confirmed that addition of the auxiliary filter material makes it possible to accelerate the entire process of water purification. Improvement of ion pair separation DYE-(R₄N)_n using calcium carbonate powder is achieved irrespective of whether water-soluble or water-insoluble quaternary ammonium salt has been used for the formation of ion pairs.

Chart 15, 16 Comparison of the efficiency of separation of 0.01M hydrolyzed dyes RO16, RB39, RBBR and RB5 with ammonium IL added in an equimolar ratio to the number of sulpho groups bound in the dye after addition of 1 and 2 g of CaCO₃ /100 mL of contaminated water

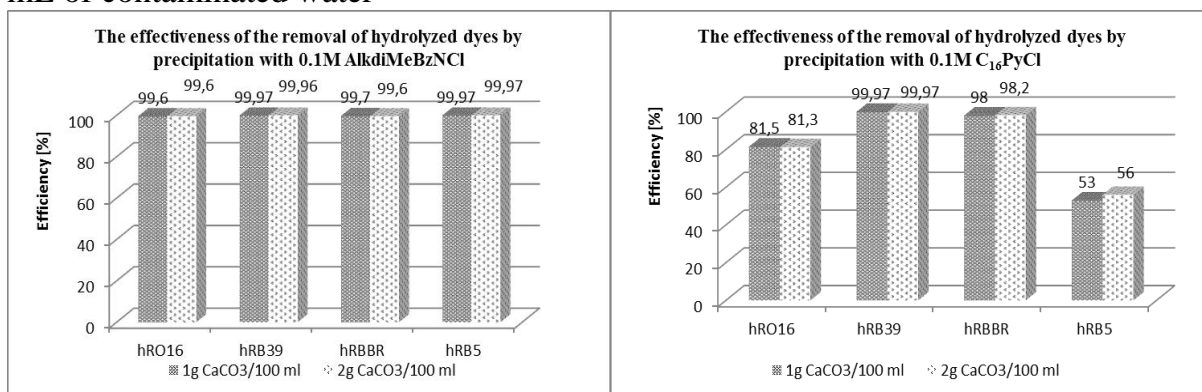
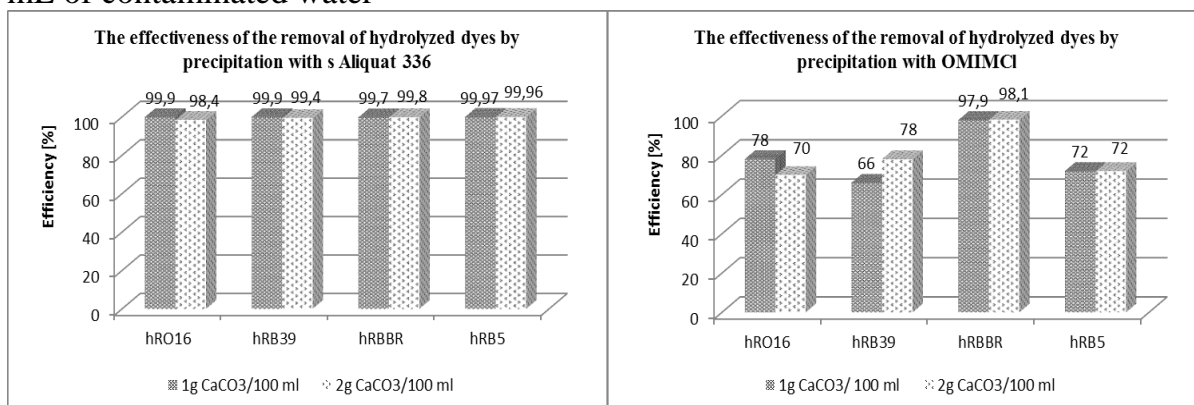


Chart 17, 18 Comparison of the efficiency of separation of 0.01M hydrolyzed dyes RO16, RB39, RBBR and RB5 with ammonium IL added in an equimolar ratio to the number of sulpho groups bound in the dye after addition of 1 and 2 g of CaCO₃ /100 mL of contaminated water



The use of powdered limestone as an auxiliary filter material in a quantity of 1 g CaCO₃/100 mL of water to some degree facilitates the separation of the DYE-(Bu₃C_xP)_n ion pairs, demonstrating a higher efficiency of decolorisation of the aqueous filtrates obtained than those obtained without the aid of filter material, via charts 12-18.

