

Treatment of model wastewater contaminated with reactive acid dyes using ionic liquids

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Abstract

The paper focuses on the simple separation of reactive acid dyes dissolved in aqueous solution using low-melting quaternary ammonium salts (ionic liquids). The effect of bulkiness of quaternary ammonium cations added in the form of readily applicable ionic liquids on the removal efficiency was studied. Especially benzyldimethylhexadecylammonium chloride combines acceptable aqueous solubility and high removal efficiency for all tested dyes. Rapid removal of dyes Reactive Orange 16, Reactive Blue 4, Reactive Orange 12, Reactive Black 5 and Reactive Black 39 from diluted aqueous solution was successfully tested using cheap and readily commercially available ionic liquid benzalkonium chloride as substitute of expensive benzyldimethylhexadecylammonium chloride liquid ion exchanger with co-action of inorganic coagulant (Al(III) or Fe(III) sulfate). The obtained removal efficiency of tested dyes from model aqueous solutions using aqueous mixture of 0.1 mol L^{-1} benzalkonium chloride and 0.4 mol L^{-1} $\text{Al}_2(\text{SO}_4)_3$ is higher than 88 %, in most cases over 97 %. The removal efficiency of benzalkonium chloride mixed with aqueous $\text{Fe}_2(\text{SO}_4)_3$ is less effective.

Keywords: reactive acid dye; ion exchange; ion-pair; coagulation; precipitation.

Introduction

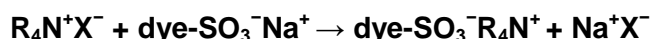
The water is most frequently used green solvent applicable for example for the production of anionic (or acid) azo dyes. Sulfonic acid groups bonded in the structures of anionic dyes make these colorants water soluble. The main method applied for the isolation of produced acid dyes from the reaction mixture is the precipitation of produced dye by salting out and subsequent filtration. The produced aqueous mother liquors contain high loads of refractory COD (Chemical Oxygen Demand) caused by dissolved polar aromatic compounds, AOX (Adsorbable Organic Halogens) if halogenated starting materials are used and high salt loads from salting out process (Scheme 1)¹.

Ionic liquids (ILs) are low melting organic salts composed by large asymmetric organic cations and inorganic or organic anions (see Figure 1 and Table 2). Some ionic liquids are water soluble, whereas the others are lipophilic and sparingly soluble². In general, their solubility depends on the nature of both cation and anion². The aqueous solubility of ionic liquids commonly diminishes with growing bulkiness of cation and anion, see Figure 1.

One of the typical property of ionic liquids is their ion exchange ability which is commonly used for synthesis of task-specific ionic liquids. The interaction between acid dyes and bulky cations of cationic surfactants has been described³⁻⁶.

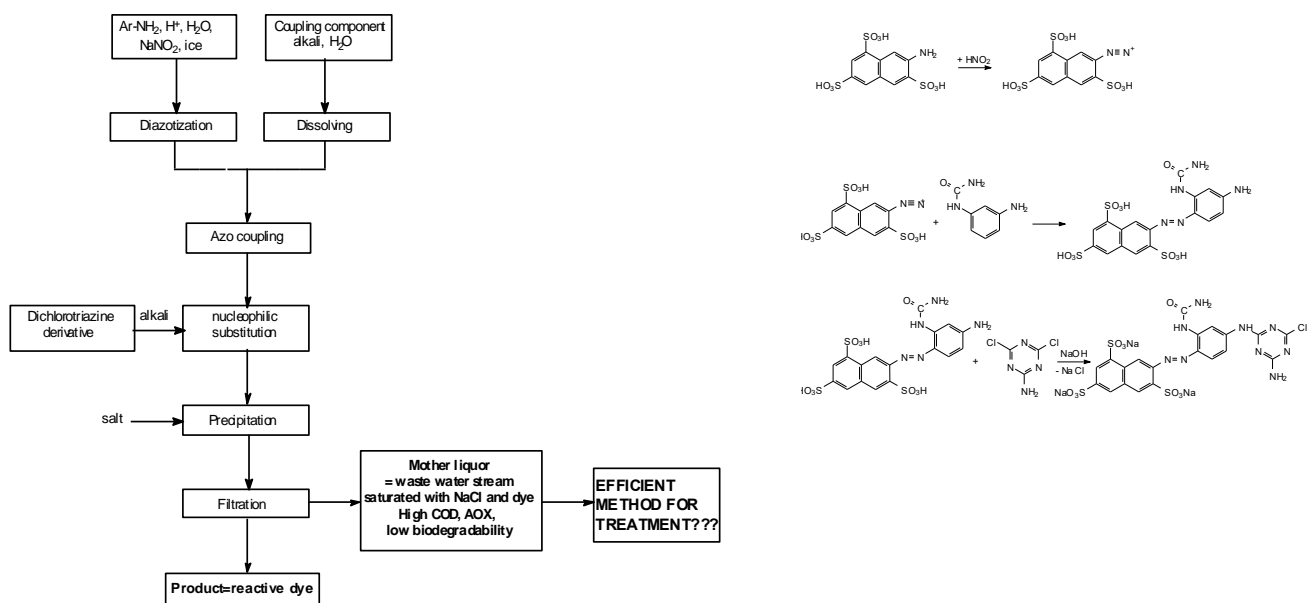
The investigation of quaternary salt-anionic dye ($\text{dye-SO}_3^- \text{R}_4\text{N}^+$) ion pair formation has shown that the importance of long-range electrical forces is basically to bring the dye anion and the ionic liquid cation close enough to enable the action of short-range noncoulombic attractive van der Waals forces and hydrophobic interactions³.

