

Chapter 12

Functionalized Ionic Liquids for the Photodegradation of Dyes



Dipesh S. Patle, Vijay Khajone, Pundlik R. Bhagat, Arvind K. Jaiswal, and
Sushil Kumar

Contents

12.1	Introduction	392
12.2	Ionic Liquids	393
12.3	Functionalization of Ionic Liquids	395
12.4	Applications of IL in Wastewater Treatment	397
12.5	Degradation of Dyes Using Functionalized Ionic Liquids	398
12.6	Case Study: Photodegradation of Organic Dyes, Methylene Blue, and Congo Red Using a Polymer-Supported Ionic Liquid Fe-Porphyrin Complex	398
	12.6.1 Synthesis of a Polymer-Supported Ionic Liquid Fe-Porphyrin Complex	398
	12.6.2 Photodegradation of Methylene Blue and Congo Red	402
	12.6.3 Possible Mechanism	405
12.7	Conclusions	406
	References	406

Abstract From the last few decades, environmental pollution is one of the major problems of the modern world. Increased industrialization has caused a serious problem of water pollution as it has led to the discharge of toxic and hazardous chemicals into the water bodies. Dyes are the main class of organic compounds that pollute the water. Hence, their effective removal is inescapable. The presence of metal ions is also a serious problem. Due to low volatility, chemical stability, and chelating abilities of ionic liquids, the application of functionalized ionic liquids can effectively reduce the amount of these pollutants.

In this chapter, the properties of ionic liquids which make them suitable for wastewater treatment are presented, and design ability of the functionalized ionic

D. S. Patle · A. K. Jaiswal · S. Kumar (✉)
Department of Chemical Engineering, Motilal Nehru National Institute of Technology,
Allahabad, Prayagraj, Uttar Pradesh, India
e-mail: dipesh-patle@mnnit.ac.in

V. Khajone · P. R. Bhagat (✉)
School of Advance Science, Vellore Institute of Technology, Vellore, Tamil Nadu, India

liquids/task-specific ionic liquids provides better opportunities to change the structures in cation and anion to achieve functionalized ionic liquid for specific pollutant removal. Therefore, recent applications of functionalized ionic liquids for the treatment of metal ions and different dyes are discussed. Later, a case study on the photodegradation with possible mechanisms of organic dyes, namely, methylene blue and congo red using a synthesized polymer-supported ionic liquid Fe-porphyrin complex is presented. Catalyst loadings of 10 mg and 12.5 mg at constant time of 60 min are found to be a better choice for the photodegradation of methylene blue and congo red dyes, respectively. The highest photodegradations of methylene blue and congo red are found to be ~78% and ~99%, respectively.

Keywords Wastewater treatment · Functionalized ionic liquids · Photodegradation · Organic dyes · Polymer supported ionic liquid iron porphyrin

12.1 Introduction

Approximately 7,00,000 tons of dyes are manufactured worldwide annually; wherein about 60% is azo dye out of which 10–15% of azo dyes is passed in the water system (Langhals 2004). Azo dyes are classified as acidic, basic, disperse, reactive, direct, and solvents/food dyes. An azo dye which is derived from benzidine, $C_{12}H_{12}N_2$ is the main segment of carcinogenicity. Textile industries use a huge amount of freshwater for dyeing and processing, which discharge large amount of chemical pollutants like organic surfactants, dyes, dispersants, alkalis, acids, solvents, and various salts into the water bodies. The presence of dyes in water creates acute aesthetic and aquatic problems by disturbing the photosynthetic reaction due to light penetration. So, it is essential to focus on wastewater treatment technologies for its reuse and recycle. From the view of an environment, severe problems such as toxicity to water bodies and foremost to carcinogenic and mutagenic effects on humans are created by the textile-based industries (Dalvand et al. 2011; Du et al. 2017). The removal/treatment of dyes from polluted wastewater is comparatively more significant than the other soluble polluted compounds, which also add the portion of biochemical oxygen demand (Holkar et al. 2016). Many methods exist to eradicate harmful dyes from wastewater such as coagulation, an electrochemical process, membrane separation process, chemical oxidation, adsorption, reverse osmosis, and biodegradation. But most of these processes are not so acceptable due to additional chemical demand, producing large amount of secondary by products with their disposal problem and monetary disadvantages. A massive amount of such dyes in wastewater is nonbiodegradable because of their complex and stable molecular structures.

The drawback with the conventional biological methods (Shankar et al. 1999) is the treatment period. Treatment period typically varies from 1 day to 6 days. In

addition, traditional processes (physical and chemical) are found to be comparatively expensive and may also lead to other secondary pollution due to the requirement of additional chemicals (Oller et al. 2011). Conventional biological procedures in association with physical/chemical processes to obtain improved decolorization of effluents may generally be costly and limited applicable. The adsorption processes using suitable adsorbents (activated carbons, charcoals, clays, diatomaceous earth, microbial biomass, compost, unmodified and modified lignocellulose, etc.) for the wastewater treatment have disadvantage of regeneration, which also increases the cost of the process. At times, it demands a very long time, and it may be ineffective for low concentrations of pollutants. Oxidation can be used to decolorize the dye effluent using various oxidizing agents such as hydrogen peroxide and ozone activated with Fe(II) salts. However, the pollutant removal mechanisms involve flocculation, and contaminants are shifted from the wastewater to the sludge, which further demands disposal in landfill (Boczkaj and Fernandes 2017; De Lima et al. 2017). Hence, the abovementioned techniques may not provide sustained solution with ecological point of view. Very recently, electrochemical treatment methods have achieved a good position as effective and efficient treatment technologies for dye effluents. However, the application of electrochemical techniques warrants a higher investment in equipment and energy requirement (Vaghela et al. 2005; Butler et al. 2011; Gautam et al. 2019).

In the recent years, researchers have used ionic liquids for various applications such as biocatalytic transformation, chemical synthesis, electrochemistry, analytical chemistry, and separation processes, because of the green characteristics of ionic liquids (Wasserscheid and Keim 2000; van Rantwijk et al. 2003; Pandey 2006; Hernández-Fernández et al. 2015). Main advantages of ionic liquids are the better possibilities of reusing and relatively easy recovery of ionic liquids. Therefore, application of ionic liquids effectively reduces the amount of waste generated during treatment process. The photodegradation of dye molecules using ionic liquids (ionic liquids), also regarded as green solvents, has advantageous over other processes with the view of environment protection. However, ionic liquids are still quite expensive. Hence, regeneration and recycling of ionic liquids are important to make a technology economically viable (Fernández et al. 2010). The scheme to reduce the amount of pollutants from industrial effluents using ionic liquids and potential sources of environmental release is presented in Fig. 12.1.

