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**COD, BOD and AOX MEASUREMENT OF FILTRATES  
FROM PRECIPITATION  
OF REACTIVE DYES BY IONIC LIQUIDS**

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*In this paper, we studied the precipitation efficiency of five anionic reactive dyes dissolved in aqueous solution using two selected quaternary salts, trihexyltetradecylphosphonium chloride (THTDPCl) and Aliquat 336, using spectroscopic measurements of different molar ratios of the dye to ionic liquid. Chemical oxygen demand (COD), biochemical oxygen demand (BOD), and adsorbable organic halogen (AOX) measurements of filtrates from precipitation were performed. The purpose of this study was to investigate the removal efficiency of reactive dyes by ionic liquids based on ammonium or phosphonium quaternary salts. According to the results, neither of the ionic liquids disturbed BOD measurements, indicating that ionic liquids are not among the biocidal substances. The results showed that an increase in the molar ratio of the ionic liquid versus the reactive dye led to a decline in all of the studied parameters.*

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## Introduction

At least 10 % of total textile dye production, or about 700,000 tons of dye per year, is released into process waters. The current physico-chemical treatments are expensive and could generate a large volume of sludge. As regulations become more stringent, the need for innovative, efficient, and economic processes to treat these effluents increases. As a consequence, there has been a growing interest in biotechnological processes [1].

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 [2,3]. 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 [4]. Ionic liquids contain a functional group that is covalently linked to its cation or anion [5]. 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 [6]. Ionic liquids have been successfully used to remove anionic dyes [Reactive Black 39 (RB), Reactive Red 45:1 (RR), Reactive Red 198 (RR198), Reactive Yellow 186 (RY), and Cibacron Brilliant Yellow 3G-P (CBY)].

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 chromospheres. The azo dyes also contain auxochromes, such as –OH or –SO<sub>3</sub>H, which are responsible for the increase in color intensity [1]. 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 [8].

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. [9,10].

## Experimental

### Materials

Ionic liquids and anionic dyes were used without further purification. Both of the ionic liquids were purchased from Aldrich Company. Aqueous solutions of anionic reactive dyes were prepared with distilled water. The chemical structures of the anionic dyes and the ionic liquids used in this work were shown in Figs 1 and 2.

### Ionic liquids

The ionic liquid Aliquat 336 (purity  $\geq 97\%$ ) was purchased from Sigma Aldrich. Trihexyltetradecylphosphonium chloride (THTDPCl; purity  $\geq 95\%$ ) was obtained from Fluka Company.

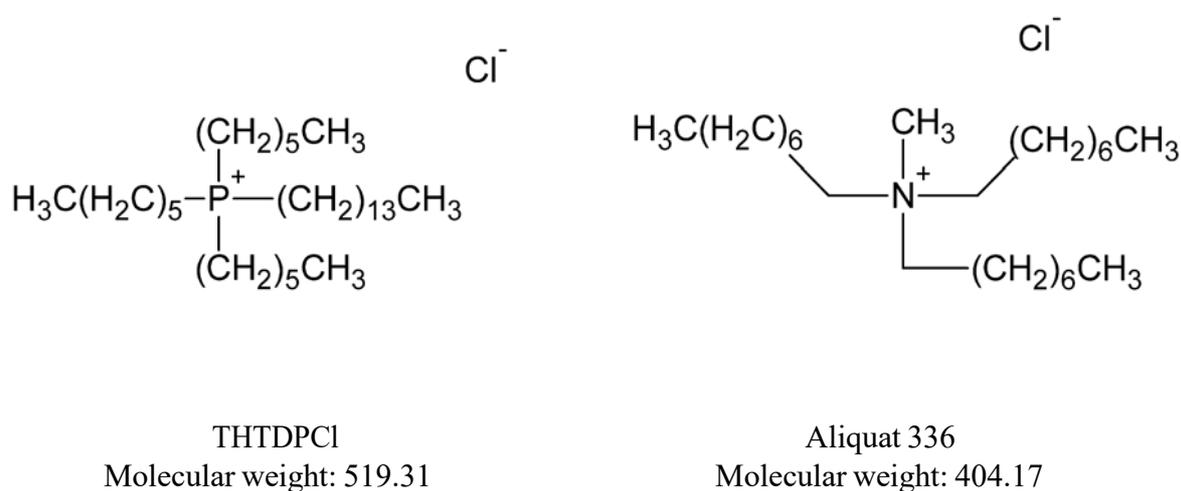
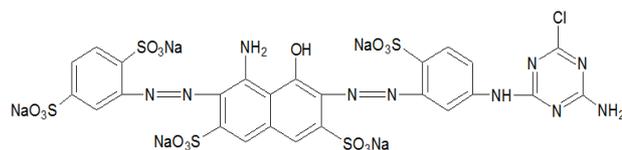