The cheap commercially available ionic liquids ideal for ion exchange reactions are usually halides (mostly chlorides) of quaternary ammonium salts. We proved earlier that the anion exchange of halide (X^-) in several ionic liquids using suitable source of larger anion (for example sodium salts of anionic dye, dye- $\text{SO}_3^- \text{Na}^+$) is very simple even in aqueous solution⁴⁻⁸:



The effect of pH on the efficiency of the formation of dye- $\text{SO}_3^- \text{R}_4\text{N}^+$ ion pairs was published elsewhere⁴.

As was observed earlier, the most effective molar ratio of used large organic cation (R_4N^+) and sulfonic acid anions bound in dye structure (dye- SO_3Na) is $\text{R}_4\text{N}^+ : \text{dye-SO}_3\text{Na} = 1 : 1$ ⁴⁻⁸.



Scheme 1: Production of reactive acid dyes, formation of RO12 as an example

Experimental part

Methods and materials

Chemicals and reagents

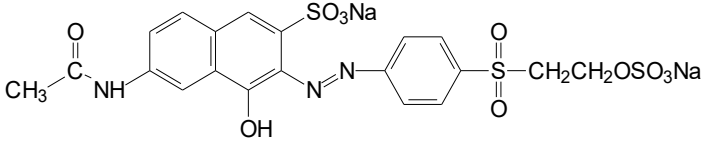
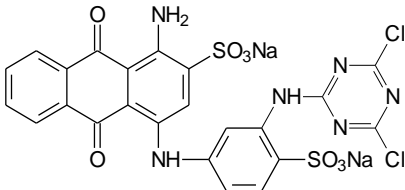
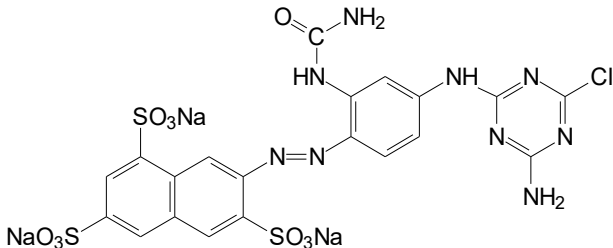
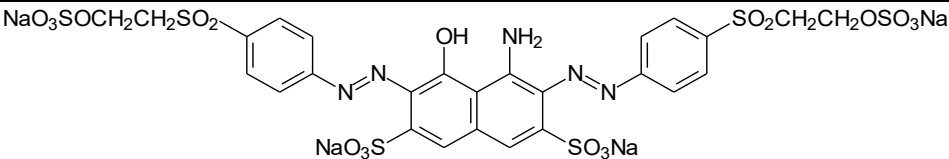
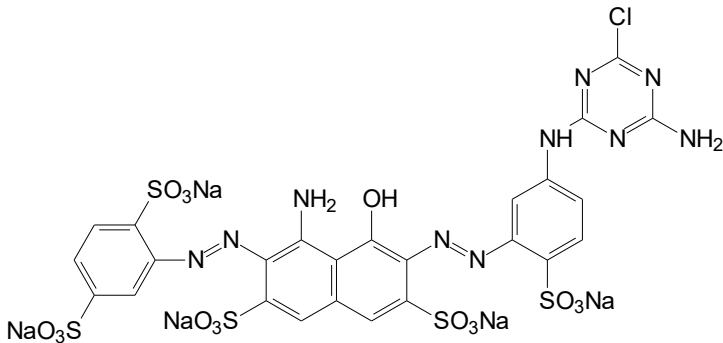
Reactive Blue 4, Reactive Blue 5, Reactive Orange 16 dyes and used ionic liquids (quaternary ammonium salts) were supplied by Sigma-Aldrich Co. Reactive Black 39 and Reactive Orange 12 was obtained from Synthesia Co. (Pardubice, Czech Republic). Stock solutions of the dyes (10×10^{-3} M) were prepared in distilled water. 100 mM stock solutions of ionic liquids were prepared in distilled water. All above mentioned chemical were obtained of highest available purity without any further purification.