12.2 Ionic Liquids

An ionic liquid is a molten salt comprising of positive charged ions, cations and negative charged ions, anions having melting point below 100 °C. Combination of bulky and asymmetrical cations such as imidazolium, pyrrolidinium, and pyridinium and evenly shaped symmetrical anions such as halides, triflate, and nitrate lowers the lattice energy which is accounted for low melting points. Ionic liquids are also known as liquid electrolytes, room temperature molten salts, low temperature molten

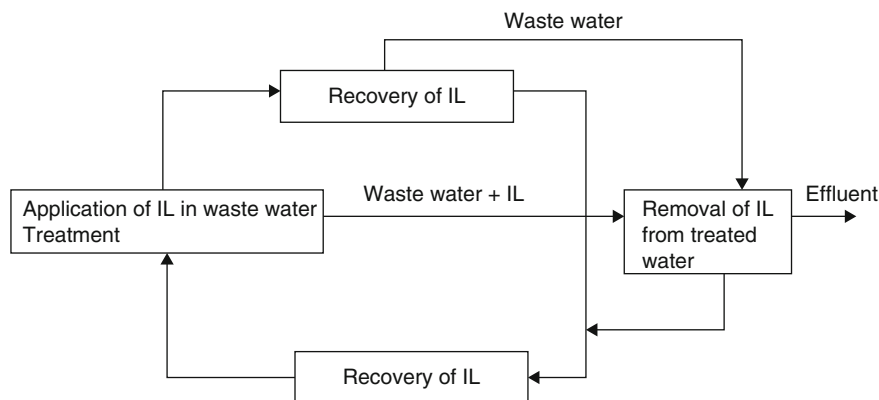
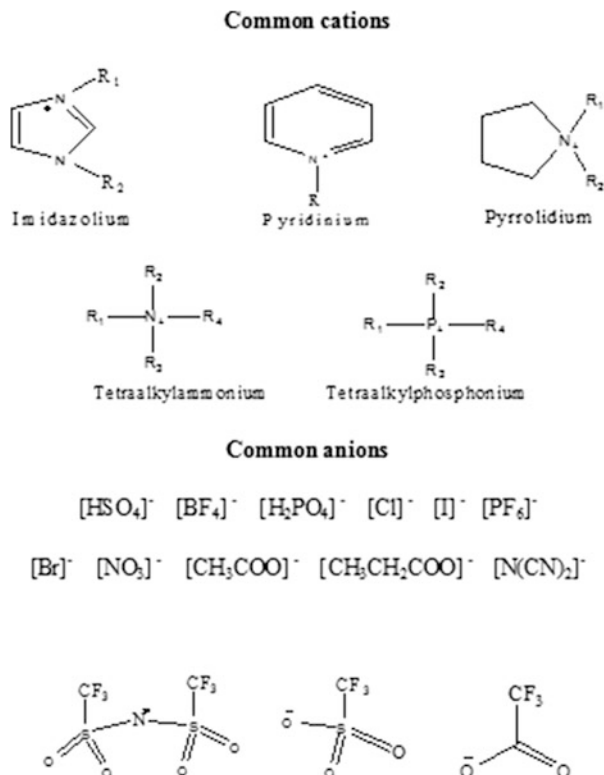


Fig. 12.1 The scheme to reduce the amount of pollutants from industrial effluents using ionic liquids (IL)

salts, ambient temperature molten salts, ionic melts, ionic fluids, fused salts, liquid salts, ionic glasses, or neoteric solvents (Wilkes 2002). Room temperature ionic liquids are salts which are in liquid state at or below room temperature. The structures of common cations and anions of ionic liquids are presented in Fig. 12.2. Ionic liquids are gaining worldwide acknowledgement from researchers as well as people in the industries for a large number of applications (Heintz and Wertz 2006).

Depending on the cation and anion, the characteristics of ionic liquids, e.g., viscosity, solubility, and cloud point, may differ. The main benefit of ionic liquids is the provision of the replacement of anion that enables developing compounds with characteristics necessary for specific application. These tuned salts are referred to as task-specific ionic liquids/functionalized ionic liquids. Moreover, non-volatility, non-flammability, and better thermal stability make ionic liquids very attractive for industrial applications. Ionic liquids also have excellent features for removal of organic pollutants and metal ions because of its low volatility, chemical stability, and chelating abilities (Domanska and Rekaewek 2009; Egorov et al. 2010; Regel-Rosocka and Wisniewski 2011). Ionic liquids consist of loosely coordinating bulky ions with the polarities comparable to alcohols. In addition to negligible vapor pressure, ionic liquids are nonexplosive and nonflammable. Ionic liquids have application in fields such as electrochemical, photo-degradation of organic compounds, catalysis and/or reaction media, drug delivery, biotransformation, solar cells, and various areas of separations (Patel and Lee 2012). The tailored ionic liquids used in reaction media and separation processes are reported to show better activity, selectivity, yields, stability, and environmental safety than conventional solvents (Dietz 2006; Han and Row 2010; Bollin and Viamajala 2012). An overview of physical properties such as density and viscosity of selected ionic liquids used in separations are presented in Table 12.1 (Han and Row 2010). The design ability of the functionalized ionic liquids/task-specific ionic liquids provides better

Fig. 12.2 Structure of common cations and anions of ionic liquids. (Sun and Armstrong 2010)

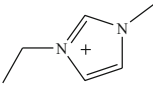
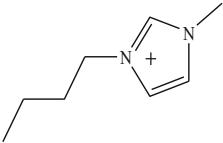
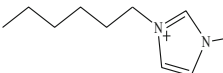
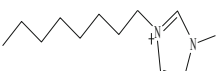

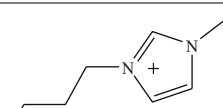
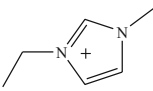


opportunities to change the structures in cation and anion, and the length of the side chain can also be altered to the organic cation to achieve tailored/ functionalized ionic liquid of special properties.

12.3 Functionalization of Ionic Liquids

The chemo-physical properties of ionic liquids depend on the cation-anion combination and the length of alkyl chain. The functionality of ionic liquids also has a strong effect on the properties. Thus, the synthesis of functionalized ionic liquids is generally performed by the integration of functional groups into the cation of ionic liquid. Till date, mostly, the imidazolium cations are functionalized, and a few functionalized anions are known. Imidazolium cations can be modified using functionalized groups such as alkyl halides, hydroxyl groups, carboxylic groups, thiol groups, alkene groups, diene groups, and so on (Ye and Shreeve 2004; Fei et al. 2005). Using the quaternization method, most of the functional groups directly added imidazolium moiety and give the desired functionalized ionic liquids. Certain functionalities require other synthetic routes to be connected to the imidazole

Table 12.1 Physical properties of ionic liquids at 25 °C

Cation	Anion	Abbreviation	Melting Point °C	Density g ml ⁻¹	Viscosity cP
	[BF ₄] ⁻	[C ₂ mim][BF ₄]	6	1.248	66
	[PF ₆] ⁻	[C ₂ mim][PF ₆]	58–62	1.373	450
	[BF ₄] ⁻	[C ₄ mim][BF ₄]	-82	1.208	233
	[PF ₆] ⁻	[C ₄ mim][PF ₆]	10	1.373	400
	[CF ₃ SO ₃] ⁻	[C ₄ mim][CF ₃ SO ₃]	16	1.290	90
	[Tf ₂ N] ⁻	[C ₄ mim][Tf ₂ N]	-8	1.404	48
	[BF ₄] ⁻	[C ₆ mim][BF ₄]	-82	1.075	211
	[PF ₆] ⁻	[C ₆ mim][PF ₆]	-61	1.304	800
	[BF ₄] ⁻	[C ₈ mim][BF ₄]	-79	1.11	440
	[Cl] ⁻	[C ₈ mim][Cl]	0	1.000	16,000
	[Tf ₂ N] ⁻	[C ₁ pyr][Tf ₂ N]	0	1.44	39
	[Br]	[C ₄ mim][Br]	65–75	1.3	1486.49
	[N(CN) ₂]	[C ₄ mim][N(CN) ₂]	-6	1.06	334
	[CH ₃ COO]	[C ₄ mim][CH ₃ COO]	-20	1,02	440
	[C ₄ SO ₃]	[C ₂ mim][C ₄ SO ₃]	1–7	1.17	180.8

Han and Row (2010)

C = alkyl group; mim = methyl imidazolium; pyr = pyridinium

backbone (Liddle and Arnold 2005). The imidazolium salts with SiOMe₃ groups can also be synthesized with greater yield using direct quaternization. The hydrophilicity of these imidazolium salts may be controlled on the surfaces of Si/SiO₂ by anion exchange (Gao et al. 2004).

