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RESEARCH ARTICLE

DYE REMOVAL STUDIES WITH IONIC LIQUIDS 1-ETHYL-3-METHYL IMIDAZOLIUM LACTATE & 2-HYDROXYETHYL-TRIMETHYL AMMONIUM L+LACTATE

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ABSTRACT

Textile industries are major source of water pollution, dyestuffs have proven to be problematic as these are most difficult to treat and recover the dye. These dye effluents are discharged in millions of gallons from different textile mills world over. These are known to affect the environment adversely reducing the dissolved oxygen thus affecting the aquatic life. Conventional treatment techniques involve physical, chemical and biological methodologies. These are not full-proof and thus new techniques are required to improve the efficiency of dye removal. Ionic liquids have been reported to be novel solvents for carrying out liquid-liquid extractions. The asymmetric cations with different combinations of anions can be explored for the removal of dye from the generated textile effluents. These could provide possible solutions to overcome this problem of textile industry.

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INTRODUCTION

To meet the demands of a growing population, textile mills are increasing in size and number thus producing more dye-containing wastewaters. As of 2012, more than 100,000 different dyes existed worldwide, and between 700,000 and 1,000,000 tons were produced each year. The textile industry utilizes about 90% of all dyes, while there remaining 10% are used in food, printing, and plastics. Approximately 280,000 tons of textile dyes are discharged through wastewater on a yearly basis worldwide. Textile industry has been the major cause of water pollution both in terms of quantity generated and difficulty of treatment. The dyes used are responsible for the increase in the COD levels of waste water and decrease in the dissolved oxygen levels thus affecting the aquatic life. Research on treatment of dye containing effluent has always been the topic of interest. New methodologies have been worked upon to develop full-proof technology for removal of dye and generate treated waters for use. (Pang and Abdullah, 2013; Wang et al., 2011) Various methods used to remove dyes from textile effluents include micellar enhanced ultrafiltration (Ahmad et al., 2006), oxidation processes using different

oxidizing agents (Neamtu et al., 2004), electrochemical degradation (Martinez-Huitle and Brillas, 2009), ozone based processes (Zhang et al., 2009), photocatalytic degradation (Bali, 2004; Siboni et al., 2011; Li et al., 2001; Nagel-Hassemer et al., 2012), electrocoagulation (Purkait et al., 2003), nanofiltration (NF) (Zhong et al., 2012; Patel et al., 2012), adsorption on various surface which include agricultural solid waste (Namasivayam and Kavitha, 2002), different minerals like bentonites (Arvanitoyannis et al., 1989), activated carbon from different sources (Kannan and Sundaram, 2001; Mezohegyi et al., 2012), and biological treatments (Khataee et al., 2010; Oller et al., 2011). The physical methods are non-effective and thus require secondary treatment coupled with them as they merely transfer the pollutants from one medium to another (Bes-Pia et al., 2003); chemical methods generate lots of sludge which involves additional cost of disposal; they are generally used in high dosage and thus not economically viable; (Kurbus et al., 2005). Ultrafiltration (UF) and nanofiltration (NF) have been reported for complete removal of all classes of dye, but certain limitations like membrane fouling have been reported. Due to low biodegradability of dyes, the conventional biological wastewater treatment processes like activated sludge are not very efficient in treating wastewater from textile industry (Muthuraman and Palanivelu, 2005). There are numerous technologies available, which are presently being applied for the extracting dye from waste water. Use

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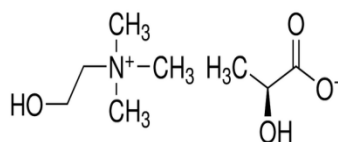
ionic liquids has not been widely used by many dye-consuming industries as only few researches have been carried out to provide sufficient proof on the effectiveness as well as versatility of ionic liquids for the purpose of dye removal. Based on the tailoring ability of ILs, either for the solvation of a wide array of compounds or for the extraction of the most diverse biomolecules from aqueous media (Taziki *et al.*, 2012), the use of IL-based aqueous two phase systems 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 possibility of exploiting ILs in the extraction of dyes from water-rich phases (Gharehbaghi and Shemirani, 2012; Chen *et al.*, 2013). Nevertheless, in these studies (Gharehbaghi and Shemirani, 2012; Chen *et al.*, 2013), hydrophobic ILs, i.e. non water-miscible ILs at temperatures close to room temperature, were employed.