Mixed aqueous solution of 0.1 M benzalkonium chloride together with 0.4 M aqueous $\text{Al}_2(\text{SO}_4)_3$ (or $\text{Fe}_2(\text{SO}_4)_3$, respectively) was prepared by addition and dissolution of 42 g (100 mmol) of benzalkonium chloride in 100 g (400 mmol) of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (or 290 g (400 mmol) of $\text{Fe}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, respectively) dissolved in 700 mL of distilled water and diluting of the obtained solution to exact 1000 mL volume using distilled water.

Analytical instruments

A spectrophotometer DR2800 (Hach-Lange, Austria) was used to measure the absorbance values of the dyes to establish their A_{\max} and concentrations. A magnetic stirrer HeITEC (Heidolph Instruments GmbH&Co.) was used for stirring of solutions.

Table 1: Description of used anionic dyes

Anionic dye	Chemical structure
Reactive Orange 16 (RO16) CAS No.: 12225-83-1 Color Index No.: 17757 $M_r = 617.54$ g/mol $\lambda_{\max} = 492$ nm	
Reactive Blue 4 (RB4) CAS No.: 13324-20-4 Color Index No.: 17757 $M_r = 637.43$ g/mol $\lambda_{\max} = 597$ nm	
Reactive Orange 12 (RO12) CAS No.: 70161-14-7 Color Index No.: 13248 $M_r = 742$ g/mol $\lambda_{\max} = 415$ nm	
Reactive Black 5 (RB5) CAS No.: 17095-24-8 Color Index No.: 20505 $M_r = 991.82$ g/mol $\lambda_{\max} = 596$ nm	
Reactive Black 39 (RB39) CAS No.: 17095-24-8 Color Index No.: 20507 $M_r = 1025.5$ g/mol $\lambda_{\max} = 610$ nm	

Precipitation of dyes by ion-pair formation

An aliquot of neat room temperature ionic liquid or of the above-mentioned 100 mM aqueous solution of ionic liquid was added into a beaker (400 mL) with the same 25 mL of 10×10^{-3} M dye solution, and the volume of solution in each beaker was replenished up to 200 mL. After 20 hours of stirring at the speed of 480 rpm and the temperature of 20 ± 1 °C, after filtration by suction and measuring dye concentration in filtrates, the maximum removal efficiency (RE %) of dyes was determined from absorbance

measurements according to the concentration absorbance standard curves at the respective maximum adsorption wavelength of the individual dye solutions (see Table 1).

Afterwards, RE % was calculated from Eq.1:

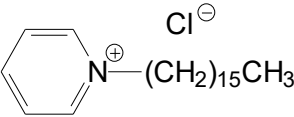
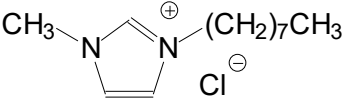
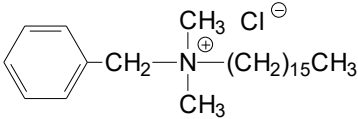
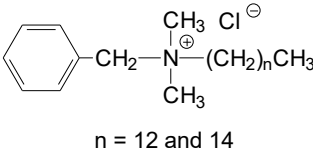
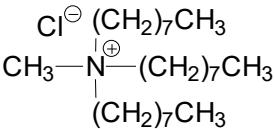
$$RE (\%) = (1 - A/A_0) \times 100 \quad (\text{Eq. 1})$$

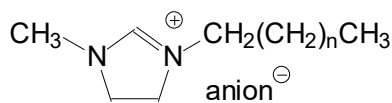
where A and A_0 denote the absorbance in the solution after and before precipitation, respectively.