Less attention was given on the synthesis of pyridinium-based functionalized ionic liquids rather than imidazolium systems. Pyridinium-based ionic liquids are successfully functionalized as the nitrile salt, 1,2,4-substitute-triazolium salts, and phosphazene-based ionic liquids. Other low melting salts have also been formed using quaternization of pyrazine and pyrimidine with alkyl and polyfluoroalkyl halides. Functionalized ammonium ionic liquids, also known as ammonium salts, have been synthesized with ether groups. The ammonium salts show enhancement in cathodic and anodic stability and provide larger electrochemical window (Zhao 2007).

12.4 Applications of IL in Wastewater Treatment

Ionic liquids have excellent features for extraction of metal ions/organic pollutants from aqueous solutions because of its low volatility, chemical stability, and chelating abilities. In this section, few recent studies are discussed particularly extraction of heavy metals/others from wastewater using functionalized and modified ionic liquids as presented in Table 12.2. Major findings of the study appeared in the literature are presented in this table.

Table 12.2 Few selected studies on the wastewater treatment using ionic liquids

Pollutants	Treated by	Major findings	Reference
Heavy metals (Cr, Cu, Cd, Ni, Pb, and Zn)	Ammonium and phosphonium-based ionic liquids (Ionic liquids)	The removal of heavy metals (Cu, Ni, and Zn) was achieved $\geq 90\%$	Fuerhacker et al. (2012)
Lead [Pb(II)]	1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (C4) and 1-hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide (C6)	These ionic liquids are modified using silica sorbents by direct immobilization on silica surface. The effect of sorbent dosage, pH, time of contact, sorbate concentration, and temperature is considered	Saleem et al. (2014)
Phthalic acid	[TBP][CF ₃ SO ₃], [OMPYR][BF ₄] and [C4DMIM][CF ₃ SO ₃]	The ionic liquids are found to be possible solvent for the treatment of organic effluent-rich water and wastewater	Pilli et al. (2014)
Phenol and phenolic compounds	Trioctylphosphine oxide 90% (Cyanex – 923) with room temperature ionic liquids, RTIL	RTIL encapsulated polymer microcapsules prepared using styrene and divinylbenzene as adsorbent can be effectively employed for the adsorption of phenol and other phenolic compounds	Archana et al. (2016)
Cu ²⁺ , Ni ²⁺ , Pb ²⁺ , Cd ²⁺ , Ag ⁺	Dendritic ionic liquids, four ionic liquids based on Tf ₂ N ⁻ and BF ₄ ⁻ anions	Extraction of Cu ²⁺ , Pb ²⁺ and Ag ⁺ cations is achieved up to 98%	Hayouni et al. (2018)
Mercury (Hg)	Polymer membrane incorporating ionic liquids [thiosalicylate (TOMATS) or salicylate (TOMAS)]	TOMATS has given better results. A PIM made of 50% cellulose triacetate, 30% TOMATS, and 20% nitrophenyl octyl ether as a plasticizer enabled the effective transport of Hg	Sergi et al. (2019)
Phenolic compounds	Ionic liquid, 1-ethyl-3-methyl imidazolium cyanoborohydride	The process conditions such as temperature, time, and phase volume ratio of ionic liquid and phenol concentration are optimized for its extraction from wastewater	Mathews et al. (2019)

12.5 Degradation of Dyes Using Functionalized Ionic Liquids

Ionic liquids have found the recent applications in fields such as electrochemical, photo-degradation of organic compounds, catalysis and/or reaction media, drug delivery, biotransformation, and various areas of separations (Patel and Lee 2012). In this section of the chapter, recent and selected studies have been presented in Table 12.3 for the degradation of various dyes such as methyl orange, methylene blue, rhodamine B, indigo blue, and Sudan III using the functionalized ionic liquids. Applicable ionic liquids are also assisted by incorporating different nanoparticles such as Ag and TiO₂. It is clear from Table 12.3 that ionic liquids can be effectively used for the effective removal of the dyes. The following section describes a case study on the photodegradation of organic dyes, namely, methylene blue and congo red, using a polymer-supported ionic liquid Fe-porphyrin complex.

12.6 Case Study: Photodegradation of Organic Dyes, Methylene Blue, and Congo Red Using a Polymer-Supported Ionic Liquid Fe-Porphyrin Complex

In this case study, a polymer-supported ionic liquid Fe-porphyrin complex was synthesized using the procedure described below. Ionic liquid complex was tested for the photodegradation of the organic dyes, namely, methylene blue and congo red. Results were analyzed using several characterization techniques.

12.6.1 Synthesis of a Polymer-Supported Ionic Liquid Fe-Porphyrin Complex

Synthesis of Poly 1-(4-(sec-butyl) benzyl)-3-(3-formyl-4-hydroxybenzyl)-1H-benzo[d]imidazol-3-ium chloride, 1-A

For the synthesis of a polymer-supported ionic liquid Fe-porphyrin complex, firstly, equal moles of poly 1-(4-s-butyl) benzyl)-1H-benzo[d]imidazole, 0.02 mol/5.284 g and 5-(chloromethyl)-2-hydroxybenz-aldehyde, 0.02 mol/3.411 g were taken and mixed in the round bottle flask of 100 mL with acetonitrile of 25 mL. The complete reaction mixture was agitated 24 h using a magnetic stirrer at ambient temperature. After completion of reaction, a new compound was formed and washed using a solvent, diethyl ether to acquire white powder form of 1D (Balange et al. 2017, 2018). The yield and melting point of the resultant compound were determined as 68.99% and 180–198 °C, respectively.

Table 12.3 Recent studies on degradation of dyes using functionalized ionic liquids

Type of dye	Ionic liquids	Major findings	Reference
Anionic dyes (methyl orange, eosin yellow, and orange G)	Imidazolium-based ionic liquids [C4mim][PF6], [C6mim][PF6], [C6mim][BF4], and [C8mim][PF6]	The extraction efficiencies of methyl orange, eosin yellows, and orange G are found as 85–99%, almost 100% and 69%, respectively, in tested water under the optimized conditions	Pei et al. (2007)
Dyes (methyl blue and chromium ions)	Hydrophobic poly(ionic liquid) of poly(3-ethyl-1-vinylimidazolium bis(trifluoromethanesulfonyl)imide) (PVI-TFSI)	The maximum adsorbed efficiencies for Cr (VI) and methyl blue are 98.0% and 97.6%, respectively, and maximum adsorption capacities of PVI-TFSI are 476.2 and 17.9 mg/g for methyl blue and Cr(VI), respectively	Hao et al. (2013)
Methyl orange (MO) and rhodamine B (RhB) Dyes	1-Butyl-3-methylimidazolium tetrafluoroborate, [Bmim]BF ₄ with Degussa P25 TiO ₂	This paper presents new insights of photocatalysis mechanism, which is occurring on functional group, TiO ₂ and the design for enhancement of photocatalytic performance	Qi et al. (2013)
Set of textile dyes (chloranilic acid, indigo blue, and sudan III)	Ionic liquids (phosphonium- and imidazolium-based) and an inorganic (aluminum sulfate) or organic salt (potassium citrate)	Authors have revealed that a proper IL and salt can be used to extract these dyes to the IL-rich phase in a single step process	Ferreir et al. (2014)
Azo dye (trypan blue)	Ionic liquid-assisted hydrothermal synthesis of TiO ₂ nanoparticles; ionic liquid: [BMI]CH ₃ SO ₃	Ionic liquid-assisted TiO ₂ nanoparticles exhibited the excellent photocatalytic activity for the photodegradation of dye and trypan blue and also reduce the amount of Cr + 6 to Cr + 3	Ravishankar et al. (2015)
Methyl orange (MO), methylene blue (MB) and rhodamine B (RhB)	Synthesized silver chloride nanoparticles and the ionic liquid trihexyl(tetradecyl) phosphonium chloride	The degradation efficiencies are found to be 98.4% for MO, 98.6% for MB, and 99.9% for RhB in 1 h	Rodríguez et al. (2017)