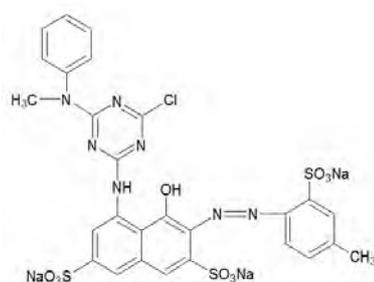
Fig. 1 Structures of the quaternary phosphonium ( $\text{R}_4\text{PCl}$ ) and ammonium chlorides ( $\text{R}_4\text{NCl}$ ) used in this study

## Reactive Dyes

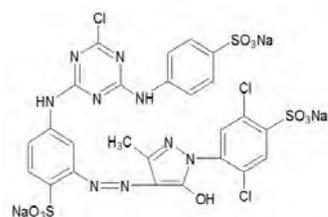
The reactive dyes (shown in Fig. 2) RB, which contains five sulfonic groups in their structure, RR and RY, which contain three sulfonic groups in their structure, and RR198, contains four sulfonic groups in its structure, were obtained from Synthesia. CBY, which contains three sulfonic groups, was supplied by Sigma Aldrich. Anionic dyes were used without further purification.



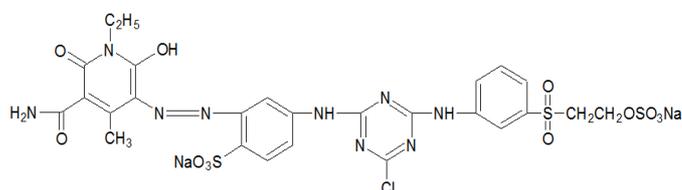
Reactive Black 39 (RB), Molecular weight: 1025.5,  $\lambda_{\max}$  = 610 nm



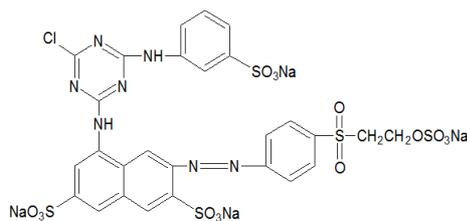
Reactive Red 45:1 (RR), Molecular weight: 771.5,  $\lambda_{\max}$  = 544 nm



Cibacron Brilliant Yellow 3G-P (CBY), Molecular weight: 872.97,  $\lambda_{\max}$  = 403 nm



Reactive Yellow 186 (RY), Molecular weight: 833.45,  $\lambda_{\max}$  = 427 nm



Reactive Red 198 (RR198), Molecular weight: 987.45,  $\lambda_{\text{max}} = 518 \text{ nm}$

Fig. 2 Chemical structures and properties of the anionic reactive dyes used in this study

## Apparatus

A UV-Vis spectrophotometer UV-160A (SHIMADZU) equipped with a 1 cm quartz cell was used for recording the visible spectra and absorbance measurements to establish the  $\lambda_{\text{max}}$  and concentrations of the dyes. A magnetic stirrer (Heidolph MR Hei-Tec, IKA<sup>®</sup> RH basic 2 and IKA<sup>®</sup> C-MAG HS 7) was used for stirring the solutions. The thermostat LT 200 was used to measure the chemical oxygen demand (COD) values (cuvette tests LCK 514, measurement range 100-2000 mg l<sup>-1</sup>; Hach Lange). The Combitherm-2 CH 3-150 heating and cooling thermostat (Biosan) was used to measure the biochemical oxygen demand (BOD) values (cuvette tests LCK 555, measurement range 4-1650 mg l<sup>-1</sup>; Hach Lange). The analyzer AOX MULTI X 2500 was used to measure the adsorbable organic halogen (AOX) values.