Co-precipitation of reactive dyes using benzalkonium chloride and $Al_2(SO_4)_3$ or $Fe_2(SO_4)_3$ flocculant

The aliquot of aqueous 0.1M benzalkonium chloride in 0.4 M $Al_2(SO_4)_3$ solution was added dropwise into the stirred 100 mL of 1×10^{-2} M aqueous dye solution and the volume of reaction mixture was replenished up to 200 mL. After 15 minutes of stirring at the speed of 480 rpm and the temperature of 20 ± 1 °C, filtration by suction and measuring dye concentration in filtrates, the maximum RE of dyes was determined from absorbance measurements (see Results and discussion chapter).

Table 2: Description of used $R_4N^+Cl^-$

Ammonium-based ionic liquids $R_4N^+Cl^-$	Structure of used $R_4N^+Cl^-$
Cetylpyridinium chloride cetylpyCl $C_{21}H_{38}ClN$ $M_r = 340.0$ g/mol M.p.: 80 – 84 °C	
1-methyl-3-octylimidazolium chloride OMIMCl $C_{12}H_{23}ClN_2$ $M_r = 230.78$ g/mol M.p.: below 20 °C	
Benzylhexadecyldimethylammonium chloride BzC16diMeNCl Average $M_r = 396.1$ g/mol M.p.: 55 – 65 °C	
Benzalkonium chloride BAC Average $M_r = 348.4$ g/mol M.p.: below 20 °C	
Methyltrioctylammonium chloride MetriOctNCl Average $M_r = 404.16$ g/mol M.p.: below 20 °C	



n = 2: 1-butyl-3-methylimidazolium salt (BMIM):

Water soluble are BMIMs containing anions:

Cl^- ; HSO_4^- ; $\text{CH}_3\text{OSO}_3^-$; BF_4^- ; $p\text{-CH}_3\text{-C}_6\text{H}_4\text{-SO}_3^-$

Water soluble are BMIMs containing anions:

PF_6^- ; $\text{CH}_3(\text{CH}_2)_7\text{SO}_3^-$

n = 6: 1-methyl-3-octylimidazolium salt (OMIM):

Water soluble are OMIMs containing anions:

Cl^- ; HSO_4^-

Water soluble are BMIMs containing anions:

BF_4^- ; PF_6^- ; $\text{CH}_3(\text{CH}_2)_7\text{SO}_3^-$; $p\text{-CH}_3\text{-C}_6\text{H}_4\text{-SO}_3^-$

Figure 1: Relationship between aqueous solubility and size of cation and anion of AlkMIM salts depicted as typical commonly used ionic liquids¹.

Results and discussion

Dye precipitation tests

Firstly there were conducted initial experiments to investigate the ability of studied dyes to form insoluble ion pairs dye- $\text{SO}_3^- \text{R}_4\text{N}^+$. For this purpose four ionic liquids (see Table 2) with different aqueous solubility, hydrophilic hexadecylpyridinium chloride (cetylpyCl, benzyltrimethylammonium chloride (BzC16diMeNCl), lipophilic, sparingly soluble 1-methyl-3-octylimidazolium chloride (OMIMCl) and practically insoluble trioctylmethylammonium chloride (MetriOctNCl), were tested as liquid ion exchangers. These ionic liquids were used in equimolar quantity to the number of sulfo groups bound in the structure of dyes (see Table 1). Trioctylmethylammonium chloride is hydrophobic, in water practically insoluble ionic liquid and it was applied neat in molten form. The other three ionic liquids were used as simply applicable 0.1 M aqueous solution. The obtained results are summarized in Figure 2. As could be seen, the removal efficiency of tested dyes increase with number of alkyl chains bound on quaternary nitrogen in ionic liquid structure used as liquid ion exchanger.

