Liquid–Liquid Extraction of Indicator Dyes into Imidazolium based Ionic Liquids

A Dissertation

submitted in partial fulfilment of the requirement
for the award of degree of

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In
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Submitted By:
SUCHITA MAHAJAN
(Reg. No. 601301013)

Under Supervision of:

Dr. Neetu Singh
Assistant Professor (CHED)

Dr. Anita Rajor
Associate Professor (SEE)

School of Energy and Environment
Thapar University, Patiala– 147004
Punjab, India
July 2015

DECLARATION

I, the undersigned, hereby declare that the research work presented in the M.tech project entitled **"Liquid–Liquid Extraction of Indicator Dyes into Imidazolium based Ionic Liquids"** has been carried out by me under the supervision and guidance of Dr. Neetu Singh, Assistant Professor, Chemical Engineering Department and Dr. Anita Rajor, Associate Professor, School of Energy and Environment, Thapar University, Patiala.

Further, I declare that no part of this dissertation has been submitted for a degree or any other qualification of any other university or examining body in India/elsewhere.

Suchita Mahajan

Suchita Mahajan

(Reg. No. 601301013)

M.tech – Environmental Science and Technology

Thapar University

Patiala

CERTIFICATE

This is to certify that the thesis entitled **"Liquid–Liquid Extraction of Indicator Dyes into Imidazolium based Ionic Liquids"**, submitted by Suchita Mahajan in partial fulfillment of the requirements for the award of degree of Master of Technology in Environmental Science and Technology, Thapar University, Patiala is an authentic work carried out by her under our supervision and guidance. To the best of our knowledge, the matter embodied in this thesis has not been submitted to any other university/institute for the award of any degree/diploma.

16/7/15

Dr. Neetu Singh
Assistant Professor
Department of Chemical Engineering,
Thapar University, Patiala

Dr. Anita Rajor
Associate Professor
School of Energy and Environment,
Thapar University, Patiala

Countersigned by:

Dr. A. S. Reddy
Head
School of Energy and Environment,
Thapar University, Patiala

Dr. S.S Bhatia
Dean of Academic Affairs
Thapar University, Patiala

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ABSTRACT

Dyed wastewater, generated by textile industries is one of the main current issues contributing to water pollution. This is due to the consumption of large amounts of dyes, textile auxiliaries and chemicals thereby discharging high volumes of polluted water containing trace metals such as Cr, As, Cu and Zn, which are capable of harming the human health and environment. The wastewaters originating from dyeing processes are generally characterized by the high content of color caused by the dyestuffs; salts; chemical oxygen demand (COD) deriving from additives such as acetic acid, detergents and complexing agents; suspended solids including fibers; high temperature and broadly fluctuating pH. Various researches have been carried out the treatment of these dyed effluents keeping in mind their harmful effects towards the environment and aquatic biota. Dye removal using Ionic Liquid (IL) is one such technique, which is still not employed on an industrial scale but has been found to be a capable dye extracting agent from textile wastewater. Since the potential of Ionic Liquid for this application is still at surface level, the major economic concerns such as process efficiency and improvement in the amount of dye removed with minimal usage of Ionic Liquid has also been kept in mind.

In the present work, a novel process, Ionic Liquid–Based Dispersive Liquid–Liquid Extraction (IL–DLLE) has been adapted for the removal of anionic (Eriochrome black T & Methyl orange) and cationic (Crystal violet & Malachite green) indicator dyes namely from aqueous solution. Three Imidazolium based Ionic Liquids ($[C_6mim][PF_6]$), ($[C_6mim][BF_4]$) and ($[C_4mim][PF_6]$) have been used for this purpose. High extraction efficiencies were observed for anionic dyes using $[C_6mim][BF_4]$ IL while $[C_4mim][PF_6]$ IL showed best results for cationic dyes. Out of all the studied dyes, maximum and minimum extraction efficiencies were obtained for Eriochrome black T and Methyl orange respectively.

To make the process economical, used IL was regenerated by Reverse Dispersive Liquid–Liquid Extraction process. Two acid stripping solutions were employed for this purpose. The IL was successfully regenerated from the IL+ dye mixture and re-used for the extraction of fresh dye solutions. The regenerated ILs also resulted in high extraction efficiencies for all the dyes studied. On the basis of these results, IL–DLLE was found to be an efficient, simple, economical and fast method for dye extraction.