Although the experiments have shown a better separation of the resulting DYE-(IL)_n ion pairs, the low affinity of the tested ion pairs for the auxiliary filter, did not prove this procedure. The most of the resulting ion pairs have no good affinity for the surface of the limestone used, the powder fraction of the auxiliary filter material is

contaminated with the tar fraction formed by the ion pair DYE-(IL)_n, the separated filter cake will not be used as a potential color filler, as it was originally intended, it would be necessary to treat it as waste.

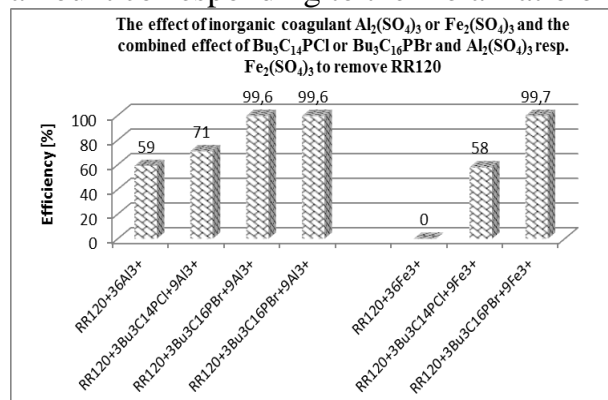
Therefore, the following experiments have been focused on verifying the improvement of ion pair separability by applying cheap inorganic coagulants which produce hydrated alumina or ferric oxides during the clarification process, that products are also potentially useful as fillers after drying.

3.3 Verification of the use of inorganic coagulants for ion pair separation efficiency of DYE-(IL)_n

The effect of adding an aqueous solution of aluminum sulphate or ferric sulphate to the separation of dyes from aqueous solutions was first tested by adding an aqueous solution of IL. And after forming DYE-(IL)_n ion pairs the aqueous solution of the respective coagulant was added. For comparison, the effectiveness of the alone coagulant for the decoloration of contaminated water was also performed. After the addition of the aqueous solution of coagulant the pH of the resulting mixture was always controlled and, if it was necessary, adjusted to 5 < pH < 7 with addition of aqueous NaHCO₃.

The aim was to find optimal dosing of the selected coagulant, in what proportion of IL to coagulant can be achieved the maximum efficiency of separation the dye from the contaminated water.

Chart 19 Comparison of the effectiveness of removal of 0.01M RR120 (with 3 SO₃Na bound) by adding the inorganic coagulant 0.1M Al₂(SO₄)₃, 0.4M Fe₂(SO₄)₃ (added in the ratio of RR120:Al³⁺(Fe³⁺)=1:36) and the effect of 0.01M Bu₃C₁₄PCL or 0.01M Bu₃C₁₆PBr followed by the addition of 0.1M Al₂(SO₄)₃ or 0.4M Fe₂(SO₄)₃ in an amount corresponding to the molar ratio of -SO₃Na:IL:Al³⁺(Fe³⁺)=1:0.5:1.5



As demonstrated by the above experimental results, the efficiency of removing RR120 from the aqueous solution can be almost quantitative even at the half-stroke of IL versus stoichiometry when excess inorganic coagulant is added.

Chart 20 Comparison of the effectiveness of removal of the reactive dye RO12 (with 3 SO₃Na bound) by adding the inorganic coagulant Al₂(SO₄)₃, Fe₂(SO₄)₃ (added in the ratio of RO12:Al³⁺(Fe³⁺)=1:9 and the effect of Bu₃C₁₄PCl or Bu₃C₁₆PBr followed by the addition of Al₂(SO₄)₃ or Fe₂(SO₄)₃ in an amount corresponding to the molar ratio of -SO₃Na:IL:Al³⁺(Fe³⁺)=1:1:5/3