To complete the separation of produced tarry-like ion pairs the reaction time 20 hours under stirring of the mixture of diluted aqueous dye solution with added ionic liquid was applied at first. In all cases part of dissolved dyes was removed, as could be seen in Figure 2. However, even under these conditions the main observed problem was the common formation of quite stable colloidal systems in case of part of used ionic liquids. These colloids disable effective isolation of produced dye- $\text{SO}_3^- \text{R}_4\text{N}^+$ ion pairs from the aqueous phase by filtration and hereby negatively influenced the observed removal efficiency. Nevertheless, using ionic liquids containing bulky cation (substituents R in $\text{R}_4\text{N}^+\text{X}^-$ are long alkyl chain, MetriOctNCl preferably) we observed practically complete separation of produced dye- $\text{SO}_3^- \text{R}_4\text{N}^+$ ion pairs.

To reduce the time for the studied separation procedure, the effect of reaction time for ion exchange reaction accompanied by decolourization between insoluble MetriOctNCl and dye dissolved in aqueous solution was investigated. To ensure efficient mass transport the two-phase system composed from aqueous solution of dye and 1-octanol solution of MetriOctNCl were used. Mentioned kinetics was studied using two structurally quite different dyes Reactive Orange 16 and Reactive Blue 4. Nevertheless, in both cases the reaction time was quite similar. After approximately 15 minutes of vigorous stirring the residual concentration of dye in aqueous solution was stabilized and removal efficiency higher than 99 % was reached, see Figure 3.

However, the application of MetriOctNCl in organic solvent was abandoned due to the environmental reasons and our interest was focused on BzC16diMeNCl as the water soluble ionic liquid with bulky cation. BzC16diMeNCl is quite expensive compound (Sigma-Aldrich Co. price is 5,500 CZK/100 grams⁷)

for the waste water treatment. In addition, this ionic liquid sometimes formed colloidal dye-SO₃⁻R₄N⁺ ion pairs which significantly reduced removal efficiency of RO12 dye. On the other hand, commonly used cationic surfactant benzalkonium chloride (alkylbenzyltrimethylammonium chloride, BAC) is very similar ionic liquid which is much cheaper (Sigma-Aldrich Co. price is 4,098 CZK/1 kg or 0.6 – 10 USD/kg from different Asian suppliers)⁹⁻¹¹. To solve problems with potential dye-SO₃⁻R₄N⁺ ion pairs colloidal mixture formation, co-action of cheap inorganic coagulant (aluminium(III) sulfate) for the removal of dye-SO₃⁻R₄N⁺ was tested and compared with co-action of ferric sulfate. After addition of equimolar quantity of BAC dissolved in excess of aqueous Al₂(SO₄)₃ (or Fe₂(SO₄)₃, respectively) the pH of the produced mixture was adjusted to pH~6 – 6.5 which is accompanied by flocculation of dye-SO₃⁻R₄N⁺ adsorbed on precipitated Al(OH)₃ (or Fe₂(SO₄)₃, respectively). The obtained results compared with action of sole Al₂(SO₄)₃ and BzC16diMeNCl are depicted in Figure 4. As could be seen, mixture of BAC and ferric sulfate is not so effective for treatment of model contaminated wastewater in comparison with mixture of BAC and aluminium sulfate.