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CHAPTER 1: INTRODUCTION

1.1Background of Study and its importance

Water is one of the most essential natural resource, unfortunately exploited the most by human being. The key reasons being increased human population, increased living standards, rapid industrialization, and urbanization. Today, approximately half of the available water is being used for domestic purposes, and the other half is consumed by the industrial and agricultural activities. Due to the unrestricted and excessive exploitation of water, today the whole world is facing water crisis. In addition to fresh water shortage, industrial activities lead to the most severe environmental pollution problems via discharge of wastewaters into the receiving water bodies. Although treatment of these wastewaters before discharging is obligatory by the relevant environmental protection legislations, all the industrial facilities in the world do not have treatment plants nor do the existing ones have adequate treatment efficiencies [1]. As a result, the water quality in the receiving environments is rapidly deteriorating. The shortage of water supplies also forces the industrialists to pay even more for their fresh water consumption and wastewater generation. All these facts force the industrialists to consider the recovery and reuse of their wastewaters, at least to a certain extent.

Water pollution due to color dyestuff industries is a topic of major concern today. Many industries use dyes extensively in different operations such as manufacturing of leather, textile, plastic, paper etc., and is posing serious ecological problems. Besides contributing significantly to many national economiesand providing employment with no required special skills, textile industries have proven themselves as threat to the water bodies due to the consumption of large quantities of water and generation of large volumes of wastewater from different steps in the dyeing and finishing processes in a symmetrical manner. Moreover the dyes used in textile industry are important sources of environmental pollution.

1.2 Textile industry and wastewater generation

1.2.1 Textile Industry

The fragmented and heterogeneous character of textile industries makes them one of the most complicated manufacturing industries. These industries consume a large quantity of chemicals, water and in turn generate large volumes of wastewater from different processes. The chemical reagents utilized are very diverse in their chemical composition, ranging from inorganic compounds to polymers and organic products.

Depending upon the used raw materials, textile industry can be classified into three categories viz., cotton, woolen, and synthetic fibers (polyester, acrylics). As shown in **Fig. 1.2.1**, the textile industry consists of a number of processes employed for converting fibers of natural origin such as cotton, silk and wool, and of synthetic origin such as nylon; first into fabrics by weaving and knitting and then into the final products by applying wet processes such as dyeing, sizing, printing, and finishing. The Cotton textile industry is one of the oldest industries in India (started in 1854, Bombay). Cotton, which is the world's most widely used fiber, is also the substrate that requires the most water in its processing. The dyeing of one kilogram of cotton with reactive dyes demands 70 to 150 L water, 0.6 to 0.8 kg NaCl and around 30–60 g dyestuff [2]. The main environmental impact comes from wet processes of the industry.

