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Complete removal of textile dyes from aqueous media using ionic-liquid-based aqueous two-phase systems

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ABSTRACT

The textiles manufacturing is one of the core industries which discharges a heavy load of chemicals during the dying process. As a result, the release of large contents of dyes through aqueous effluents leads to both environmental and economic concerns. Aiming at developing more benign methodologies than those studied hitherto, this work proposes a novel approach to remove dyes from aqueous discharges by the use of ionic liquid (IL)-based aqueous two-phase systems (ATPS). A detailed study on the partition coefficients and extraction efficiencies of a set of textile dyes (chloranilic acid, indigo blue and sudan III) using ATPS composed of ILs (phosphonium- and imidazolium-based) and an inorganic (aluminium sulphate) or organic salt (potassium citrate) is here addressed. The gathered data allow the evaluation of the IL chemical structure, the nature of the salt, as well as the pH of the aqueous medium. The results obtained reveal that a proper selection of the IL and salt can lead to the complete extraction of the three dyes to the IL-rich phase in a single-step procedure. Moreover, the dyes recovery to further allow the reuse of the IL-rich phase is also described. This new approach, using hydrophilic ILs, is consequently more environmentally friendly and could be envisaged as a promising process for reducing the pollution of wastewaters.

1. Introduction

Dyes are widely used in various industries including the textile, leather tanning, paper, plastics, food, cosmetic, printing, among others, for the colouration of their related products [1–4]. Unfortunately, and despite all their interest, the dyes commonly employed have a synthetic origin and are based on complex aromatic structures which make them highly stable and resistant to biodegradation [5,6]. Annually, 1 million tons of dyes are produced worldwide [2], and 10–15% of them are discharged by the textile industry [7]. Wastewaters of these industries are a considerable source of pollution and it was already demonstrated that they largely affect the photosynthetic activity [4,8]. Moreover, most of these dyes and their metabolites are toxic and potentially carcinogenic in nature, thus affecting the aquatic biota and human health [4]. In this context, environmental regulations are becoming stricter in what concerns the discharge and removal of dyes from aqueous effluents [8,9].

Different methods for the removal of dyes from water and wastewaters have been investigated, and these include biological, physical (membrane filtration, adsorption, coagulation, flocculation, precipitation, reverse osmosis, ion exchange, etc.) and chemical (oxidation, ozonation, etc.) processes [8]. However, most of these techniques display major drawbacks, such as a high-running cost, low-removal efficiency, and a labour-intensive operation. Therefore, the development of alternative and cost-effective removal strategies is a top priority in the treatment of dye-containing wastewaters [3,8]. Liquid–liquid extraction has often been a preferred choice in separation processes; yet, this approach commonly requires the use of volatile and toxic organic solvents [10]. Aiming at avoiding the use of organic solvents as extractive phases, aqueous two-phase systems (ATPS) have been introduced as an alternative strategy [11]. ATPS consist of two aqueous-rich phases usually formed by polymer/polymer, polymer/salt, or salt/salt combinations [12,13]. The basis for the solutes partitioning in ATPS is a direct result of their selective distribution between the two phases, governed by the affinity of the target molecule for a given phase [14]. In recent years, it was demonstrated that ionic liquids (ILs) are viable alternatives [15] to common polymer-based ATPS, which usually present narrower differences in their phases polarities [16] and hence display significant limitations on their extraction efficiencies.

ILs have attracted a wide attention in diverse areas of chemistry, biotechnology and environmental engineering, mainly due to

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their unique combination of physicochemical properties: negligible volatility, non-flammability, high thermal and chemical stability, and a large liquid temperature range [17]. These properties have contributed to their widespread recognition of more environmentally-friendly compounds and as potential solvents for the replacement of the noxious volatile organic compounds currently used in industrial processes [18,19].

Even though some controversy has appeared in literature regarding the lack of a complete life cycle assessment on ILs [20], hydrophilic or water-soluble ILs present, in general, a rather low toxicity [21], whereas their negligible vapour pressure at atmospheric conditions is already a good marker envisaging the reduction of atmospheric pollution. Moreover, the physicochemical properties of ILs can be tailored by the proper choice of their cation/anion combinations, and which allows them to be tuned for specific applications, such as in extraction processes [12,22]. Certainly, the replacement of a conventional process by an alternative strategy based on new solvents must be more environmentally attractive, *i.e.*, the new solvents should have a small life cycle impact, allow a high degree of reusability, and lead to high yields and to an easy separation [23,24]. Therefore, solvents such as ILs are potential alternatives only if they fulfill the previous requirements. Since ILs are tunable compounds it is possible to synthetize ILs with a low environmental footprint and a small life cycle impact [24,25]. Yet, their recovery and reuse are mandatory features when large scale applications are foreseen.

Based on the tailoring ability of ILs, either for the solvation of a wide array of compounds or for the extraction of the most diverse biomolecules from aqueous media [12], the use of IL-based ATPS to extract and remove dyes typically discharged by the textile industry is described in this work envisaging their potential application in the treatment of aqueous effluents. Recent publications reported the use of ILs in the extraction of dyes from water-rich phases [26–32]. Nevertheless, in these studies [26–32], hydrophobic ILs, *i.e.* non water-miscible ILs at temperatures close to room temperature, were employed. Most of the hydrophobic ILs contain fluorinated ions which are environmentally less benign and some of them even tend to be unstable in aqueous media (leading to the release of fluoridic acid [33]). Fluorinated ILs also tend to be more expensive than halogen-based counterparts. Furthermore, the toxicity of ILs mainly depends on their hydrophobicity, and hydrophilic ILs are recognized as more environmentally friendly compounds [21]. Finally, it was previously shown that IL-based ATPS can lead to complete extractions and high concentration factors of a wide variety of compounds by a proper tailoring of the IL chemical structure and by modification of the salting-out agent [34–36], further guaranteeing the potentiality of IL-based ATPS for the complete removal of textile dyes from aqueous media.