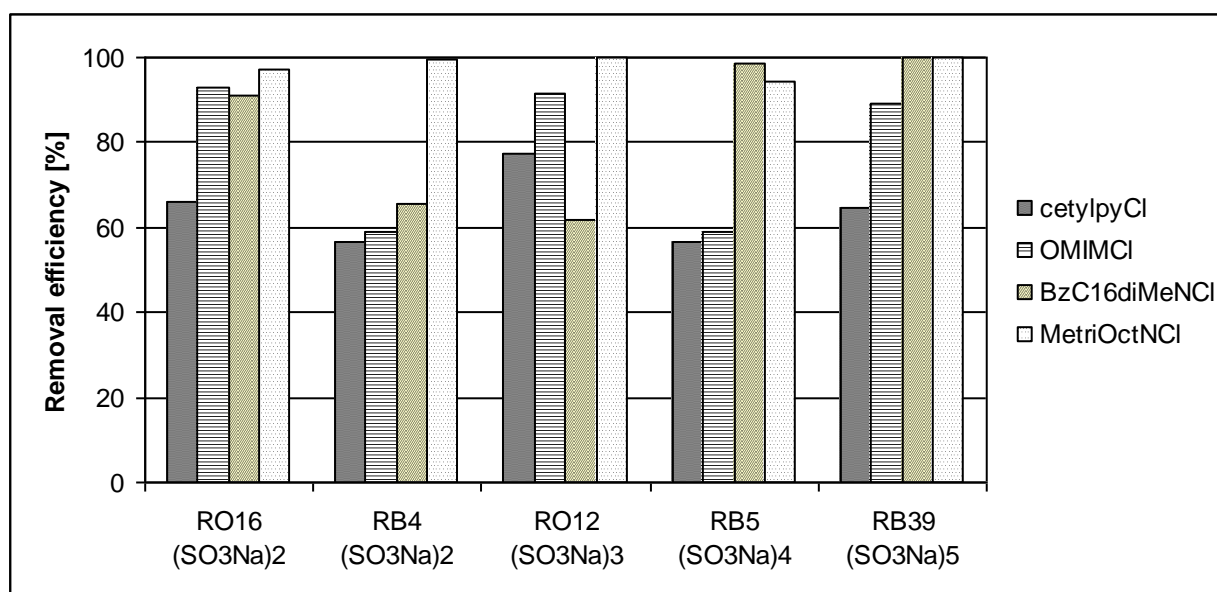


Figure 2: Removal efficiency of 5 tested dyes with different number of bound -SO₃Na groups using equimolar quantities of 4 different ionic liquids.

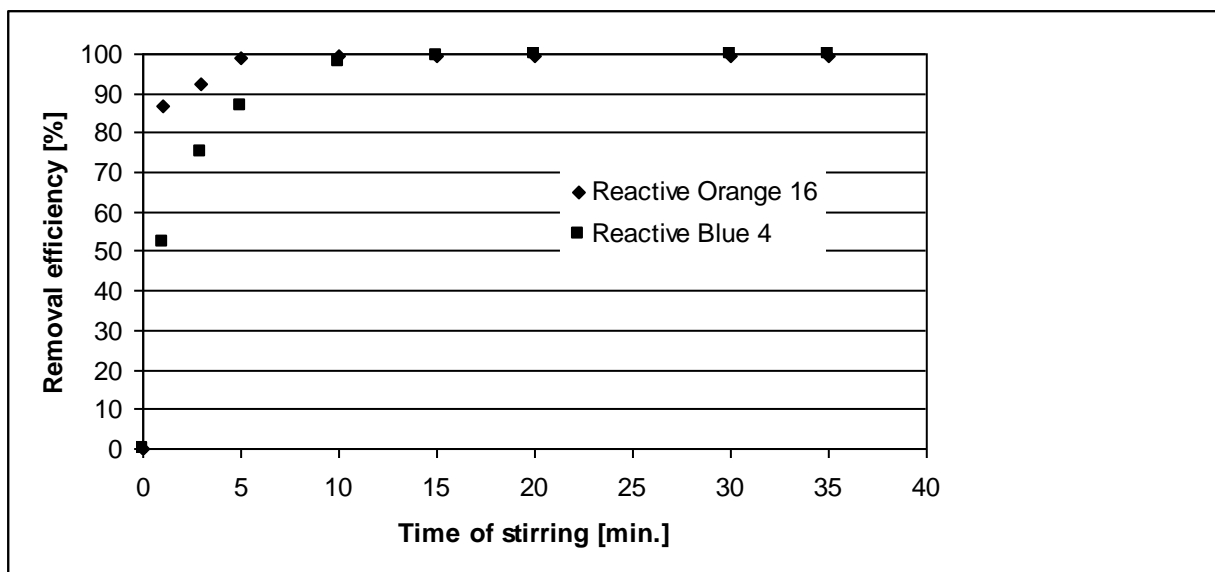


Figure 3: Removal efficiency of two dyes from 2.5 mM aq. solution (500 mL) using 10 mmol of MetriOctNCl dissolved in 1-octanol (10 mL) under stirring at 480 rpm