(continued)

Table 12.3 (continued)

Type of dye	Ionic liquids	Major findings	Reference
Anionic azo dyes, methyl orange	Silver nanostructures in ionic liquid media (1-butyl-3-methylimidazolium tetrafluoroborate)	Results confirmed that Ag nanostructures using silver nitrate incorporated in ionic liquid media have shown good photocatalytic efficiency for the degradation of dyes	Park et al. (2019)

¹H NMR (400 MHz, DMSO-d₆): δ 0.52 (s, 1H), 0.74 (br. 1H), 1.08 (br. 1H), 1.29 (s, 1H), 1.92 (s, 1H), 5.65 (s, 4H), 7.36 (br. 6H), 7.73 (br. 1H), 10.13 (d, 2H, J = 8.97 Hz), 15.79 (br. 1H). ¹³C NMR (100 MHz, DMSO-d₆): 190.77, 161.74, 159.18, 136.94, 135.46, 131.29, 129.18, 127.15, 122.94, 118.64, 114.49, 49.76. FT-IR – (KBr, v/cm⁻¹): 3377.36, 3018.60, 2926.01, 1654.92, 1612.49, 1558.48, 1487.12, 1444.68, 1371.39, 1282.66, 1249.87, 1188.15, 1151.50, 1016.49, 929.69, 842.89, 744.52, 698.23, 632.65, 540.07, 497.63, 424.34.

Synthesis of 3-(2-carboxyethyl)-1-(3-formyl-4-hydroxybenzyl)-1H-benzo[d]imidazol-3-ium bromide, 1-B

The synthesis of 3-(2-carboxyethyl)-1-(3-formyl-4-hydroxybenzyl)-1H-benzo[d]imidazol-3-ium bromide was carried out according to the procedure given in (Muskarwar et al. 2013; Khiratkar et al. 2016) with slight modification. 5-(1-H-benzo[d]imidazole-1-yl) methyl-2-hydroxybenzaldehyde (BMSA), 7.56 g/30 mmol was stirred for 1 h in toluene solution of 50 ml at 60 °C. Then, 3-bromopropionic acid of 6.08 g/40 mmol in toluene was added drop wise for 30 min and stirred for next 14 h at 85 °C. After this, the whitish solid product was obtained, after the decantation of toluene and washing with ethyl acetate, 3 × 20 mL and diethyl ether, 3 × 25 mL with yield of 73.33%, and melting point of 205 °C.

¹H NMR (400 MHz, DMSO-d₆): δ 2.63 (s, 2H), 4.33 (s, 2H), 5.35 (s, 2H), 6.67 (s, 1H), 7.15 (s, 1H), 7.29 (s, 1H), 7.50 (d, 1H, J = 19.52 Hz), 7.75 (s, 1H), 9.24 (s, 1H), 9.58 (s, 1H), 9.88 (s, 1H), 10.55 (s, 1H), 12.32 (1H, br), 15.58 (1H, br), ¹³C NMR (100 MHz, DMSO-d₆): 190.97, 172.31, 161.49, 161.32, 142.40, 142.57, 136.53, 129.55, 127.12, 126.01, 125.24, 122.90, 118.48, 116.31, 114.47, 114.34, 113.51, 65.36, 49.56, 33.21, 15.63. FT-IR – (KBr, v/cm⁻¹): 3360, 3120, 1720, 1560, 1440, 1249, 1184, 1128, 989, 823, 744, 626, 495.

Synthesis of 1,1'1''-(((20-(5-((3-(4-(sec-butyl)benzyl)-1H-benzo[d]imidazole-3-ium-1-yl)methyl)-2-hydroxyphenyl)porohyrin-5,10,15-triyl)tris(4-hydroxybenzene-3,1-diyl))tris(methylene))tris(3-(2-carboxyethyl)-1H-benzo[d]imidazole-3-ium) tribromide chloride, (PSILPP) ligand 1-C

1-(4-(sec-butyl)benzyl)-3-(3-formyl-4-hydroxybenzyl)-1H-benzo[d]imidazol-3-ium chloride, **1-A** of 1.01 g/2.5 mmol and 3-(2-carboxyethyl)-1-(3-formyl-4-hydroxybenzyl)-1H-benzo[d]imidazol-3-ium bromide, and **1-B** of 3.039 g/7.5 mmol were mixed thoroughly in propionic acid, 20 mL at 60 °C for 30 min.

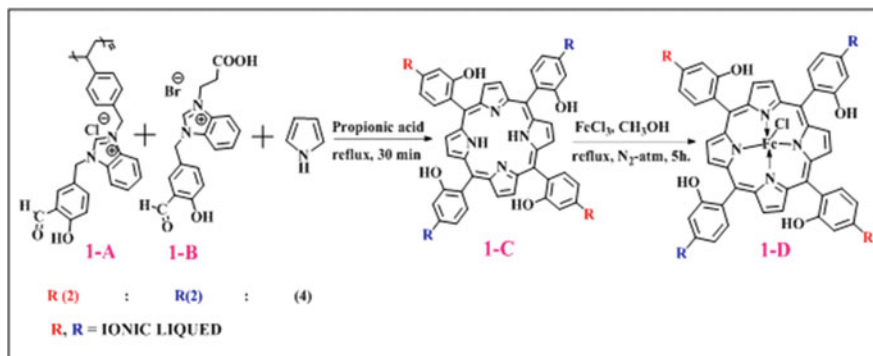


Fig. 12.3 Synthesis of polymer-supported ionic liquid Fe-porphyrin complex

To the mixture, pyrrole of 0.67 g/10 mmol in propionic acid of 15 mL was fed gradually for 30 min with controlled stirring for next 60 min at 130–140 °C. The purple solid product was then obtained. This was separated by removal of 2/3 propionic acid using rotary evaporator and finally washing with methanol followed by diethyl ether, 3 × 25 mL. The NH protons inside the ring of porphyrins acquired acidic character and therefore can get deprotonated to provide porphyrin to ions (Rabbani et al. 2016; Min et al. 2019). %Yield = 71.99% and melting point = above 250 °C were found.