## 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  $\text{SO}_3^-$  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 the ionic liquid. The mixture 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  $\lambda_{\text{max}}$  of the dye, and then calculated according to the following formula

$$\text{concentration of sample (mol l}^{-1}\text{)} = \frac{\text{absorbance of sample} \cdot \text{concentration of stock solution}}{\text{absorbance of stock solution}}$$

It was necessary to integrate the dilution factor to the formulation above. Finally, the exact concentration of dye was calculated and the COD, BOD<sub>5</sub>, and AOX values were determined.

## Results and Discussion

In previous experiments, we found that THTDPCl and Aliquat 336 had the desired ability to precipitate the anionic reactive dyes from aqueous solution. We performed a comparison of the absorbance, COD, BOD, and AOX parameters from the measurements of the precipitation process between phosphonium (THTDPCl) or ammonium (Aliquat 336) ionic liquid and the reactive anionic dye (RB, RR, CBY, RY, RR198).

### Absorbance Measurements

The ionic liquids THTDPCl and Aliquat 336 have been shown to precipitate dyes quantitatively, and they are very effective when used for the precipitation of reactive dyes. The removal efficiency of the dyes was at least 99.8 % in all cases when a 1:1 molar ratio of IL to the SO<sub>3</sub><sup>-</sup> groups in the dye was used, as determined by measuring the absorbance after 20 hours of stirring (Tables I and II).

Table I Efficiency of dye removal by THTDPCl

Dye	RB	RR	CBY	RY	RR198
Removal efficiency, %	99.95	99.92	99.88	99.88	99.89

Table II Efficiency of dye removal by Aliquat 336

Dye	RB	RR	CBY	RY	RR198
Removal efficiency, %	99.96	99.93	98.9	99.88	99.9

In addition to the 1:1 molar ratio of the IL to the SO<sub>3</sub><sup>-</sup> groups in the dye, we also used ratios of 1:1 to 1:6 of the dye to ionic liquid for RB removal by THTDPCl (Fig. 3), and molar ratio of 1:1 to 1:3 of RR to Aliquat 336 (Fig. 4). We saw increasing efficiency of dye removal from 35 % to 99.96 % for the precipi

tation of RB by THTDPCl, while the precipitation efficiency of RR by Aliquat 336 increased from 39 % to 99.7 %.

