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Short communication

Extraction and recovery of azo dyes into an ionic liquid

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Abstract

The azo dyes are commonly used in the leather and textile industries as they are quite versatile in nature. However, they are neither totally utilised during the process, nor are they recovered at the end of the process. In fact, in the leather industry, typically about 10–15% of the dye is discharged with the effluent creating both environmental and economic issues. Hence, there is a need to remove the residual dye from the large volume of aqueous effluent. In this study, for the first time, azo dyes employed in the leather industry have been successfully extracted into a neutral ionic liquid, with an extraction efficiency of 98%, potentially providing a method of minimizing pollution of waste-waters. The extraction of the dye into the ionic liquid also provides a potential analytical approach to determination of these dyes.

Keywords: Ionic liquids; Extraction; Azo dyes; Effluent; Leather industry; Red dye; Blue dye; Recovery

1. Introduction

The process of leather making involves a number of unit operations, including dyeing, that utilize large quantities of water. It has been estimated that nearly 40–45 l of water per kilo of raw-hides are used by tanneries for processing finished leather [1]. The azo dyes are some of the most commonly used in the leather and textile industries as they are quite versatile in nature [2]. Approximately half of all known dyes are azo dyes, making them the largest group of synthetic colourants. The azo dyes are neither totally utilised during the process, nor are they totally recoverable at the end of the process. In fact, during the process of dyeing in the leather industry, typically about 10–15% of the dye is discharged with the effluent. Hence, there is a need to remove the residual dye from the large volume of aqueous effluent in order to avoid the significant environmental issues that discharge into the ecosystem can produce.

In leather processing, dye-containing effluents are typically treated by physical (absorption), chemical and biological methods [3]. The drawback with all of these methods is the duration of the treatment, which normally ranges from 24 h to 6 days.

Adsorbents suitable for wastewater treatment include charcoals, activated carbons, clays, soils, diatomaceous earth, activated sludge, compost, and living plant communities. It was suggested by Laszlo [4] that biomass such as chitin, chitosan, microbial biomass, unmodified lignocellulose, chemically modified cellulose and lignocellulose could also be used for decolorization of dyes containing effluents. The disadvantage of adsorption processes is that the adsorbent needs to be regenerated, which adds to the cost of the process, and is sometimes very time-consuming.

Chemical treatments for decolorization of wastewater include reduction, oxidation, complexation reactions, ion exchange and neutralization. Oxidation is the most commonly used chemical decolorization process. In most cases the oxidizing agent is hydrogen peroxide, which, due to its stability in the pure form, needs to be activated. Decolorization methods differ in the way in which hydrogen peroxide is activated. Fenton's reagent (hydrogen peroxide, activated with Fe(II) salts) is very suitable for the oxidation of wastewaters. However, since the mechanism involves flocculation, impurities are transferred from the wastewater to the sludge, which still needs disposal in land-fill [5]. Thus, these methods do not provide an ecologically acceptable long term solution. An alternative to hydrogen peroxide is ozone. The use of ozone for purposes of wastewater treatment

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began in the early 1970s. Although the original purpose of oxidation with ozone was disinfection of potable water, it can also be used to remove many toxic chemicals from wastewaters, to facilitate the decomposition of detergents, chlorinated hydrocarbons, phenols, pesticides and aromatic hydrocarbons [6]. However, ozone has a rather short half-life in water, decomposing in about 20 min.

The bacterial species capable of removing the colour from dye effluent are reported to do so mainly by adsorption into their cell membranes. The degradation of dye chemicals in wastewater by the bacterial species was achieved only by enzymatic reduction/oxidation reactions [7]. However, the products of azo dye degradation [8] are mostly aryl amines which are more carcinogenic and toxic than the original effluents. There are reports that enzymes [9], both fungal as well as bacterial, have been employed in dye wastewater treatment. In some cases, traditional biological procedures were combined with physical or chemical treatment processes to achieve better decolorization but chemical or physico-chemical methods are generally costly, less efficient and of limited applicability.

Electrochemical processing is yet another recent method [10–13] for the treatment of dye effluents. However, the implementation of electrochemical methods involves a large investment in equipment.

In recent years, room temperature ionic liquids (ILs) have been extensively investigated [14–18] for use as replacement solvents for numerous applications including clean synthesis and extractions. For example, the use of ionic liquids as solvents in polymerisation reactions has recently been reported [19–24]. The major advantage with using these ionic liquids is their ability to dissolve a wide range of organic and ionic compounds to an appreciable extent. Their lack of volatility, polarity and their high thermal stability are also important features. Given that they are, in some cases, water immiscible, it has been proposed that ionic liquids may prove effective in liquid–liquid extraction processes, such as selectively extracting from an aqueous phase compounds that are more soluble in the ionic liquid.

Recently ionic liquids have thus been employed in separation processes [16,17,25]. Some of the studies include: stripping of non-volatile aromatic solutes from an ionic liquid loaded phase using supercritical CO_2 [16]; using a crown ether as extractant to enhance metal ion partitioning to an ionic liquid phase from water [17] and effective liquid/liquid partitioning of thymol blue, an indicator, using CO_2 and NH_3 gases to activate the 'proton switching' of phase preference [25]. However, there is no reference to ionic liquids being used for the extraction of azo dyes.