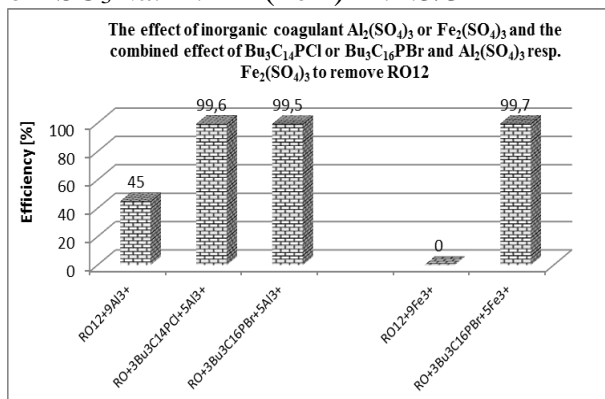


Chart 21, 22 Comparison of effect of precipitation and flocculation on efficiency of removal of reactive dyes with Bu₃C₁₄PCl and subsequent addition of Al₂(SO₄)₃ in various molar ratios of the dye:IL:Al³⁺

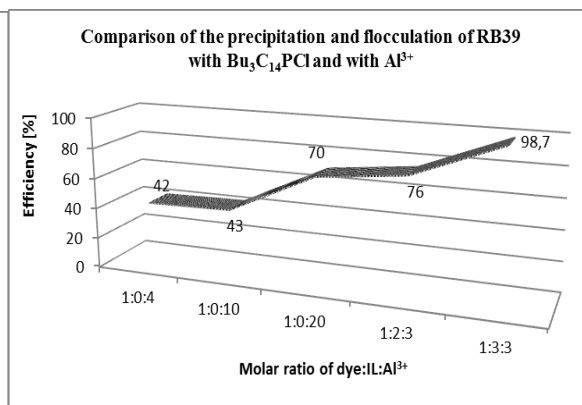
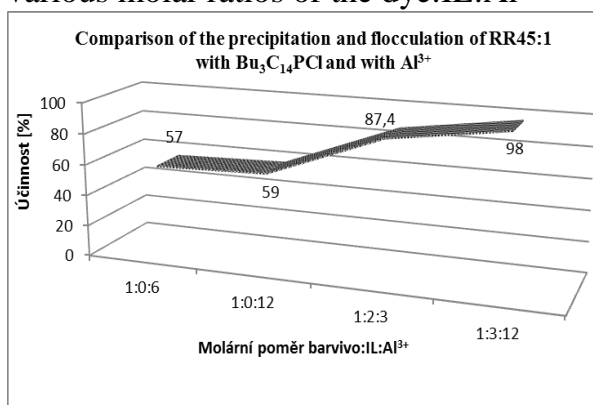


Chart 23, 24 Comparison of effect of precipitation and flocculation on efficiency of removal of reactive dyes with C₁₆Me₃NBr and subsequent addition of Al₂(SO₄)₃ in various molar ratios of the dye:IL:Al³⁺