$^1\text{H NMR}$ (400 MHz, DMSO- d_6): δ -1.006 (s, 2H), 0.05(t, 5H, $J = 7.62$ Hz), 0.24 (s, 2H), 1.21(q, 3H, $J = 7.88$ Hz), 1.54(s, 3H), 1.99(q, 2H, $J = 6.1$ Hz), 3.74(q, 3H, $J = 7.21$ Hz), 4.72(brs, 5H), 6.17(s, 7H), 6.57(m, 9H), 6.69(q, 4H, $J = 3.17$ Hz), 6.84 (q, 7H, $J = 3.00$ Hz), 6.98(d, 4H, $J = 8.58$ Hz), 7.07(q, 4H, $J = 3.19$ Hz), 7.10(s, 5H), 8.49(s, 6H), 8.86(s, 2H), 12.21(s, 2H). FT-IR - (KBr, ν/cm^{-1}): 3026, 2929, 1712, 1610, 1560, 1502, 1438, 1330, 1255, 1182, 991, 827, 744, 601, 464.

Synthesis of 1,1'1''-(((1⁹-(5-((3-(4-(*sec*-butyl)benzyl)-1H-benzo[d]imidazole-3-ium-1-yl)methyl)-2-hydroxyphenyl)-1²,1³-dihydro-1¹²H,3²H-1¹ λ^2 -1(12,3)-1 λ^2 -5,8-(azeno)pyrrolo[1,2-b][1]zinc[2,1]diazacycloundecina-3(5,2)-pyrrolacycloheptaphan-5-ene-14,2,4-triyl)tris(4-hydroxybenzene-3,1-diyl)tris(methylene))tris(3-(2-carboxyethyl)-1H-benzo[d]imidazole-3-ium) tribromide chloride, polymer supported ionic liquid iron porphyrin complex 1-D

Polymer-supported ionic liquid iron porphyrin complex was successfully prepared and characterized by the different methods. The complex ligand **1-C** of 0.903 g/0.5 mmol and FeCl_3 of 0.097 g/0.6 mmol were charged to methanol and stirred initially for 30 min at atmospheric temperature. Later, above mixture was subjected to reflux at a temperature of 75 °C for 5 h in the inert atmosphere of nitrogen. The synthesized product was then isolated by periodic washing using methanol, and it was dried in the oven for 2 h at a temperature of 80 °C. Finally, a purple color powder of polymer-supported ionic liquid iron porphyrin complex was obtained as given in Fig. 12.3 with yield of 79.93% and melting point of above 250 °C.

FT-IR – (KBr, v/cm^{-1}): 3248, 1714, 1608, 1562, 1506, 1438, 1259, 1189, 1132, 993, 829, 746, 592, 505, 422.

12.6.2 Photodegradation of Methylene Blue and Congo Red

The synthesized polymer-supported ionic liquid iron porphyrin catalyst was used to photodegrade the two azo dyes, methylene blue and congo red under the simulated light and normal air at specific values of pH. The photodegradation results are shown in Figs. 12.4 and 12.5. The process parameters used in photodegradation were optimized to maximize the degradation. In the process of optimization, photodegradation of dyes in visible light was investigated by changing one variable, and remaining variables were kept constant. After getting one optimum parameter, next parameter study was carried out keeping fixed other variables to find optimum photodegradation. First, the photodegradation of methylene blue using this catalyst with different quantities was optimized under simulated light at temperature of 25 °C. The results are presented in Table 12.4 as serial numbers 1–5 and Fig. 12.4, 1B.

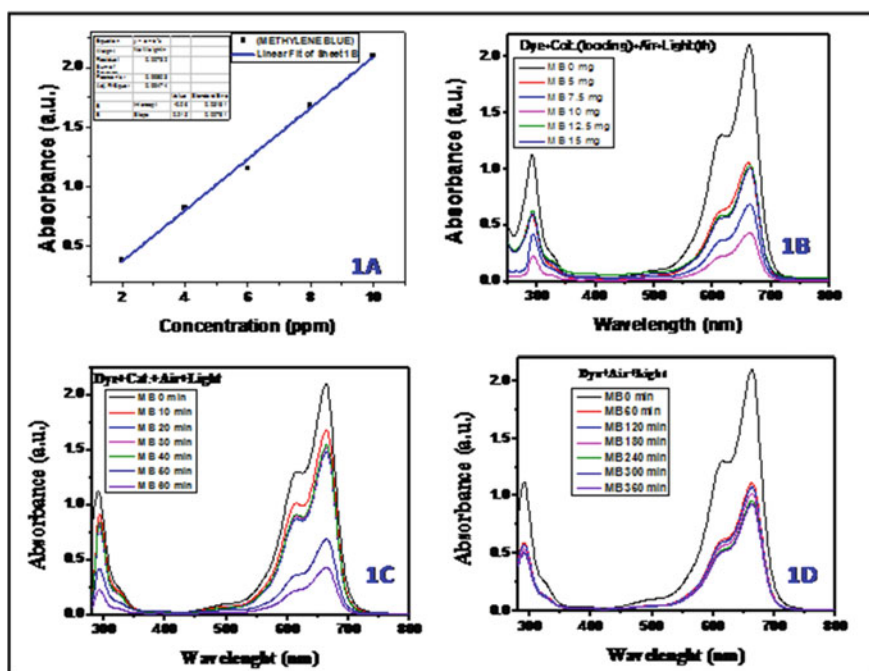


Fig. 12.4 Methylene blue, MB dye (A) R-square value, (B) catalyst loading, (C) time variation of 10 mg catalyst and atmospheric air, and (D) time variation of atmospheric air. (Carried out at pH of ~5 in the presence of 5 W LED light)

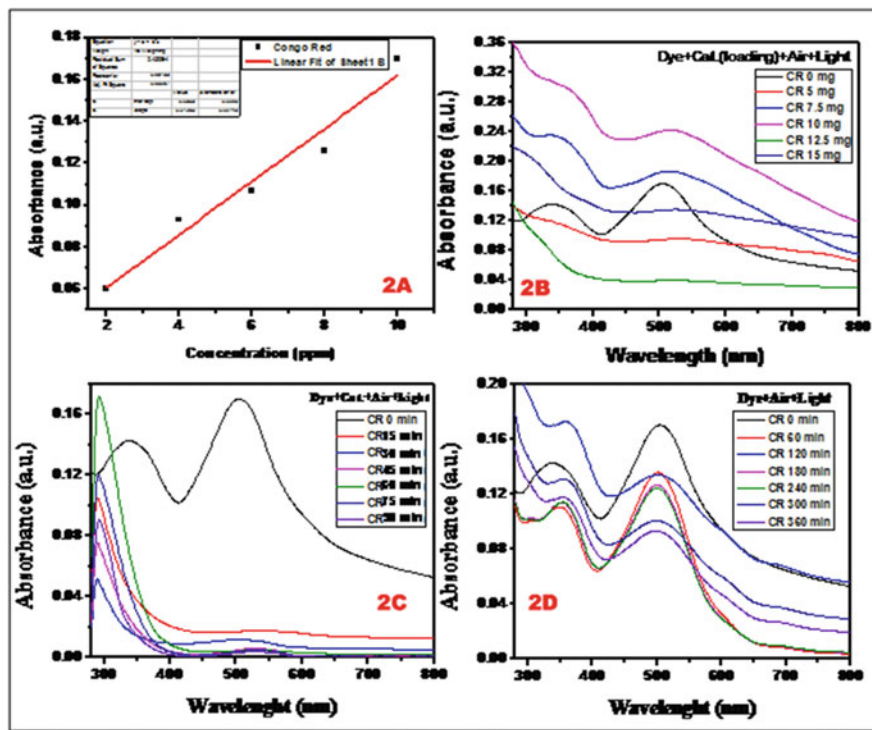


Fig. 12.5 Congo red, CR dye (A) R-square value, (B) catalyst loading, (C) time variation of 12.5 mg catalyst and atmospheric air, and (D) time variation of atmospheric air. (Carried out at pH of ~ 5 in the presence of 5 W LED light)