A number of studies have been conducted that examined the use of ionic liquids in the extraction of various dyes (Visser *et al.*, 2000; Vijayaraghavan *et al.*, 2006; Ali *et al.*, 2006; Pei, 2007; Liand Xin, 2008; Fan *et al.*, 2011). For these extractions to be viable, the dye components obviously must partition into the ionic liquid or organic layer, thus vacating the wastewater (aqueous layer). No mechanism of extraction was formally determined, but curiously, the researchers concluded that hydrophobicity of an ionic liquid has no effect on extraction efficiency. This seemingly contradicting study was conducted by Pei *et al.* in 2007. In this work, four different ionic liquids were used, including C4 mim PF6, 1-hexyl-3-methylimidazolium hexafluorophosphate (C6mimPF6), 1-hexyl-3-methylimidazolium tetrafluoroborate (C6mimBF4), and 1-octyl-3-methylimidazolium hexafluorophosphate (C8mimPF6). The anionic dyes used were methyl Orange, eosin yellow, and Orange G, and the extractions were performed over a wide range of pH values. It was observed that the ILs possessing longer alkyl chains were more efficient at extraction. Not much work has been reported on disperse dyes and direct dyes. In this paper the efficiency of removal has been compared with of two different classes of dye and two different ionic liquids. The cations of the ionic liquids are different and the anion is the same.

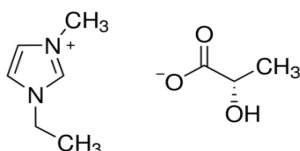
Experimental

A) Ionic liquids were procured from Sigma Aldrich. The ionic liquids used for the study are:

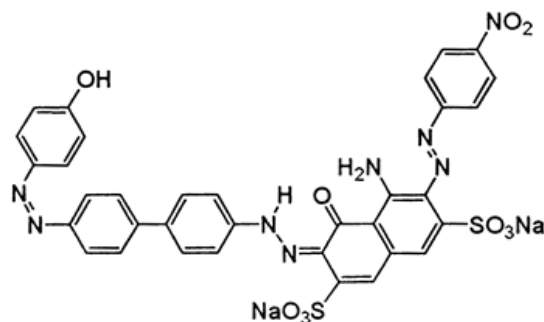
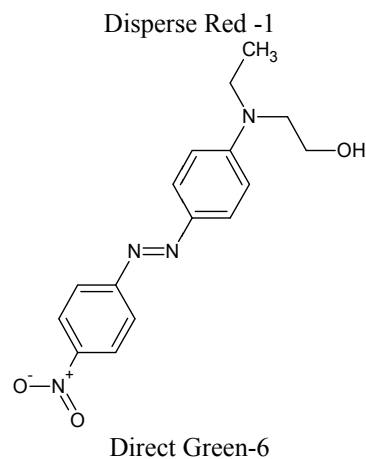
1. 2-Hydroxyethyl-trimethyl ammonium L+ lactate



2. 1-Ethyl-3-methyl imidazolium lactate



b) Dyes used for the study are: Disperse dye red-1 and Direct dye Green-6



The concentrations of dye and ionic liquid used for the study are 500mg/liter (500ppm) and 0.1% ionic liquid, respectively. The absorbance spectra for the dyes were noted using a Colorimeter- Systronics at different wavelengths to determine the λ_{max} for the dye. Standard curves were plotted by taking the absorbance at the λ_{max} for the different concentrations of the dye. The standard curve were used to determine the different concentration of the dye after treatment with the ionic liquid. The studies have been carried at different phase ratios of dye and ionic liquid. The ionic liquid volumes have been increased keeping the dye constant. The ratios of ionic liquid used for the study varied from 10 to 100 ml. The % efficiency of removal was calculated using the formula

$$\% \text{ efficiency} = 1 - \frac{C_f}{C_o}$$

Where, C_o is initial concentration of the dye and C_f is the final concentration in ppm.

RESULTS AND DISCUSSION

The results of % removal of dyes with different ionic liquids are tabulated in Table-1. The %removal of disperse dye is lower in case of 2-Hydroxyethyl-trimethyl ammoniums L+ lactate with higher volumes of ionic liquid while using lesser volume of ionic liquid, the % removal is much better as given in column three of Table1. However in case of direct dye, better removal has been observed with higher volumes of ionic liquid. And at lower ratios much less removal has been observed. The cation part of ionic liquid has a hydroxyl group which is probably causing different types of interactions with the dye. The interactions possible in case of direct dye are more as compared to the disperse dye. The disperse dye has a hydrophobic chain which may be responsible for such results. However, in case 1-ethyl-3-methylimidazolium-L(+)-lactate the cation part of the ionic liquid has no such polar groups.

Table 1. % Removal of dyes using different ionic liquids

No	Phase ratios (Dye:IL*)	2-Hydroxyethyl-trimethyl ammonium L+ lactate - (HL) (% Removal)		1-ethyl-3-methylimidazolium-L(+)-lactate (EL) (% Removal)	
		Disperse Dye	Direct Dye	Disperse Dye	Direct Dye
1	1:10	50	100	90	90
2	1:05	50	80	61	60
3	1:02	75	50	24	60
4	1: 01	75	20	15	20