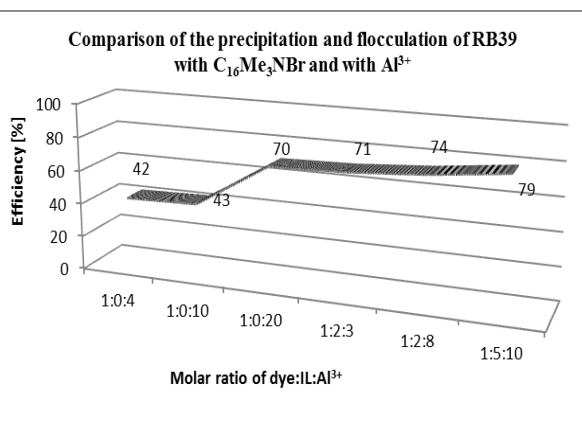
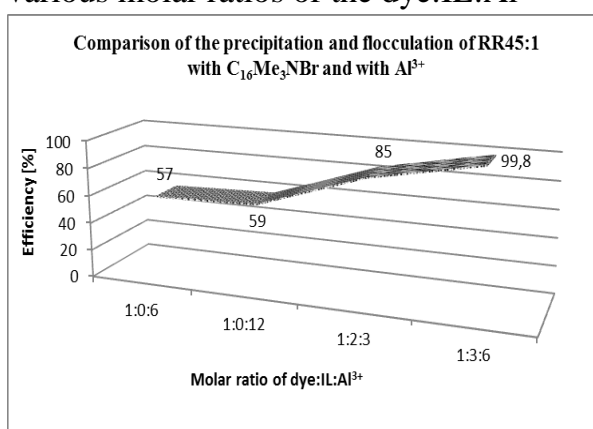
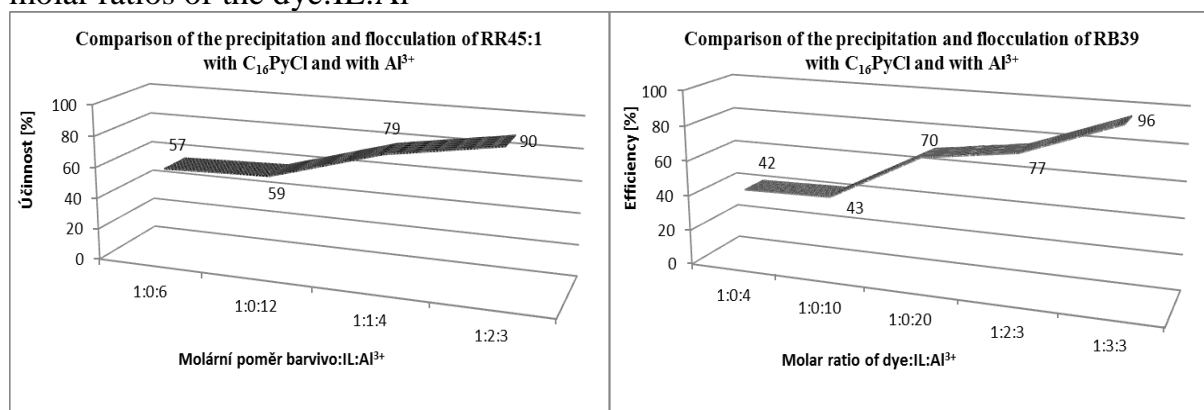


Chart 25, 26 Comparison of effect of precipitation and flocculation on efficiency of removal of reactive dyes with $C_{16}PyCl$ and subsequent addition of $Al_2(SO_4)_3$ in various molar ratios of the dye:IL: Al^{3+}



3.4 Effect of the structure of $R_4P^+X^-/R_4N^+X^-$ and Al^{3+}/Fe^{3+} solutions used on salt removal activity of selected reactive dyes after precipitation and flocculation

To simplify the dye removal procedure from contaminated water, the possibility of dispensing both ionic and inorganic coagulants simultaneously was verified. The following graphs compare the results of the separation of reactive dyes, the "number" abbreviated as the amount of IL added to 1 mole in the contaminated water-dyed dye.

Chart 27, 28 Comparison of the effect of inorganic coagulant 0.1M $Al_2(SO_4)_3$ or 0.4M $Fe_2(SO_4)_3$ and mixtures of 0.1M AlkdiMeBzNCl + 0.1M $Al_2(SO_4)_3$ or 0.4M $Fe_2(SO_4)_3$ on the efficiency of the removal of reactive dyes