It was found from Table 12.4 as serial number 12 and Fig. 12.4, 1D that only 22.42% of methylene blue was degraded in 60 min without using catalyst, under atmospheric air irradiation. On the other hand, 46.78% degradation efficiency of methylene blue was obtained with 5 mg catalyst as shown in Table 12.4, serial number 1 and Fig. 12.4, 1B. The improvement in the degradation efficiencies was observed as 65.31% and 77.76% with higher catalyst loadings of 7.5 mg and 10 mg, respectively, as given in Table 12.4, serial numbers 2–3 and Fig. 12.4, 1B. Comparatively less improvement was observed in photodegradation of methylene blue with the catalyst loading above 10 mg as shown in Table 12.4, serial numbers 4–5, and Fig. 12.4, 1B. This implies that the photo-induced electrons and holes are produced at lesser rate with high catalyst loadings and leads to a limiting factor for degradation. Catalyst loading of 10 mg is found to be a better choice for the photodegradation of methylene blue.

The photodegradation of congo red using polymer-supported ionic liquid iron porphyrin with different amounts of catalyst at atmospheric temperature of 25 °C under simulated sunlight was studied as given in Table 12.5 from serial numbers 1–5 and Fig. 12.5, 2B. Without catalyst, 21% of congo red was only able to degrade

Table 12.4 Total optimum conditions of methylene blue dye degradation with or without polymer-supported ionic liquid Fe-porphyrin complex catalyst (10 ppm and 25 mL)

S. no.	Catalyst (ILPSFePc) (mg)	Air	Time (Min)	% Degradation
1	5	Atm.	60	46.78
2	7.5	Atm.	60	65.31
3	10	Atm.	60	77.76
4	12.5	Atm.	60	77.92
5	15	Atm.	60	78.11
6	10	Atm.	10	21.38
7	10	Atm.	20	27.31
8	10	Atm.	30	28.88
9	10	Atm.	40	30.69
10	10	Atm.	50	68.26
11	10	Atm.	60	78.09
12	–	Atm.	60	22.42
13	–	Atm.	120	30.45
14	–	Atm.	180	51.01
15	–	Atm.	240	54.34
16	–	Atm.	300	55.25
17	–	Atm.	360	56.15

Table 12.5 Optimization of parameters for degradation of congo red dye with or without polymer-supported ionic liquid Fe-porphyrin complex catalyst (25 mL of 10 ppm)

S. no.	Catalyst (ILPSFePc) (mg)	Air	Time (Min)	% Degradation
1	5	Atm.	60	41.7
2	7.5	Atm.	60	–8.41
3	10	Atm.	60	51.76
4	12.5	Atm.	60	76.05
5	15	Atm.	60	78.21
6	12.5	Atm.	15	41
7	12.5	Atm.	30	54.52
8	12.5	Atm.	45	68.05
9	12.5	Atm.	60	77.64
10	12.5	Atm.	75	98.82
11	12.5	Atm.	90	99.11
12	–	Atm.	60	21
13	–	Atm.	120	22.76
14	–	Atm.	180	25.88
15	–	Atm.	240	27.64
16	–	Atm.	300	41.17
17	–	Atm.	360	45.29

under atmospheric air irradiation in 60 min, whereas 41.7% removal was accomplished with 5 mg of catalyst as presented in Table 12.5 and Fig. 12.5, 2B. The increased removal was noticed at higher loadings of the catalyst, where -8.41% and 51.76% degradation were observed with catalyst loadings of 7.5 mg and 10 mg, respectively, as represented in Table 12.5, serial numbers 2–3, and Fig. 12.5, 2B. The negative value of degradation efficiencies may be attributed to the formation of few chromophore groups during the photodegradation. Similar findings were obtained by Kharazi et al. (2018); Khajone et al. (2019).

The rate of improvement was enhanced with 12.5 mg photocatalyst but found lesser thereafter, in serial numbers 4–5 of Table 12.5 and Fig. 12.5, 2B, which means that the photodegradation rate can be controlled by the production rate of photo-induced electrons and holes at these higher catalyst dosages. Next, the influence of duration was also influenced on photodegradation of congo red using the optimized catalyst loading of 12.5 mg in 25 mL at 10 ppm concentration. The progress in the degradation efficiencies was detected from 41% to 98.82% with respect to duration from 15 min to 75 min as presented in Table 12.5, s. no. 6–10. However, there was no appreciable enhancement with more duration, Table 12.5 at s. no. 11. It was found that there was no significant degradation in absence of photocatalyst as given in Table 12.5, s. no. 12–17.

12.6.3 Possible Mechanism

The possible mechanism of the dye degradation by polymer-supported ionic liquid iron porphyrin catalyst is given in Fig. 12.6. When exposed to replicated sunlight,

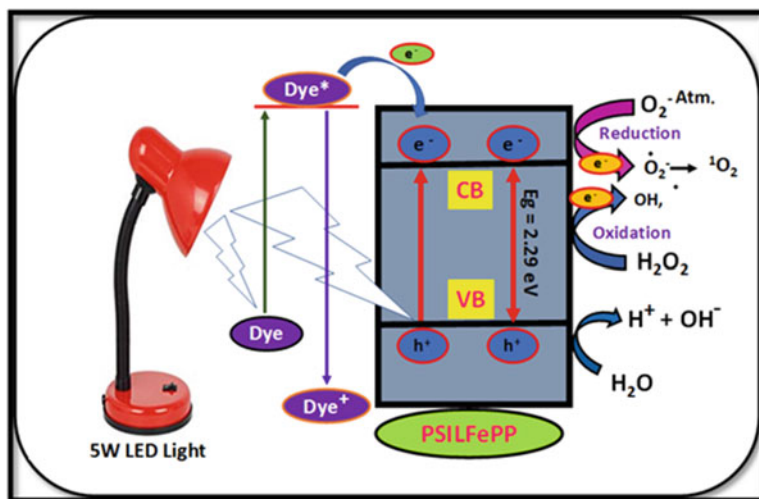
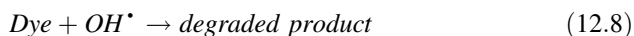
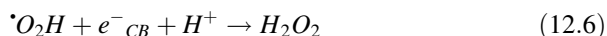
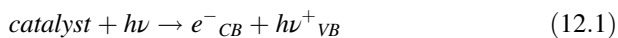


Fig. 12.6 Plausible mechanism for dye degradation by polymer-supported ionic liquid Fe-porphyrin complex (PSILFePP)

electrons could reduce O_2 to $O_2^{\cdot-}$ and the OH^- and OH^\cdot radicals could be formed with the photo-generated holes. More radicals are generated due to the higher separation efficacy of electron–hole pairs in the developed photocatalyst. These generated radicals such as $^\cdot OH$ and $O_2^{\cdot-}$ and 1O_2 were found to be responsible for the photodegradation of methylene blue and congo red. Equations (12.1, 12.2, 12.3, 12.4, 12.5, 12.6, 12.7, and 12.8) illustrate the creation of radicals.