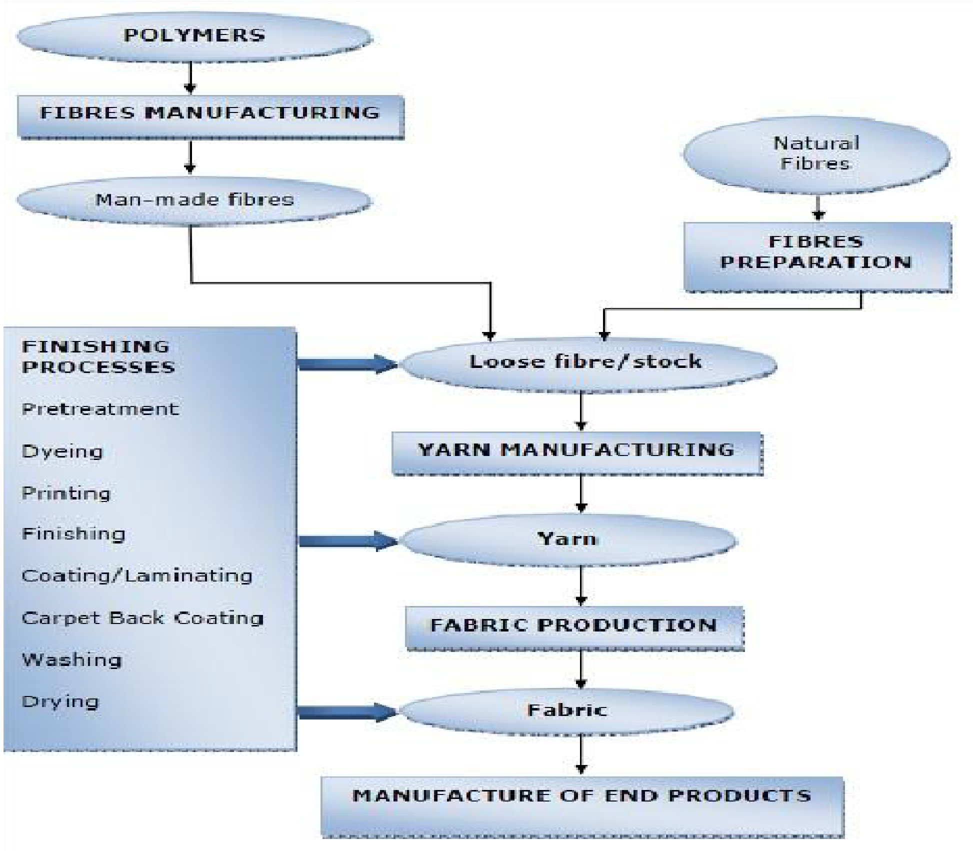


Fig. 1.2.1: Layout of processes in the textile industry **(Sources of pollution, prevention and abatement: textile industry)**

Wastewater from printing and dyeing units is often rich in color, containing residues of reactive dyes and chemicals, such as complex components,many aerosols,various waste chemical pollutants such as sizing agents, wetting agents, complexing agents, dyes, pigments, softening agents, stiffening agents, fluorocarbon, surfactants, oils, wax and many other additives which are used throughout the processes. These pollutants contribute to high suspended solids (SS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), heat, color, acidity, alkalinity and much more hard-degradation materialswhich cause aesthetic as well as other health problems to the surrounding ecosystem. The toxic effects of dyestuffs and other organic compounds, as well as acidic and alkaline contaminants, from industrial establishments on the general public are widely accepted. At present, the dyes are mainly aromatic and heterocyclic compounds, with colordisplay groups and polar groups. The structure is more complicated and stable, resulting in greater difficulty to degrade the printing and dyeing wastewater.

Indian cities produce nearly 40,000 million liters of sewage every day and barely 20 percent of it is treated, according to "Excreta Does Matter", a new report released by the Centre for Science and Environment (CSE)[3]."The untreated waste dumped into rivers seeps into groundwater, thereby creating a ticking health bomb in India," concludes the report[3]. Weak or non-existent enforcement of environmental laws, rapid urban development and a lack of awareness about the dangers of sewage are all blamed for water pollution. "Untreated sewage is killing Indian rivers," the report stated[3]. A 2011 survey by the Central Pollution Control Board (CPCB) revealed only 160 out of nearly 8,000 towns had both sewerage systems and a sewage treatment plant [4]. Therefore, understanding and developing effective printing-dye industrial wastewater treatment technology is environmentally important [4]. Taking the example of wool, silk, jute and cotton industries i.e., Reliance Industries, Allahabad (man-made fiber); Shri Lakshmi Cotsyn Ltd., Fatehpur and A.R. Polymers, Fatehpur, the Ganges River located nearby has been receiving approximately one million m^3 per day of untreated dyed wastewater per day from these textile units. This river water, which was once known for its economic, social, cultural and religious values, and was a potential source of water for agriculture, aquaculture, hydro-power generation, industry, and household consumption, has consequently turned reddish and bluish in color due to the presence of dyed effluents like Arsenic and Chromium(**Fig. 1.2.2**) which carry significant health risks for humans, as well as environmental risks for the sustainability of the ecosystem services provided by the Ganga. Ganga Action Plan (GAP) was one of the proposals suggested to reduce the amount of untreated raw sewage deposited in the Gangariver[5].

Fig. 1.2.2: Pollution due to dyed effluents, Arsenic and Chromium in the Ganga river nearby Allahabad, India

Textile industries typically generate 200–500 L of wastewater per kg of finished product [6]. In order to reduce water consumption, wastewater treatment is necessary for water reuse in the textile industries [7]. Different techniques currently used for the treatment of textile effluents are based on carbon adsorption, membrane separation, chemical precipitation, photo degradation, biodegradation and electrolytic chemical treatment. The merits and demerits of the current methods of dye removal from industrial effluents are listed in the**Table1.2.1**.[8].