Hence, in this communication, the extraction and distribution ratios of azo dyes into a hydrophobic ionic liquid have been determined by means of UV–vis spectrophotometric methods. The results show that the extraction can be used for both analytical and dye recovery purposes. The ionic liquid chosen for this study is *N*-butyl, *N*-methyl pyrrolidinium bis(trifluoromethanesulfonyl) amide, abbreviated as $[\mathrm{p}_{14}][\mathrm{tf}_2\mathrm{N}]$, a well known and particularly stable, hydrophobic ionic liquid [26].

2. Experimental

2.1. Materials

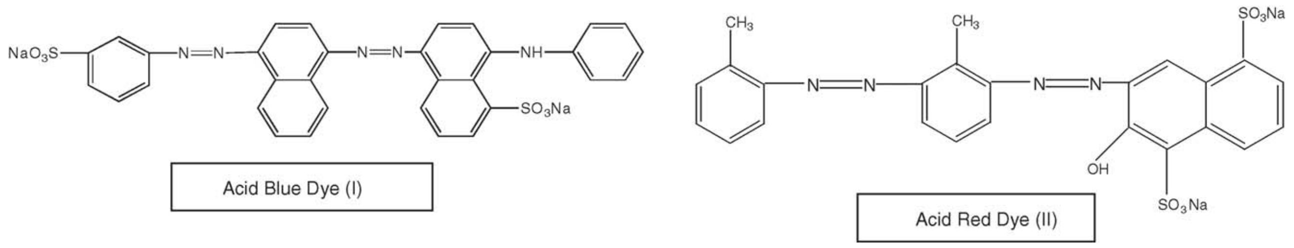
Analytical grades of two typical azo dyes, namely Navy 5RE, an acid blue dye (**I**, 1-[4-(3-phenylsulfonic acid)azo-1-naphthylazo]-4-anilino-naphthlene-5-sulfonic acid, disodium salt) and acid red dye (**II**, 1-[2-tolyl-4-(2-tolylazo)-azo]-2-hydroxy-3,6-disulfonic acid, di-sodium salt) (Scheme 1) were used as received. Analytical reagents of lithium bis (trifluoromethanesulfonyl) amide (LiTFSA), *N*-methyl pyrrole, iodobutane and dichloromethane (DCM) were used without further purification.

2.2. Synthesis of ionic liquid

The synthesis of ionic liquid was made by using the procedure given in the literature [27]. Typically $[\mathrm{p}_{14}][\mathrm{tf}_2\mathrm{N}]$ ionic liquid separates out as viscous liquid after stirring the aqueous solutions of p_{14} I and LiTFSA at room temperature for 2 h. The crude ionic liquid is washed with DCM solvent and the solvent is evaporated to obtain the pure ionic liquid.

2.3. Method of analysis

The partitioning of dyes in ionic liquid was determined by UV–vis spectroscopy. The decrease in dye concentration in the aqueous phase with respect to time was monitored. The initial absorbance and the absorbance of the aqueous red and blue dye solutions, after each extraction with IL, at different time intervals were measured. The absorbance of blue dye was measured at 566.5 nm and the red dye at 524.5 nm.



Scheme 1. Chemical structure of acid blue and red dyes.

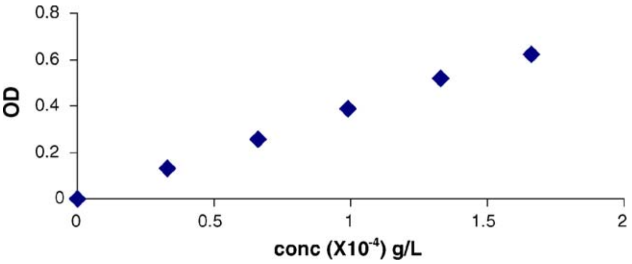


Fig. 1. Concentration vs. absorbance—calibration of neutral blue dye.

3. Results and discussion

Initially 0.5 wt.% solution of the respective dyes were made up in water and from this stock solution 1 ml taken and diluted 10-fold. A calibration graph was prepared for both the dye solutions in water and an example for the blue dye is presented in Fig. 1. Then optimisation of ionic liquid to aqueous phase volume ratio was carried out for a given aqueous dye (blue) solution with different quantities of IL and the results are presented in Table 1. These also allow the distribution coefficient (D) of the dye between IL and water to be calculated as follows:

$$D = \frac{[\text{dye}]_{\text{IL}}}{[\text{dye}]_{\text{aq}}}$$

These show a clear constancy across the trials conducted, as required, with D being very close to two, indicating a reasonable preference for the dye in the IL phase.