To test the ability of IL-based ATPS to extract/remove textile dyes from aqueous effluents, different ATPS composed of several ILs and two distinct salts were investigated here, with the aim of evaluating the influence of the IL structural features, the nature and salting-out ability of the salt employed, and the pH of the aqueous medium. The partition coefficients and extraction efficiencies of three current textile dyes, sudan III, indigo blue and chloranilic acid (Fig. 1), for the IL-rich phase were experimentally determined at 25 °C. Whenever necessary, the ternary phase diagrams (IL + salt + water), which allows the identification of the monophasic/biphasic regimes, were also determined at 25 °C.

2. Materials and methods

2.1. Chemicals

The ILs studied in this work were: 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (triflate), $[C_2mim][CF_3SO_3]$ (purity 99 wt%); 1-butyl-3-methylimidazolium trifluoromethanesulfonate (triflate), $[C_4mim][CF_3SO_3]$ (purity 99 wt%); 1-butyl-3-methylimidazolium tosylate, $[C_4mim][Tos]$ (purity 98 wt%); 1-butyl-3-methylimidazolium dicyanamide, $[C_4mim][N(CN)_2]$ (purity > 98 wt%); tetrabutylphosphonium bromide, $[P_{4444}]Br$ (purity 95 wt%); tributylmethylphosphonium methylsulphate, $[P_{4441}][CH_3SO_4]$ (purity 96–98 wt%); tri(isobutyl)methylphosphonium tosylate, $[P_{i(444)1}][Tos]$ (purity 98 wt%); and tetrabutylphosphonium chloride, $[P_{4444}]Cl$ (purity 97 wt%). The chemical structures of the investigated ILs are depicted in Fig. 2. The phosphonium-based ILs were kindly supplied by Cytec Industries Inc. whereas the imidazolium-based compounds were purchased from Iolitec. Before use, all ILs were purified and dried, for a minimum of 48 h, under constant agitation, at moderate temperature (≈80 °C) and under vacuum, to reduce their volatile impurities to negligible values. After this step, the purity of each IL was also confirmed by ^1H and ^{13}C NMR spectra and found to be in accordance with the purity levels given by the suppliers.

The salts used were the inorganic salt aluminium sulphate, $Al_2(SO_4)_3$ (⩾98.0 wt% pure), and the organic salt potassium citrate, $K_3C_6H_5O_7{\cdot}H_2O$ (⩾99 wt% pure), acquired from Himedia and Sigma–Aldrich, respectively.

The water employed was ultra-pure water, double distilled, passed by a reverse osmosis system and further treated with a Milli-Q plus 185 water purification equipment.

The dyes used were sudan III and chloranilic acid (>99 wt% pure), both from Merck, and indigo blue (>95 wt% pure) acquired from Sigma–Aldrich.

2.2. Phase diagrams and tie-lines

Most of the phase diagrams of the ATPS used here have been previously reported in literature [37,38]. Nonetheless, novel ternary phase diagrams were also determined in this work to expand the study on the ILs and salts influence through the extraction efficiencies of the three dyes. The ILs investigated for the creation of ATPS comprise imidazolium- and phosphonium-based compounds whereas the salts used include an inorganic and an organic salt, $Al_2(SO_4)_3$ and $K_3C_6H_5O_7$, respectively. The novel ternary phase diagrams (IL + salt + water) were determined at 25 °C and atmospheric pressure with the organic salt for the following ILs: $[C_2mim][CF_3SO_3]$, $[C_4mim][Tos]$, $[P_{4444}]Br$, $[P_{4441}][CH_3SO_4]$ and $[P_{i(444)1}][Tos]$.

The binodal curves of the ternary phase diagrams were determined through the cloud point titration method at 25 (±1) °C and atmospheric pressure [39,40]. Aqueous solutions of $K_3C_6H_5O_7$ and aqueous solutions of the different hydrophilic ILs at variable concentrations were prepared gravimetrically, and used for the determination of the binodal curves. Drop-wise addition of the aqueous organic salt solution to each IL aqueous solution, or *vice versa*, was carried out until the detection of a cloudy solution (biphasic region), followed by the drop-wise addition of ultra-pure water until the detection of a clear and limpid solution (monophasic region). Drop-wise additions were carried out under constant stirring. The ternary system compositions were determined by the weight quantification of all components added within $\pm 10^{-4}$ g (using an analytical balance, Mettler Toledo Excellence XS205 DualRange). All the calculations considering the weight fraction or molality of the citrate-based salt were carried out discounting the complexed water.

The tie-lines (TLs), which allow the inspection on the coexisting phases' compositions, were determined by a gravimetric method originally described by Merchuk et al. [41]. In this method, a mixture at the biphasic region (IL + salt + water) was gravimetrically prepared within $\pm 10^{-4}$ g, vigorously stirred, and left for at least 12 h at (25 ± 1) °C to reach the complete separation and equilibration