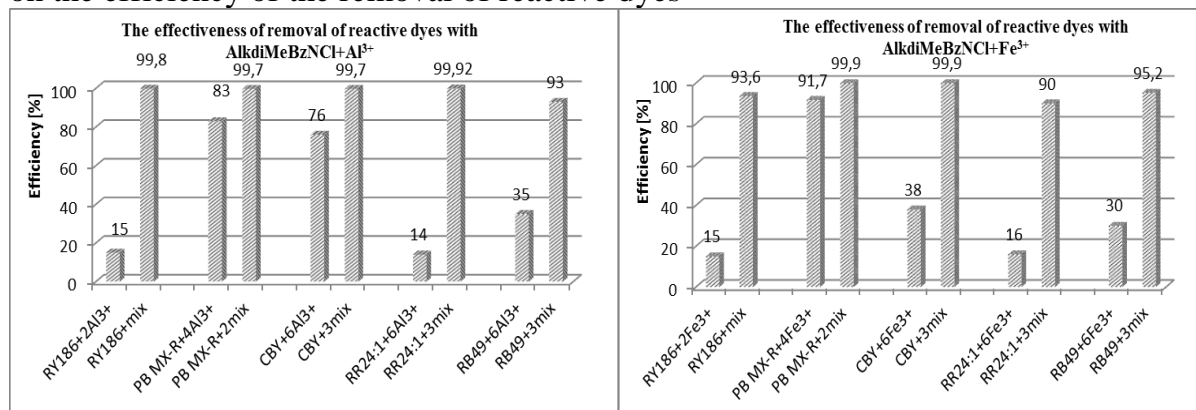


Chart 29, 30 Comparison of the effect of inorganic coagulant 0.1M $\text{Al}_2(\text{SO}_4)_3$ or 0.4M $\text{Fe}_2(\text{SO}_4)_3$ and mixtures of 0.1M $\text{BdMeSACl} + 0.1\text{M } \text{Al}_2(\text{SO}_4)_3$ or 0.4M $\text{Fe}_2(\text{SO}_4)_3$ on the efficiency of the removal of reactive dyes

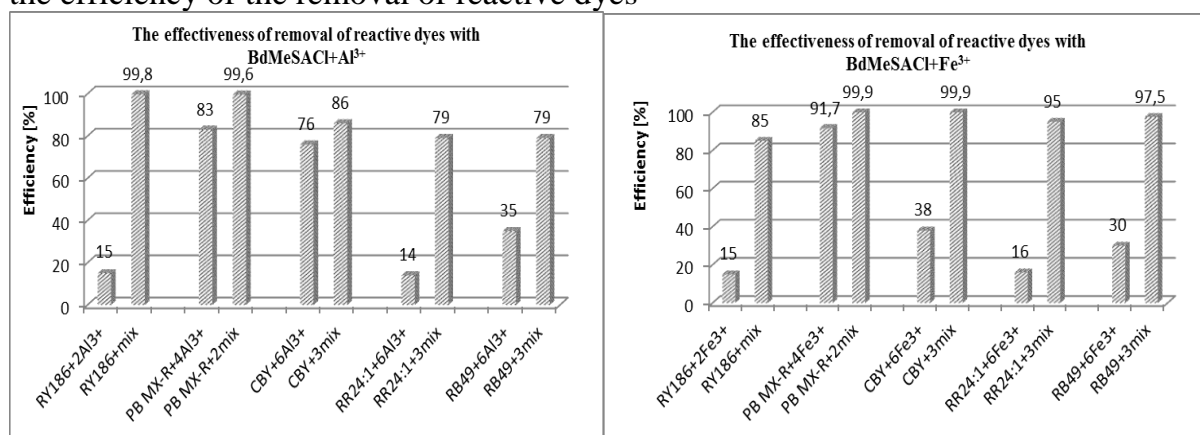
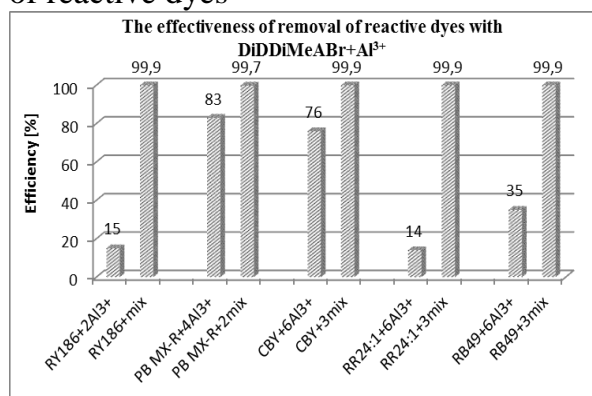


Chart 31 Comparison of the effect of inorganic coagulant 0.1M $\text{Al}_2(\text{SO}_4)_3$ and mixtures of 0.05M $\text{DiDDiMeABr} + 0.1\text{M } \text{Al}_2(\text{SO}_4)_3$ on the efficiency of the removal of reactive dyes



The very good results of the combined action of ILs and subsequently inorganic coagulants led to the preparation of aqueous solutions of the commercially available ionic liquid of benzalkonium-chloride (AlkdiMeBzNCl), which not only provided some of the best efficiency for the separation of the acid dyes tested but was additionally miscible with water which allows the preparation of mixed aqueous solutions of AlkdiMeBzNCl dissolved in an aqueous solution of the selected inorganic coagulant.