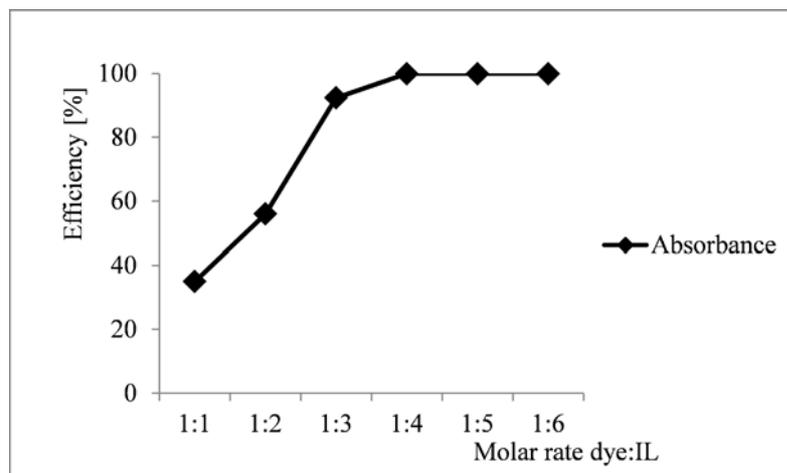


Fig. 3 Effect of the amount of THTDPCl added on the precipitation of RB

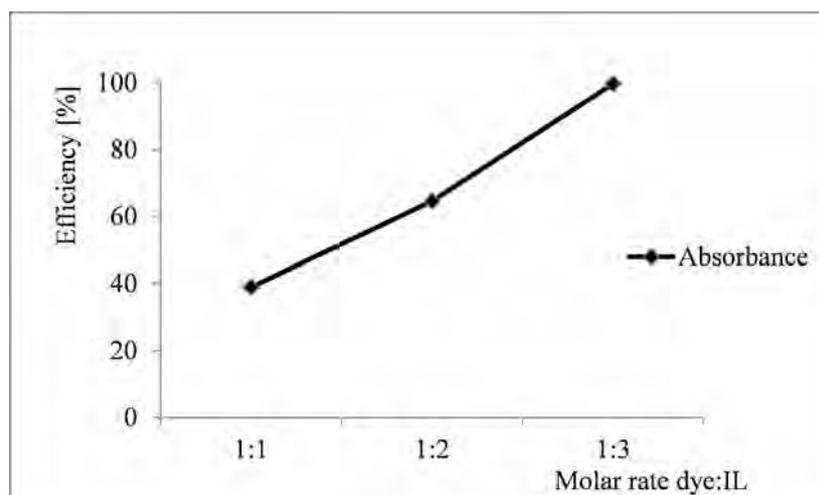


Fig. 4 Effect of the amount of Aliquat 336 added on the precipitation of RR

### Comparison of COD and BOD Values

The filtrates from precipitation were used to determine other important parameters, such as COD, BOD, and AOX values.

When the molar ratio of  $R_4PCl$  to  $SO_3^-$  was increased from 1:1 to 1:5 or more, the removal efficiency of RB rapidly increased from approximately 30 % to more than 99 % due to the formation of less soluble ion pairs of higher molecular mass.

For the precipitation of RR by ammonium salt, Aliquat 336 in molar ratios

of dye to IL of 1:1 and 1:2, there was an increase in the BOD value in the filtrates (Table III). It was clear that in these two cases, the Aliquat 336 ionic liquid had a negative effect on the removal of the dye. Removal efficiency of RR was less than 60 %, and the COD and BOD values were very high. Higher efficiency of dye removal was achieved only when Aliquat 336 was added in molar ratio of 1:1.

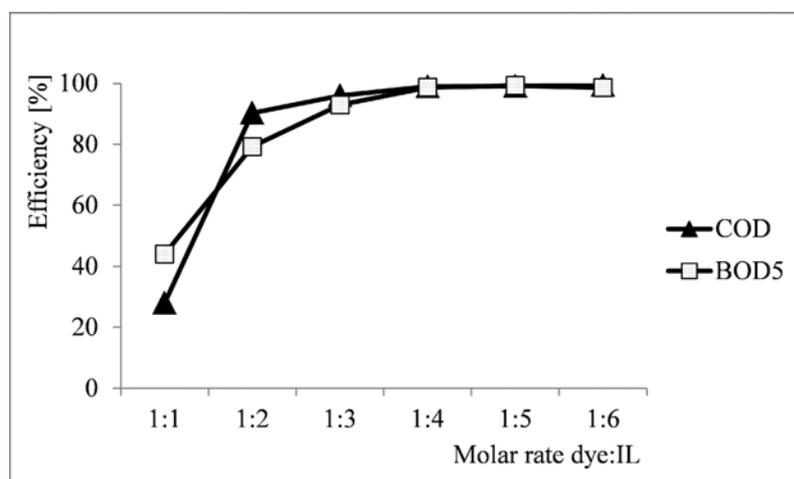


Fig. 5 Comparison of the COD and BOD parameters in filtrates obtained from precipitation of RB by THTDPCI in molar ratios ranging from 1:1 to 1:6

The COD value must always be higher than the BOD value, because it is impossible to biochemically oxidize all biomass to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . There always remains a constant component (about 10 %) that is not biodegradable. The proportion of biodegradable substances in wastewater is estimated from the ratio of BOD to COD. The higher this value, the more readily degradable a substances in the wastewater [11]. Therefore, these two filtrates are very biodegradable.

Table III BOD and COD values for filtrates obtained from precipitation of RR by Aliquat 336 using different molar ratios

Molar ratio dye:IL	COD dye stock solution $\text{mg l}^{-1}$	COD filtrate $\text{mg l}^{-1}$	BOD dye stock solution $\text{mg l}^{-1}$	BOD filtrate $\text{mg l}^{-1}$
1:1	8500	6280	1030	6080
1:2	8500	3070	1030	6800
1:3	8500	314	1030	730

## Determination of AOX in Filtrates After Precipitation of Dyes by ILs

The concentration of the obtained filtrates is  $0.005 \text{ mol l}^{-1}$ , and since 1025.5 g RB dye contains 35.5 g Cl, then  $(1025.5 \times 0.005) \text{ g dye RB}$  contains 0.1775 g Cl. From the above calculation, theoretically in 1L of the  $0.005 \text{ mol}$  filtrate is 177.5 mg of organically bound chlorine.