Table1.2.1: Merits and demerits of the current methods of dye removal from industrial effluents

Physical/chemical/biological methods	**Merits**	**Demerits**
Fentons reagent	Effective decolorization of both soluble and insoluble dyes.	Sludge generation
Ozonation	Applied in gaseous state: no alteration of volume	Short half-life (20 min)
Photochemical	No sludge production	Formation of by-products
NaOCl	Initiates and accelerates azo-bond cleavage	Release of aromatic amines
Electrochemical destruction	Breakdown compounds are non-hazardous	High cost of electricity
Activated carbon	Good removal of wide variety of dyes	Very expensive
Membrane filtration	Removes all dye types	Concentrated sludge production
Ion exchange	Regeneration: no adsorbent loss	Not effective for all dyes
Irradiation	Effective oxidation at lab scale	Requires a lot of dissolved O_2
Electrokinetic coagulation	Economically feasible	High sludge production
Activated sludge process	High efficiency in COD removal	Incomplete color elimination, bulking problems

According to “The Environment (Protection) Rules”, 1986,the standards for effluents from textile wastewater are listed in **Table1.2.2**.

Table 1.2.2: Standards for effluents from Textile Industry (CPCB)

Parameter	Concentration (mg/L) not to exceed, except pH
pH	5.5 – 9.0
Total suspended solids	100
Bio-chemical oxygen demand (BOD)	30
Chemical oxygen demand (COD)	250
Total residual chlorine	1
Oil and grease	10
Total chromium as Cr	2
Sulphide as S	2
Phenolic compounds as C_6H_5OH	1

- Where the treated effluent is discharged into municipal sewer leading to terminal treatment plant, the BOD may be relaxed to 100 mg/L and COD to 400 mg/L.
- The quantity of effluent (liter per kilogram of product) shall not exceed 100, 250 and 80 in composite cotton textile industry, composite woolen textile industry and textile processing industry, respectively (CPCB).

1.2.2 Overview of Textile Processes

Textile industries receive and prepare fibers, transform fibers into yarn, thread, or webbing; convert the yarn into fabric or related products; and dye and finish these materials at various stages of production. Textile processing industries include pre-treatment (desizing, scouring, bleaching, mercerizing, washing) drying, dyeing, printing and finishing processes. A schematic overview of Cotton fabric production in Indiais shown in **Fig. 1.2.3**[9].

1.2.3 Different Types of Processes in Textile Processing Industries

Desizing: Sizing applied to warp yarns prior to weaving or warp knitting by the slashing process must be removed prior to dyeing or finishing assuring even and uniform application of the dye or finish. Sizes can consist of starches, modified starches, and adhesives based on synthetic organic polymers. Starches and modified starches may generally be removed by dilute acid or enzyme treatment, whereas synthetic adhesive sizes can be removed by specialized short washing treatments.

Bleaching: It involves elimination of unwanted color from textiles. These are three processes: sodium hypochlorite bleaching; hydrogen peroxide bleaching and sodium chlorite bleaching. Hypochlorite is one of the oldest industrial bleaching agents. For bleaching, textiles are soaked with bleaching agents and then temperature is raised to the recommended levels. Then the textiles are thoroughly washed and dried.

Mercerization: It is carried out by treating cotton material with a strong solution of sodium hydroxide (about 18–24%) and washing-off the caustic after 1 to 3 min, while holding the material under tension. Cotton is known to undergo a longitudinal shrinkage upon impregnation with this solution. This process provides luster and strength to textiles.

Dyeing: It is the treatment of fiber or fabric with chemical pigments/dyes to impart color. In this process, water is used to transfer dyes and in the form of steam to heat the treatment baths. Cotton, which is the world’s most widely used fiber, is a substrate that requires a large amount of water for processing.

Drying: The purpose of drying process is to reduce or eliminate the water content of the yarns or fabrics after wet processes applied in dyeing. In the textile mill, drying process is applied via contact driers at a temperature of 140° C in order to reduce the water content of the rope from 68% to 78%.