4. CONCLUSION

The aim of this dissertation was to verify the possibility of simple and effective removal of water-soluble dyes, namely acid azo dyestuffs, by the action of tetrasubstituted phosphonium and ammonium salts (IL_s) to form poorly soluble ion pairs of $\text{DYE}-(\text{IL})_n$, with the potential for further utilization of such separated dyes. The intention was to verify the relationship between the structure of quaternary ammonium and phosphonium salts tested and their efficiency on the separation of tested dyes from model aqueous solutions. The quaternary ammonium and phosphonium salts used in many cases have the properties of ionic liquids, which may

be advantageous in the event of subsequent manipulation with them on an operational scale.

The dye removal efficiency from model wastewater was evaluated by comparing the absorbance of the starting dye solutions and the resulting filtrates in the area of the absorption maximum of the tested dye. As an additional method for evaluating the efficiency of removing the dyes from the solutions, the determination of AOX, COD, BOD or ICP-OES in selected experiments was used, the resulting ionic liquids were analyzed by NMR spectroscopy.

In order to achieve rapid and efficient separation, the possibility of adsorbing the DYE-(IL)_n ion pairs into the cheap inorganic materials, for example used as fillers in polymers, was subsequently verified. Therefore, the possibility of using ionic liquids with the addition of powdered calcium carbonate as a possible auxiliary filter material has been investigated. This process led to shortening the separation time of the DYE-(IL)_n ion pairs from the aqueous phase. The best results were obtained by using tetradecyl-tributylphosphonium-chloride (Bu₃C₁₄PCl) and benzalconium-chloride (AlkdiMeBzNCl) with water-insoluble tetradecyltrihexylphosphonium-chloride (Hex₃C₁₄PCl) and Aliquat 336 with water-miscible ionic liquids. However, a filter cake consisting of a mixture of CaCO₃ with a bonded tar pitch ion DYE-(IL)_n, formation of a non-homogeneous mass.

Subsequently, the possibility of using ionic liquids with the co-operation of inexpensive inorganic coagulants, aluminum sulphate and ferric sulphate, was tested, which during the coagulation and flocculation form the corresponding (hydr)oxides used as fillers in the polymers. For the effective separation of dyes from water, the use of concentrated aqueous solutions of aluminum or ferric sulphate with ionic liquids with a bulky organic cation proved to be beneficial. In these experiments, it has been shown that even for the very efficient removal of dyes from contaminated water, a bellow stoichiometric amount of ionic liquid can be used provided that an excess of inorganic coagulant is applied to the mixture.

The best results were obtained by using water-miscible ionic liquids with tetradecyltributylphosphonium-chloride (Bu₃C₁₄PCl) and benzalkonium-chloride (AlkdiMeBzNCl). Addition of an aqueous solution containing a mixture of an aluminum sulphate or ferric sulphate ionic liquid results in neutralizing within a few minutes to form well separable flakes of the respective metal hydroxides, which are very efficiently sorbed by the interaction of ionic liquids with the dyes formed by the ion pairs. Sludge separated by filtration can be easily dried by standing in the air. Within this dissertation thesis prepared samples of dried sludge DYE-(IL)_n/M(OH)₃, where M=Al or Fe, are currently tested as potential low-grade dyes/fillers for coloring the mixture of surfactants used as part of hygiene products for sanitary technology.

The results obtained led to the patenting of the procedure for the application of selected ionic liquids dissolved in an aqueous solution of inorganic coagulants for the effective separation of acidic dyes from contaminated waters (patent University of Pardubice CZ303942) and to publishing obtained results in the reviewed and impacted journals listed in the list of published works.