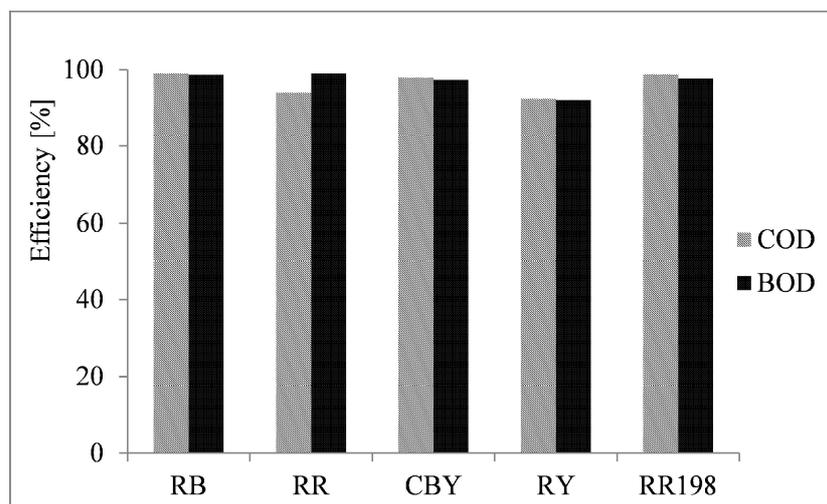


Fig. 6 Comparison of COD and BOD values in filtrates obtained from precipitation of dyes with phosphonium quarternary salt for a 1:1 molar ratio of IL to the  $\text{SO}_3^-$  groups in the dyes

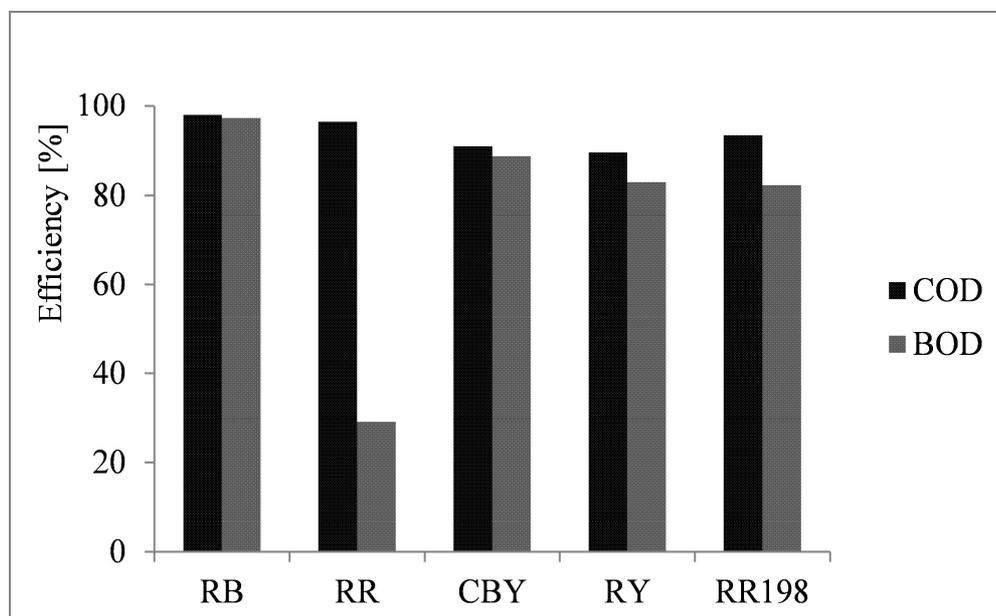


Fig. 7 Comparison of COD and BOD values in filtrates obtained from precipitation of dyes by ammonium quarternary salt for a 1:1 molar ratio of IL to the  $\text{SO}_3^-$  groups in the dyes

Figure 8 shows a decrease of AOX values in filtrates obtained from precipitation of the RB dye by the ionic liquid THTDPCl for increasing molar ratios of the dye to IL. Also, theoretically, an AOX value of  $0.01 \text{ mol l}^{-1}$  RB stock solution is 355 mg organically bound chlorine. For an AOX value of  $0.01 \text{ mol l}^{-1}$  RB stock solution, we measured 217 mg organically bound chlorine using the AOX MULTI X 2500 analyzer.