The optimised IL quantity was found to be around 0.5 ml per millilitre aqueous solution as the efficiency was found to be maximum at this quantity (Table 1). Then at the optimized IL quantity, samples from the aqueous layer were drawn at different intervals and the absorbance of these samples were obtained. It was found (Table 2) that the leaching of the dyes from the aqueous to the ionic liquid layer takes place almost instantaneously under the conditions of mixing applied.

A similar set of leaching experiments were carried out in IL for these dye samples after the dye is acidified to pH ~3. The results of leaching experiments are given in Table 3. It is observed that in the first extraction the leaching proceeds to an extent of about of about 50% for the blue dye and an extent of 25% for the red dye. Repeated extractions (two to three times) with fresh IL yielded 95% extraction of the dyes into the ionic liquid. In both the cases, for both dye samples, the leaching is almost complete in 30 min and there was no further change after overnight stirring.

Table 2
Extraction of neutral dyes into an ionic liquid

Dye	Abs (nm)	Time (min)	Residual conc. ($\times 10^{-4}$ g/l) after single extraction	Residual conc. ($\times 10^{-4}$ g/l) after third extraction
Blue	566.0	0	1.66	–
		10	1.33	0.35
		30	1.01	0.24
		60	0.73	0.08
		1440	0.68	0.10
Red	523.0	0	1.53	–
		10	1.33	0.25
		30	0.99	0.19
		60	0.93	0.05
		1440	0.93	0.05

Table 3
Extraction of acidified dyes into an ionic liquid

Nature of dye	Abs (nm)	Time (min)	Residual conc. ($\times 10^{-4}$ g/l)
Blue	561.0	0	1.66
		10	1.44
		30	1.15
		60	0.73
		1440	0.66
Red	523.0	0	1.71
		10	1.68
		30	1.47
		60	1.40
		1440	1.37

Experiments were also carried out with real tanning effluent dye (red) samples to extract the dyes using ionic liquid. The results are given in Table 4. The results indicate that in the case of the effluent sample, in spite of the presence of other components, the ionic liquid is able to leach the red dye to an extent of about 26% initially (first extraction) and, after subsequent extractions (four times) with fresh ionic liquid, eventually yields almost complete extraction (98%). Thus, the hydrophobic ionic liquid has been successfully employed to extract the azo dyes from the effluent dye samples with extraction efficiency of close to 100%. The dyes can be subsequently separated from the IL/dye extracts by washing with a small quantity of a mixture of iso-

Table 1
Optimisation of ionic liquid extraction process

Vol. of aqueous soln. (ml)	Vol. of IL (ml)	Initial conc. of aqueous layer ($\times 10^{-4}$ g/l)	Final conc. of dye in aqueous layer ($\times 10^{-4}$ g/l)	Conc. of dye in IL ($\times 10^{-4}$ g/l)	Efficiency[a]	Distribution coefficient (D)
1.00	0.10	1.66	1.37	2.80	0.17	2.04
1.00	0.20	1.66	1.18	2.40	0.29	2.03
1.00	0.30	1.66	1.03	2.10	0.38	2.04
1.00	0.40	1.66	0.917	1.85	0.45	2.02
1.00	0.50	1.66	0.830	1.66	0.50	2.00
1.00	0.70	1.66	0.689	1.39	0.58	2.02

[a] Calculated as the ratio of concentration of aqueous layer (after extraction) to that of initial concentration of aqueous layer.

Table 4
Extraction of red dyes from an effluent sample into an ionic liquid

Dye	Abs (nm)	Time (min)	Residual conc. ($\times 10^{-4}$ g/l) after single extraction	Residual conc. ($\times 10^{-4}$ g/l) after fourth extraction
Red	523.0	0	1.43	–
		10	1.08	0.19
		30	0.85	0.15
		60	0.76	0.05
		1440	0.80	0.05

propyl alcohol and water (1:1 by volume). This mixture remains immiscible with the IL, which can therefore, be separated and reused.

To quantify the extent of loss of IL into the aqueous phase, the solubility of ionic liquid in water was determined gravimetrically by weighing equal volumes of ionic liquid and water and stirring for about 2 h. A known weight of aqueous layer was evaporated to dryness, cooled and weighed. The equilibrium solubility of the ionic liquid in water was found to be 0.028 mM. This amount of IL being lost into an effluent stream would be significant issue in both environmental and economic terms, however, the IL ions can be easily recovered from the aqueous phase by the use of ion exchange resins. Complete recycling of the IL means that the cost of the IL is not a significant factor other than in the establishment stage.

4. Conclusions

It is now possible to use a hydrophobic IL to extract azo dyes, used in leather industry from dilute aqueous solution for both analytical and recovery purposes. The effectiveness of dye removal from wastewater depends on the type and number of interactions of other dissolved species and may vary for different dyes, but in all cases is related to the hydrophobic nature of the dye. The hydrophobic nature of the ionic liquid used here provides an ideal solvent for solutes that are ionisable but nonetheless hydrophobic in nature, as evidenced by the favourable distribution coefficient. Thus, these studies suggest an alternate and novel method of using a hydrophobic ionic liquid to extract, analyze and recover commercial azo dyes. Studies related to other types of dyes with different ionic liquids are underway.

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