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Using tunability of ionic liquids to remove methylene blue from aqueous solution

Massoud Kermanioryani[a], M.I. Abdul Mutalib[a], Girma Gonfa[a], Mohanad El-Harbawi[b], Faizureen Afzal Mazlan[a], Kallidanthiyil Chellappan Lethesh[c,*], Jean-Marc Leveque[d,*]

[a] Department of Chemical Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 32610 Perak, Malaysia
[b] Chemical Engineering Department, King Saud University, Riyadh 11421, Saudi Arabia
[c] Centre for Biofuel and Biochemical Research, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 32610 Perak, Malaysia
[d] Department of Fundamental and Applied Sciences, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 32610 Perak, Malaysia

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ABSTRACT

The liquid-liquid extraction of Methylene Blue (MB) from aqueous solution was undertaken with 5 hydrophobic ionic liquids (ILs) based on bis(trifluoromethylsulfonyl)imide anion [NTf_2] for comparison purpose where three of them were of commercial origin, 1-butyl-3-methyl imidazolium [BMIm], 1-hexyl-3-methylimidazolium [HMIm] and 1-octyl-3-methylimidazolium [OMIm] cations and the two other were purposely designed for this work, 1-hexyl-2-phenylimidazolium [HPhIm], and 1-benzyl-3-methyl-imidazolium [BnMIm]. Several parameters such as the place and nature of the aromatic ring, the length of the side alkyl chain and the ability to form hydrogen bonding were investigated to evaluate their impact on extraction performances. Results show that the incorporation of the functional group (aromatic group) not only led to excellent results of dye removal compared to commercially available ones but allowed easier recovery and subsequent reuse of the functionalized ILs. Conductor like Screening Model for Real Solvents (COSMO-RS) calculations were also performed to see the structural variations of the ILs their extraction capabilities of MB from water. The finding of this study may assist in reducing the pollution of wastewater from dye industries.

1. Introduction

Nowadays, dyes are increasingly used in many sectors of industry such as textiles printing, paper industry and much more. This wide range of applications result in high discharging of dye effluents into the environment. These effluents usually remain untreated or undergo improper/incomplete treatment before being channelled to the water, which is mainly responsible for skin and respiratory diseases [1–3]. Discharging dyes into the water resources can cause serious environmental damage, as the dye will form a colour layer on the water surface, which consequently reduces the light penetration that has the potential to endanger the aquatic ecosystems [4,5]. Therefore, it is important to remove the dyes before discharging the water into the environment to avoid any health hazards to human beings as well as destruction of the ecosystem. Dyes are usually derived from aromatic organic materials, allowing thus the partial absorption of the visible light, and their solubility in water is insured by a charged functional group, which may be azoic, anionic or cationic [6]. Cationic (or basic) dyes normally have a quaternary ammonium substituent, Methylene Blue (MB) being one of the most known representatives [7].

Several studies have been conducted for the treatment of effluents in a way to recover the chemicals and to recycle the processed water. Haghi recently pointed out that different ways of dyes treatment could be classified into biological, chemical and physical treatments [8]. However, these methods display some disadvantages such as lengthy processes, cost for regeneration of adsorbents in adsorption process, toxicity of chemicals in biological treatment and short half-life time of ozone in ozonation process for dye removal [9–12].

Ionic liquids (ILs) have recently attracted high interest on many domains of chemistry sciences due to some of their remarkable properties such as high thermal and chemical

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[*] Corresponding authors.
E-mail addresses: lethesh.chellappan@petronas.com.my (K.C. Lethesh), jm.leveque@petronas.com.my (J.-M. Leveque).

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stabilities, very low vapour pressure enabling their full recycling and tunability through adequate molecular design of some of their physical properties among density and viscosity [13]. Moreover, due to their negligible or non-measurable vapour pressure, they can be an ideal replacement for conventional organic solvents in liquid-liquid processes as they may be more easily recycled and reused than the latters [14]. By considering not only the large number of cation/anion combinations but also the possibility to structurally modify these ions, this family of compounds may provide a breakthrough to design an optimized IL, which can be utilized for particular processes such as dye removal from wastewaters. The use ILs for the removal of various type of dyes from aqueous solutions was investigated by various research groups around the world [15–20]. For example imidazolium-based ILs with $[PF_6]^-$ and $[BF_4]^-$ anions were successfully used for the removal of azo dyes from waste water [18]. In another study, *N*-alkyl-*N*-methylpyrrolidinium based cations with bis(trifluoromethanesulfonyl)amide anion were employed for the extraction of acid blue and acid red dyes [16]. From these pioneer studies, it was acknowledged that the application of ILs in dye removal showed some interesting potential but somehow still needs to be further studied to match the characteristics of an IL that would lead to an optimum extraction efficiency while recovering/reusing the IL to increase the economical attractiveness of the process. For that reason, we designed new third-generation ILs, namely Task Specific Ionic Liquids (TSILs), by incorporating aromatic groups in the effort to enhance IL/dye affinities through favoured π-π interactions. The extraction efficiency of the newly synthesized functionalized ILs has been compared with commercially available ones.