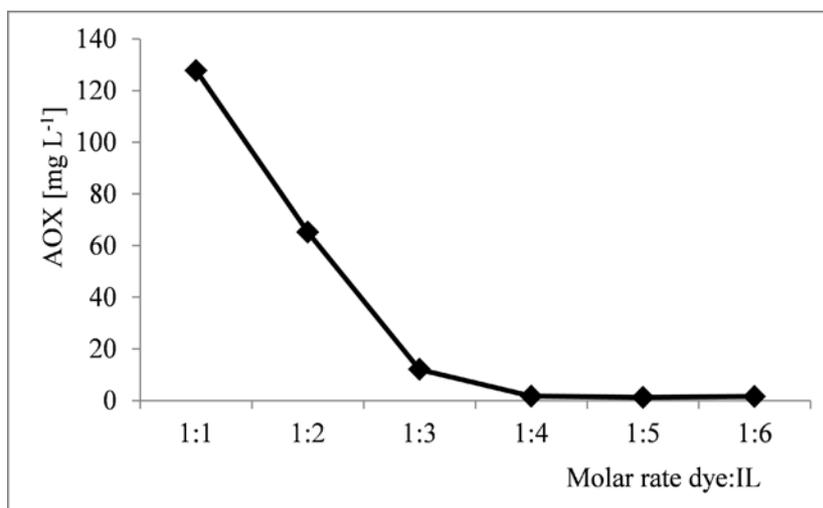


Fig. 8 Decreasing AOX values in filtrates obtained from precipitation of RB with phosphonium quaternary salt in increasing molar ratios of dye to IL using an AOX MULTI X 2500 analyzer

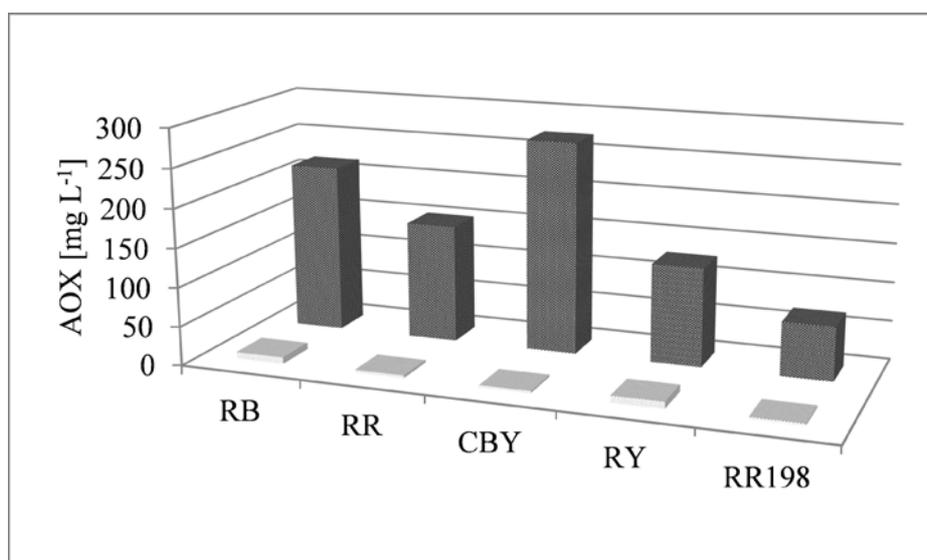


Fig. 9 Comparison of the AOX values for filtrates obtained from precipitation of reactive dyes by phosphonium quaternary salt in a 1:1 molar ratio of IL to the  $\text{SO}_3^-$  dye group

Figures 9 and 10 show comparisons of the AOX values obtained from precipitation of reactive dyes by both of ionic liquids in a 1:1 molar ratio of IL to the  $\text{SO}_3^-$  dye group. It is apparent that there is a substantial difference in the decrease in AOX values in filtrates in both of figures. For a molar ratio 1:1 of reactive dyes to THTDPCl, AOX values decreased by 94 % after 24 hours of reaction time. For a molar ratio of reactive dyes to Aliquat 336 of 1:1, the AOX values decreased by 93 % after 24 hours of reaction time.