12.7 Conclusions

This study presents the recent applications of functionalized ionic liquids for the removal of metal ions and different dyes. An up-to-date review of the recent articles is presented in the first part. Later, a case study focusing on the application of a polymer-supported ionic liquid Fe-porphyrin complex for the photodegradation of organic dyes, namely methylene blue and congo red, is presented. It was observed that a polymer-supported ionic liquid Fe-porphyrin complex could be effectively used for the removal of organic dyes. This may pave a way for the efficient removal of the organic pollutants from the wastewater.

Acknowledgments The authors acknowledge SIF DST-VITFIST, the SEM facility at SBST, and RGEMS (VIT, Vellore) for allowing them to use the analytical instruments.

References

- Archana V, Meera KM, Begum S, Anantharaman N (2016) Studies on removal of phenol using ionic liquid immobilized polymeric micro-capsules. *Arab J Chem* 9:371–382. <https://doi.org/10.1016/j.arabjc.2013.03.017>
- Balinge KR, Khiratkar AG, Bhagat PR (2017) Polymer supported Zn-salen complexes: an effective one-pot oxidative esterification of aldehydes to carboxylic esters. *J Mol Liq* 242:1085–1095. <https://doi.org/10.1016/j.molliq.2017.07.105>

- Balinge KR, Khiratkar AG, Muskawar PN, Thenmozhi K, Bhagat PR (2018) Facile access to polymer supported zinc–salen complex: highly efficient heterogeneous catalyst for synthesizing hydantoin, thiohydantoin and Schiff bases in aqueous medium. *Res Chem Intermed* 44:2075–2097. <https://doi.org/10.1007/s11164-017-3215-x>
- Boczkaj G, Fernandes A (2017) Wastewater treatment by means of advanced oxidation processes at basic pH conditions: a review. *Chem Eng J* 32:608–633. <https://doi.org/10.1016/j.cej.2017.03.084>
- Bollin PM, Viamajala S (2012) Reactive extraction of triglycerides as fatty acid methyl esters using Lewis acidic chloroaluminate ionic liquids. *Energy Fuels* 26:6411–6418. <https://doi.org/10.1021/ef301101d>
- Butler E, Hung YT, Yeh RL, Suleiman Al Ahmad M (2011) Electrocoagulation in wastewater treatment. *Water SA* 3:495–525. <https://doi.org/10.3390/w3020495>
- Dalvand A, Gholami M, Joneidi A, Mahmoodi NM (2011) Dye removal, energy consumption and operating cost of electrocoagulation of textile wastewater as a clean process. *Clean-Soil Air Water* 39:665–672. <https://doi.org/10.1002/clen.201000233>
- De Lima LB, Pereira LO, de Moura SG, Magalhães F (2017) Degradation of organic contaminants in effluents-synthetic and from the textile industry-by Fenton, photocatalysis, and H₂O₂ photolysis. *Environ Sci Pollut Res* 24(7):6299–6306. <https://doi.org/10.1007/s11356-016-6973-x>
- Dietz M (2006) Ionic liquids as extraction solvents: where do we stand? *Sep Sci Technol* 41:2047–2063. <https://doi.org/10.1080/01496390600743144>
- Domanska U, Rekawek A (2009) Extraction of metal ions from aqueous solutions using Imidazolium based ionic liquids. *J Solut Chem* 38:739–751. <https://doi.org/10.1007/s10953-009-9402-7>
- Du C, Xue Y, Wu Z (2017) Microwave-assisted one-step preparation of macadamia nut shell-based activated carbon for efficient adsorption of reactive blue. *New J Chem* 41:15373–15383. <https://doi.org/10.1039/C7NJ03208K>
- Egorov VM, Djigailo DI, Momotenko DS, Chernyshov DV, Torocheshnikova II, Smirnova SV, Pletnev IV (2010) Task-specific ionic liquid trioctylmethylammonium salicylate as extraction solvent for transition metal ions. *Talanta* 80(3):1177–1182. <https://doi.org/10.1016/j.talanta.2009.09.003>
- Fei Z, Zhao D, Geldbach TJ, Scopelliti R, Dyson PJ, Antonijevic S, Bodenhausen G (2005) *Angew Chem Int Ed* 44:5720. <https://doi.org/10.1002/anie.200500207>
- Fernández JF, Neumann J, Thöming J (2010) Regeneration, recovery and removal of ionic liquids. *Curr Org Chem* – in press, Alexander K (ed), (InTech) ISSN 1385-2728
- Ferreir AM, Coutinho JAP, Fernandes AM, Freire MG (2014) Complete removal of textile dyes from aqueous media using ionic-liquid-based aqueous two-phase systems. *Sep Purif Technol* 128:58–66. <https://doi.org/10.1016/j.seppur.2014.02.036>
- Fuerhacker M, Haile TM, Kogelnig D, Stojanovic A, Keppler B (2012) Application of ionic liquids for the removal of heavy metals from wastewater and activated sludge. *Water Sci Technol* 65(10):1765–1773. <https://doi.org/10.2166/wst.2012.907>
- Gao Y, Twamley B, Shreeve JM (2004) *Inorg Chem* 43:3406. <https://doi.org/10.1021/ic049961v>
- Gautam K, Kamsonlian S, Kumar S (2019) Removal of reactive black 5 dye from wastewater using electro-coagulation: equilibrium isotherms and kinetic study. *J Water Chem Technol*. <https://doi.org/10.1515/zpch-2017-1044>
- Han D, Row KH (2010) Recent applications of ionic liquids in separation technology. *Molecules* 15:2405–2426. <https://doi.org/10.3390/molecules15042405>
- Hao M, Zhiguo J, Kong J (2013) Hydrophobic poly(ionic liquid) for highly effective separation of methyl blue and chromium ions from water. *Polymers* 5:1203–1214. <https://doi.org/10.3390/polym5041203>
- Hayouni S, Robert A, Maes C, Conreux A, Marin B, Mohamadou A, Bouquillon S (2018) New dendritic ionic liquids (DILs) for the extraction of metallic species from water. *New J Chem* 42:18010–18020. <https://doi.org/10.1039/C8NJ01921E>