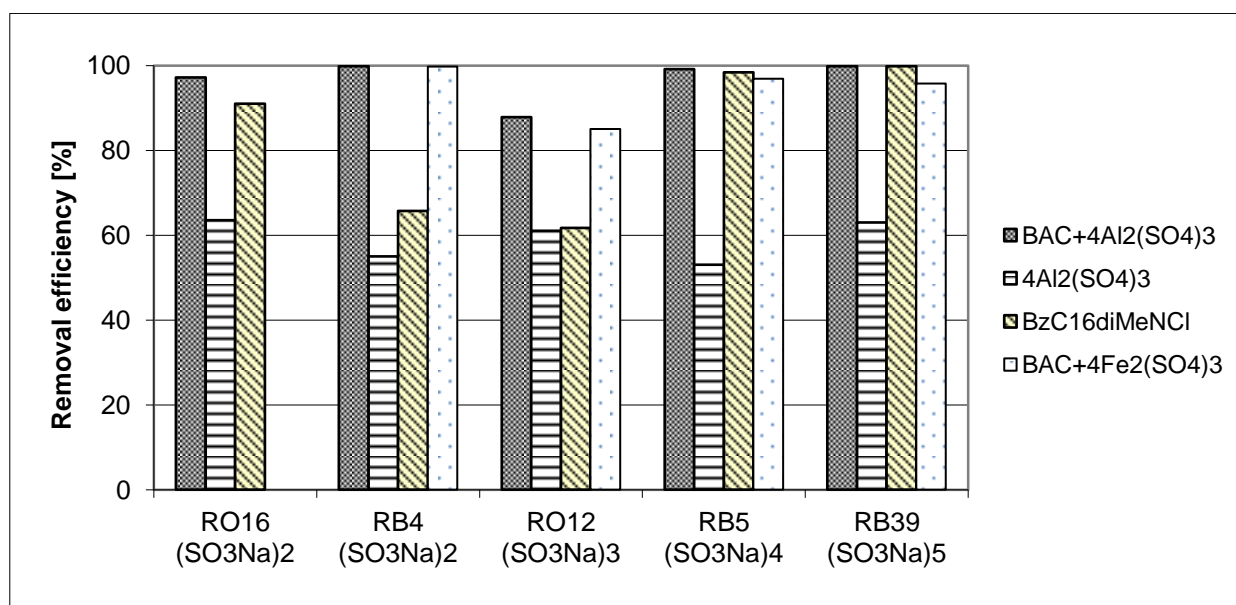


Figure 4: Comparison of removal efficiency obtained using mixture of aqueous 0.1M BAC in 0.4 M Al₂(SO₄)₃ (or Fe₂(SO₄)₃) with the same quantity of Al₂(SO₄)₃ and with action of 0.1M BzC16diMeNCl

Conclusions

In this study the applicability of ion exchange accompanied by precipitation between acid dye anions and ionic liquid cations was studied using five different commercially available ionic liquids and five commonly used reactive textile dyes.

It was demonstrated that tested ionic liquids added in equimolar quantity to the sulfo groups bound in the dye structure enable precipitation of dye-SO₃⁻R₄N⁺. The formation of insoluble ion pairs dye-SO₃⁻R₄N⁺ potentially enables simple removal of studied dyes from the aqueous solution. We proved that increasing size of cation in used ionic liquid (accompanied with increasing of hydrophobicity of ionic liquid) improve effective removal of tested reactive acid dyes from the aqueous solution.

In this point of view ionic liquid benzyldimethylstearylammonium chloride (or much more cheaper benzalkonium chloride), which are both water soluble and very effective for dye removal, was chosen as available candidate for optimization of decolourization procedure. Addition of 0.1M benzalkonium chloride dissolved in 0.4M aqueous $\text{Al}_2(\text{SO}_4)_3$ in the equimolar quantity (with respect to the concentration of sulfo groups bound in dye structure) is crucial for the almost quantitative precipitation after few minutes of action and subsequent simple removal of tested dyes from the aqueous solution by sedimentation/filtration. In comparison, addition of 0.1M benzalkonium chloride dissolved in 0.4M aqueous $\text{Fe}_2(\text{SO}_4)_3$ in the equimolar quantity (with respect to the concentration of sulfo groups bound in dye structure) is less effective for removal of tested dyes. The comparable results were obtained by action of neat hydrophobic methyltrioctylammonium chloride, however, the reaction time is much longer (around 15 minutes) and the addition of precise quantity of this viscous ionic liquid and subsequent separation of produced tarry-like ion pair is problematic.

In conclusion, cheap and commercially available aqueous benzalkonium chloride solution mixed with four equivalents of aqueous $\text{Al}_2(\text{SO}_4)_3$ was proved as the most effective precipitation agent for the tested dyes.

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