In this investigation, 1-hexyl-2-phenyl-imidazolium bis(trifluoromethanesulfonyl) imide [HPhIm][NTf_2], 1-benzyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl) imide [BnMIm][NTf_2], 1-butyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl) imide [BMIm][NTf_2], 1-hexyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl) imide [HMIm][NTf_2] and 1-octyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl) imide [OMIm][NTf_2] were used for methylene blue (MB) removal from aqueous solution. Moreover, Conductor like Screening Model for Real Solvents (COSMO-RS) model was used to understand the effect of structural variations of the ILs on the extraction process. COSMO-RS is a quantum chemistry based statistical thermodynamics model for the prediction of thermodynamic properties of fluids and liquid mixtures [21–23]. Activity coefficient is an important parameter for preliminary selection of solvents for selective extraction of solute component from a mixture [24–26].

2. Experimental

2.1. Chemicals

Commercial ionic liquids, [BMIm][NTf_2] (≥98%) and [HMIm][NTf_2] (≥99%), 1-bromo hexane (≥98%), 2-phenyl imidazole (≥95%), benzyl chloride (≥99%) and 1-methyl imidazole (≥99%) were purchased from Merck (Germany, France) and used as received without any further purification. [OMIm][NTf_2] (≥99.5%) was purchased from Solvionic (France). Sodium bis(trifluoromethanesulfonyl)amide (≥97%) and methylene blue (MB, dye content, ≥82%) were supplied by Sigma-Aldrich (USA). Dichloromethane (≥99.6%), acetonitrile (≥99.8%), and ethyl acetate (≥99.99%) were purchased from Fisher Scientific (UK). Aqueous solutions were prepared with doubly distilled water.

2.2. Preparation of ionic liquids

2.2.1. Synthesis of 1-hexyl-2-phenyl-imidazolium bis(trifluoromethanesulfonyl)amide [HPhIm][NTf_2]

1-Bromohexane (2.8 mL, 0.02 mol) was added dropwise into a solution of 2-phenyl-imidazole (2.88 g, 0.02 mol) in acetonitrile (20 mL) under stirring at room temperature and the resulting solution was then refluxed at 82 °C for 72 h. The obtained product was then washed twice with 20 mL of ethyl acetate and dried on a rotary evaporator at 323 K under reduced pressure and yellowish viscous liquid of 1-hexyl-2-phenyl-limidazolium bromide was obtained. In the second step, an aqueous solution of $NaNTf_2$ was added to 1-hexyl-2-phenylimidazolium bromide dissolved in a minimum amount of distilled water and stirred for further 24 h to ensure completion of the anion metathesis. The IL phase made a separate layer with water. The water was decanted and the ionic liquid was washed many times with water until the washing water gave no precipitate with $AgNO_3$ solution. The water was then removed using a rotary evaporator and the ionic liquid obtained was further dried in vacuum line at 328 K for 24 h. [HPhIm][NTf_2] was obtained as a pale yellow liquid with 97% yield (9.90 g). ^1H NMR (500 MHz, MeOD) δ = 0.85 (t, 2H), 1.25 (m, 2H), 1.75 (m, 2H), 4.04 (t, 3H), 4.88 (s, 1H), 7.68 (m, 5H), 7.93, (m, 2H).

2.2.2. Synthesis of 1-benzyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)amide [BnMIm][NTf_2]

The same experimental procedure affording [HPhIm][NTf_2] was followed for the preparation of [BnMIm][NTf_2] from benzyl chloride (2.53 g, 0.02 mol) and methyl imidazolium (1.64 g, 0.02 mol) and the colourless IL was obtained with yield 98% (8.80 g). ^1H NMR (500 MHz, MeOD) δ = 3.33 (m, 2H), 5.41 (s, 3H), 7.44 (m, 5H), 7.58 (m, 2H), 8.95 (s, 1H).

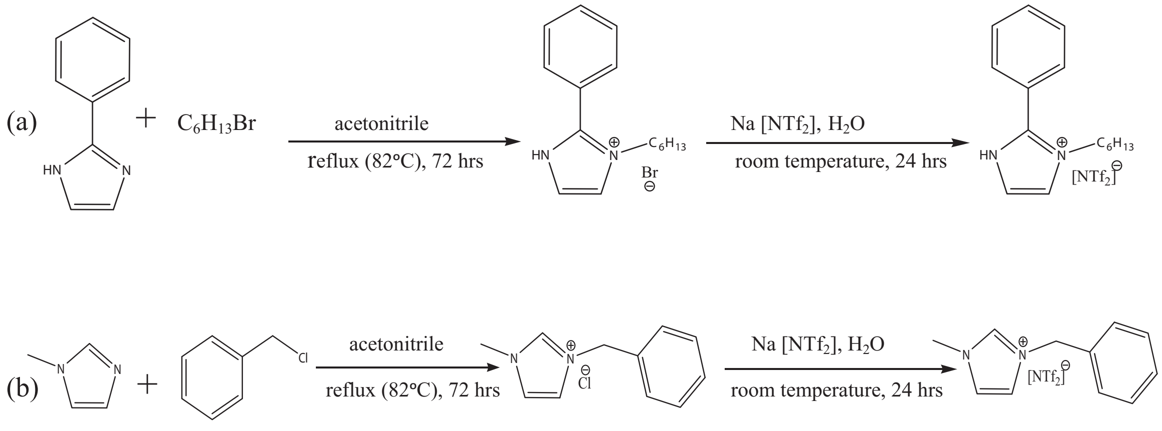

Fig. 1. General route for the synthesis of new TSILs: (a) [HPhIm][NTf_2] and (b) [BnMIm][NTf_2].