List of references

- [1] CALVAR, N., GONZÁLEZ, E. J., DOMÍNGUEZ, Á. Acoustic, volumetric and osmotic properties of binary mixtures containing the ionic liquid 1-butyl-3-methylimidazolium dicyanamide mixed with primary and secondary alcohols, *J. Chem. Therm.*, 2012, Vol. 50, pp. 19-29.
- [2] RAO, V. G., MANDAL, S., GHOSH, S. Aggregation behavior of Triton X-100 with a mixture of two room-temperature ionic liquids: can we identify the mutual penetration of ionic liquids in ionic liquid containing micellar aggregates?, *J. Phys. Chem. B*, 2012.
- [3] AUDRIETH, L. F., LONG, A., EDWARDS, R. E. Fused onium salts as acids. Reactions in fused pyridinium hydrochloride, *J. Am. Chem. Soc.*, 1936, Vol. 58, pp. 428.
- [4] VALIZADEH, H., AMIRI, M., HOSSEINZADEH, F. Nanoparticles of organosilane-based nitrite ionic liquid immobilized on silica for the diazotization of aniline derivatives and subsequent synthesis of azo dyes, *Dyes and pigments*, 2011, Vol. 92, pp. 1308-1313.
- [5] PEI, Y., LIU, J., YAN, Z. Association of ionic liquids with cationic dyes in aqueous solution: a thermodynamic study, *J. Chem. Thermodynamics*, 2012, Vol. 47, pp. 223-227.
- [6] PITTER, P. *Hydrochemie*, 1999, pp. 302-303. ISBN 80-7080-340-1.
- [7] VALIZADEH, H., AMIRI, M., SHOMALI, A. Ionic liquid 1-(3-trimethoxysilylpropyl)-3-methylimidazolium nitrite as a new reagent for the efficient diazotization of aniline derivatives and *in situ* synthesis of azo dyes, *J. Iran. Chem. Soc.*, 2011, Vol. 2, pp. 495-501.
- [8] GRELUK, M., HUBICKI, Z. Sorption of SPANDS azo dye on polystyrene anion exchangers: equilibrium and kinetic studies, *Journal of hazardous materials*, 2009, Vol. 172, pp. 289-297.
- [9] MAZMANCI, M. A., UNYAYAR, A. Decolorization efficiency of *Funalia trogii* under static condition: Effect of C: N ratios, 2010.
- [10] MUTHURAMAN, G., PALANIVEU, K. Selective extraction and separation of textile anionic dyes from aqueous solution by tetrabutyl ammonium bromide, *Dyes and pigments*, 2005, Vol. 64, pp. 251-257.
- [11] ABSALAN, G., ASADI, M., KAMRAN, S. Removal of reactive red-120 and 4-(2-pyridylazo) resorcinol from aqueous samples by Fe₃O₄ magnetic nanoparticles using ionic liquid as modifier, *Journal of hazardous materials*, 2011, Vol. 192, pp. 476-484.
- [12] LI, Ch., XIN, B., XU, W. Study on the extraction of dyes into a room-temperature ionic liquid and their mechanisms, *J. Chem. Tech. Biotechnol.*, 2007, Vol. 82:, pp. 196-204.

List of Student's Published Works

1. Weidlich T., Martinková J.: Application of Tetraphenyl- and Ethyltriphenylphosphonium Salts for Separation of Reactive Dyes from Aqueous Solution, *Separation Science and Technology*, 47, 2012, s. 1-6
2. Václavíková J., Bandžuchová L., Mikulášek P.: COD, BOD, and AOX measurements of filtrates obtained from the precipitation of reactive dyes by ionic liquids, *Scientific Papers of the University of Pardubice*, 19, 2013, s. 173-184
3. Weidlich T., Martinková J.: Removal of acid dyes from aqueous effluents using ionic liquids, *Vlákna a textil*, 23, 2016, s. 219-223
4. Weidlich T., Fulínová T., Kovářová D., Václavíková J.: Treatment of model wastewater contaminated with reactive acid dyes using ionic liquids, *Waste forum*, 2, 2018, s. 108-116
5. Patent: Weidlich T., Martinková J.: Způsob srážení barviv z vodných roztoků, CZ303942 (B6) 3.7.2013 (PV2012-359)