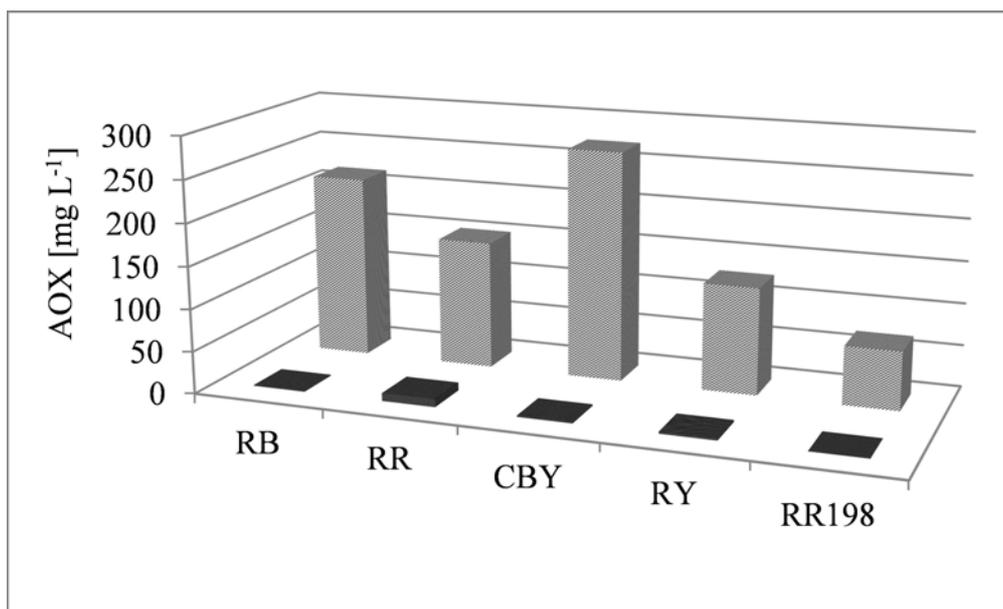


Fig. 10 Comparison of the AOX values for filtrates obtained from precipitation reactive dyes by ammonium quaternary salt in a 1:1 molar ratio of IL to the  $\text{SO}_3^-$  dye group

## Conclusion

The removal of five anionic reactive dyes (RB, RR, CBY, RY, and RR198) from aqueous solutions was studied using THTDPCl and Aliquat 336. The maximum removal efficiencies of the studied reactive dyes were achieved using equimolar quantities of THTDPCl (quarternary phosphonium salt) and Aliquat 336 (quarternary ammonium salt). These results indicate that this one-step process is promising for the precipitation of anionic dyes during wastewater treatment, especially for the textile industry.

The precipitated salts were characterized by determining the COD, BOD, and AOX values. The precipitation process using phosphonium and ammonium ionic liquids as the precipitation reagent and reaction medium was used for the precipitation of reactive anionic dyes from water solution. These ionic liquids, THTDPCl and Aliquat 336, were shown to precipitate the dyes quantitatively. The

aim of our paper was to compare the efficiency of removal of reactive dyes using ionic liquids in model waste waters. The efficiency of removal of the dyes was analyzed using a UV-Vis spectrophotometer. The results indicated that both the ionic liquids were very efficient in the removal of the studied reactive dyes. With a growing number of  $\text{SO}_3^-$  groups in dye molecule, the solubility of the dye in an aqueous environment is growing too; consequently, the efficiency of removal of the dye increases from model wastewater using ionic liquid. In summary, anionic reactive dye RB prepared at 0.01 M is very biodegradable. Furthermore, the studied ionic liquids do not disturb BOD measurements, indicating they are not biocidal substances.

## Acknowledgement

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