- Heintz A, Wertz C (2006) Ionic liquids: a most promising research field in solution chemistry and thermodynamics. *Pure Appl Chem* 78:1587–1593. <https://doi.org/10.1351/pac200678081587>
- Hernández-Fernández F, de los Ríos PJ, Mateo-Ramírez AF, Godínez C, Lozano-Blanco LJ, Moreno JJ, Tomás-Alonso F (2015) New application of supported ionic liquids membranes as proton exchange membranes in microbial fuel cell for waste water treatment. *Chem Eng J* 279:115–119. <https://doi.org/10.1016/j.cej.2015.04.036>
- Holkar CR, Jadhav AJ, Pinjari DV, Mahamuni NM, Pandit AB (2016) A critical review on textile wastewater treatments: possible approaches. *J Environ Manage* 182:351–366. <https://doi.org/10.1016/j.jenvman.2016.07.090>
- Khajone VB, Balinge KR, Patle DS, Bhagat PR (2019) Synthesis and characterization of polymer supported Fe-phthalocyanine entangled with carboxyl functionalized benzimidazolium moiety: a heterogeneous catalyst for efficient visible-light-driven degradation of organic dyes from aqueous solutions. *J Mol Liq* 288:111032. <https://doi.org/10.1016/j.molliq.2019.111032>
- Kharazi P, Rahimi R, Rabbani M (2018) Study on porphyrin/ZnFe₂O₄@polythiophene nanocomposite as a novel adsorbent and visible light driven photocatalyst for the removal of methylene blue and methyl orange. *Mater Res Bull* 103:133. <https://doi.org/10.1016/j.materresbull.2018.03.031>
- Khiratkar AG, Muskawar PN, Bhagat PR (2016) Polymer-supported benzimidazolium based ionic liquid: an efficient and reusable Brønsted acid catalyst for Biginelli reaction. *RSC Adv* 6:105087–105093. <https://doi.org/10.1039/C6RA23781A>
- Langhals H (2004) Color chemistry. Synthesis, properties and applications of organic dyes and pigments. By Heinrich Zollinger, Wiley Online Library. Liddle ST, Arnold PL *Organometallics*. 24, 2597 <https://doi.org/10.1002/anie.200385122>
- Liddle ST, Arnold PL (2005) Synthesis of heteroleptic cerium(III) anionic amido-tethered N-heterocyclic carbene complexes. *Organometallics*. 24:2597–2605. <https://doi.org/10.1021/om050061b>
- Mathews C, Bhosale VK, Kulkarni PS, Kamble SP (2019) Removal of phenol from organic system using ionic liquids. *Curr Environ Eng* 6:1. <https://doi.org/10.2174/2212717806666190408154507>
- Min KS, Kumar RS, Lee JH, Kim KS, Lee SG, Son YA (2019) Synthesis of new TiO₂/porphyrin-based composites and photocatalytic studies on methylene blue degradation. *Dyes Pigments* 160:37–47. <https://doi.org/10.1016/j.dyepig.2018.07.045>
- Muskawar PN, Kumar SS, Bhagat PR (2013) Carboxyl-functionalized ionic liquids based on Benzimidazolium cation: study of Hammett values and catalytic activity towards one-pot synthesis of 1-amidoalkyl naphthols. *J Mol Liq* 380:112–117. <https://doi.org/10.1016/j.molcata.2013.09.026>
- Oller I, Malato S, Sa'nchez-Pe'rez JA (2011) Combination of advanced oxidation processes and biological treatments for wastewater decontamination-a review. *Sci Total Environ* 409:4141–4166. <https://doi.org/10.1016/j.scitotenv.2010.08.061>
- Pandey S (2006) Analytical applications of room-temperature ionic liquids: a review of recent efforts. *Anal Chim Acta* 556:38–45. <https://doi.org/10.1016/j.aca.2005.06.038>
- Park H, Shamim AH, Nallal M, Park S, Park KH (2019) Synthesis of silver nanostructures in ionic liquid media and their application to photodegradation of methyl orange. *Nanomater Nanotech* 9:1–9. <https://doi.org/10.1177/1847980419836500>
- Patel DD, Lee JM (2012) Applications of ionic liquids. *Chem Rec* 12:329–355. <https://doi.org/10.1002/tcr.201100036>
- Pei YC, Wang JJ, Xuan XP, Fan J, Fan M (2007) Factors affecting ionic liquids based removal of anionic dyes from water. *Environ Sci Technol* 41:5090–5095. <https://doi.org/10.1021/es062838d>
- Pilli SR, Mohanty K, Banerjee T (2014) Extraction of Phthalic Acid from Aqueous Solution by Using Ionic Liquids: A Quantum Chemical Approach. *International Journal of Thermodynamics* 17(1):42–51. <https://doi.org/10.5541/ijot.482>

- Qi L, Yu J, Jaroniec M (2013) Enhanced and suppressed effects of ionic liquid on the photocatalytic activity of TiO₂. *Adsorption* 19:557–561. <https://doi.org/10.1007/s10450-013-9478-7>
- Rabbani M, Heidari-Golafzani M, Rahimi R (2016) Synthesis of TCP/PP/ZnFe₂O₄@ZnO nanohollow sphere composite for degradation of methylene blue and 4-nitrophenol under visible light. *Mater Chem Phys* 179:35–41. <https://doi.org/10.1016/j.matchemphys.2016.05.005>
- Ravishankar TN, Sureshkumar K, Dupont J, Ramakrishnappa T, Nagaraju G (2015) Ionic liquid-assisted hydrothermal synthesis of TiO₂ nanoparticles and its applications towards the photocatalytic activity and electrochemical sensor. *J Exp Nanosci* 10. <https://doi.org/10.1080/17458080.2015.1014870>
- Regel-Rosocka M, Wisniewski M (2011) Ionic liquids in separation of metal ions from aqueous solutions, applications of ionic liquids in science and technology, Prof. Scott Handy (ed), (InTech) ISBN: 978-953-307-605-8. <https://doi.org/10.5772/23909>
- Rodríguez CB, Rodríguez PI, Corchero R, Rodil R, Rodil E, Arce A, Soto A (2017) Photocatalytic degradation of methyl orange, methylene blue and rhodamine B with AgCl nanocatalyst synthesised from its bulk material in the ionic liquid [P6 6 6 14]Cl. *Water Sci Technol* 75 (1–2):128–140. <https://doi.org/10.2166/wst.2016.499>
- Saleem S, Saqib ANS, Mujahid A, Hanif M, Mustafa G, Mahmood T, Waseem A, Khan AR (2014) Extraction of Pb(II) from water samples by ionic liquid-modified silica sorbents. *Desalin Water Treat* 52:40–42. <https://doi.org/10.1080/19443994.2014.922497>
- Sergi D, Gemma E, Claudia F (2019) System for mercury preconcentration in natural waters based on a polymer inclusion membrane incorporating an ionic liquid. *Journal of Hazardous Materials* 371:316–322. <https://doi.org/10.1016/j.jhazmat.2019.03.017>
- Shankar M, Sekaran G, Sadullah S, Ramasami T (1999) *J Chem Tech Biotechnol* 74:337. [https://doi.org/10.1002/\(SICI\)1097-4660\(199904\)74:4<337::AID-JCTB39>3.0.CO;2-U](https://doi.org/10.1002/(SICI)1097-4660(199904)74:4<337::AID-JCTB39>3.0.CO;2-U)
- Sun P, Armstrong DW (2010) Ionic liquids in analytical chemistry. *Anal Chim Acta* 661:1–16. <https://doi.org/10.1016/j.aca.2009.12.007>
- Vaghela SS, Jethva AD, Mehta BR, Dave SP, Ramachandria G (2005) *Environ Sci Technol* 39:2848. <https://doi.org/10.1021/es035370c>
- van Rantwijk F, Madeira LR, Sheldon RA (2003) Biocatalytic transformations in ionic liquids. *Trends Biotechnol* 21. [https://doi.org/10.1016/S0167-7799\(03\)00008-8](https://doi.org/10.1016/S0167-7799(03)00008-8)
- Wasserscheid P, Keim W (2000) Ionic liquids: new “solutions” for transition metal catalysis. *Angew Chem Int Ed* 39:3772–3789. [https://doi.org/10.1002/1521-3773\(20001103\)39:21<3772::AID-ANIE3772>3.0.CO;2-5](https://doi.org/10.1002/1521-3773(20001103)39:21<3772::AID-ANIE3772>3.0.CO;2-5)
- Wilkes JS (2002) A short history of ionic liquids—from molten salts to neoteric solvents. *Green Chem* 4:73–80. <https://doi.org/10.1039/b110838g>
- Ye C, Shreeve JM (2004) *J Org Chem* 69:8561. <https://doi.org/10.1021/jo048383x>
- Zhao D (2007) Design, synthesis and applications of functionalized ionic liquids, (Thesis) M.Sc. in Chemistry, Xinan Petroleum University, Nanchong, China et de nationalité chinoise. <https://doi.org/10.5075/epfl-thesis-3531>