*IL- Ionic Liquid

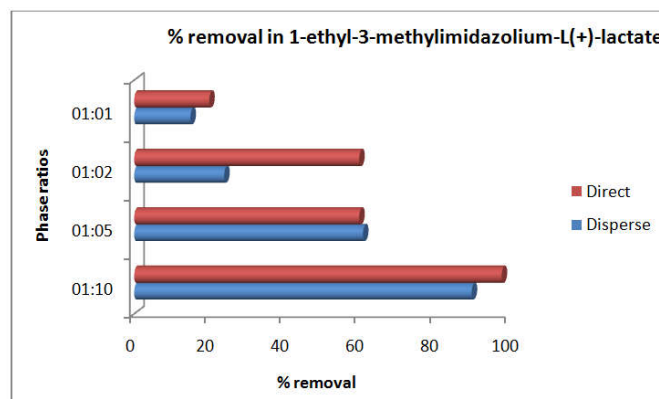


Fig.4. % removal of direct dye and disperse dye with 1-Ethyl-3-Methylimidazolium Lactate (+)

Thus the results observed are almost comparable. At lower ratios the removal is 15% in case of disperse dye and 20% in case of direct dye while at higher ratios 1:10 the removal is 90% in case of both disperse dye and direct dye, Figure 1 and Figure 2 present these results. Figure 3 and Figure 4 show the % removal of dye with two ionic liquids and dyes.

In 2-Hydroxyethyltrimethylammonium- L(+) Lactate, the removal of direct dye is better at higher ratios of ionic liquid and is better for disperse dye at lower ratios. However in case 1-ethyl-3-methylimidazolium-Lactate-L(+), overall better results have been observed with direct dye. Thus it can be concluded that the asymmetric cationic moiety of the ionic liquid has affected % removal along with type of dye being extracted.

Conclusion

Type of ionic liquid and quantity of ionic liquid affect the % dye removal. Cations in the ionic liquids have effect on the % removal of dye.

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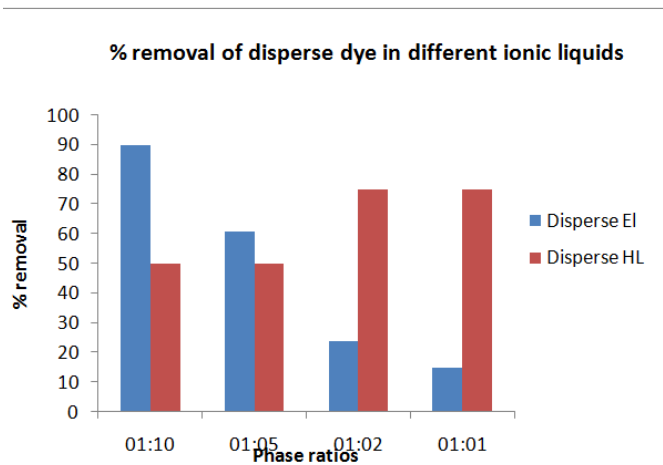


Fig.1. % Removal of Disperse dye in different ionic liquids

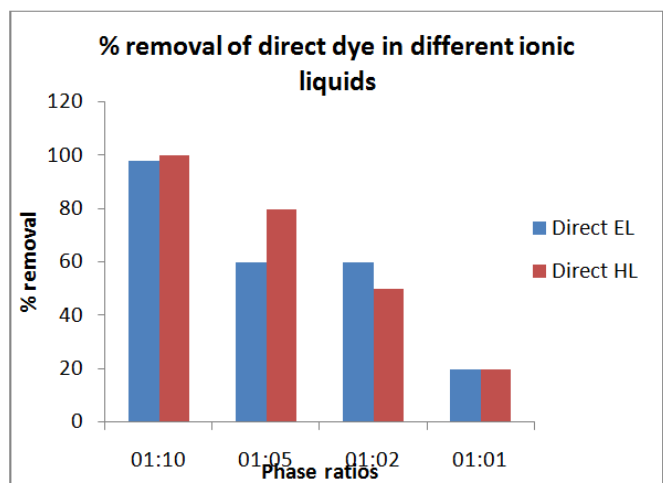


Fig.2. Effect of removal of direct dye with two different ionic liquids

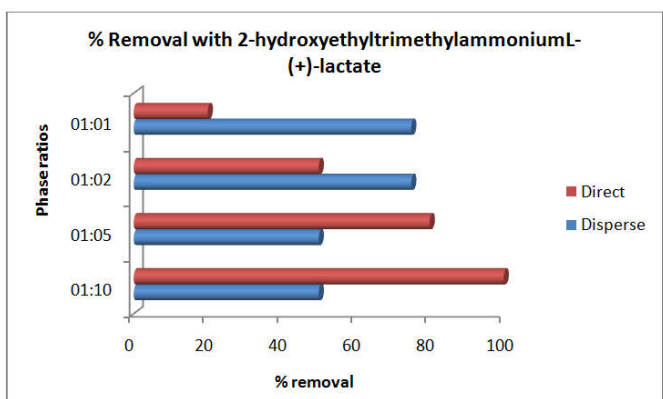


Fig.3. % removal of direct and disperse dye in 2-Hydroxyethyltrimethylammonium- L(+) Lactate

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