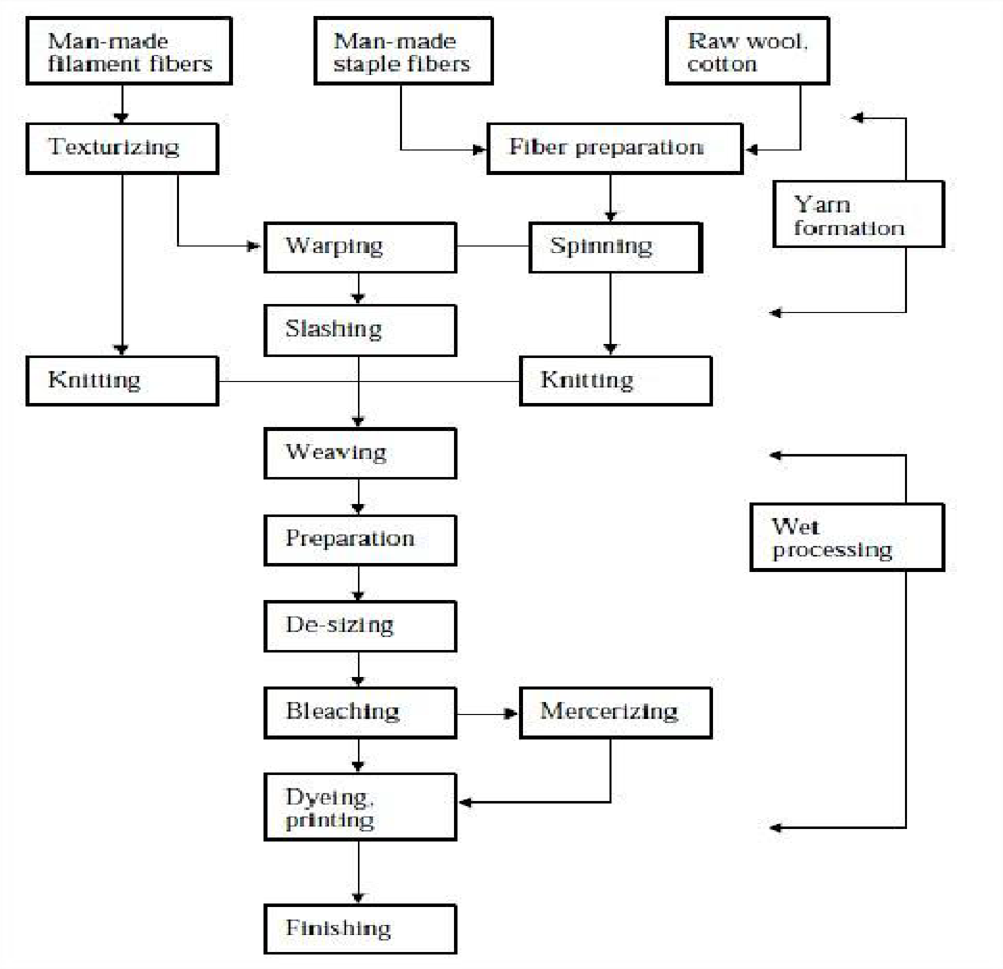


Fig. 1.2.3: Schematic overview of Cotton fabric production in India

According to the dyeing properties, the dye classes are acid, basic, direct, disperse, mordant,reactive, sulfur and vat dyes (**Table 1.2.3**). Each dye class is suitable to a specific type of fiber and hence the fixation rate of each class of dye is different.

Printing: It is generally defined as 'localized dyeing,' i.e., dyeing that is confined to certain portion of the fabric that constitutes the design. It is a form of dyeing in which the essential reactions involved are the same as those in dyeing. In dyeing, color is applied in the form of a solution, whereas in printing, color is applied in the form of a thick paste of the dyes.

Finishing: Both natural and synthetic textiles are subjected to a variety of finishing processes. This is done to improve specific properties in the finished fabric and involves the use of a large number of finishing agents for softening, cross-linking, and waterproofing. All of the finishing processes contribute to water pollution. Among the products that are used in textile finishing, the most ecologically friendly ones are formaldehyde-based cross-linking agents that bestow desired properties, such as softness and stiffness that impart bulk and drape properties, smoothness, and handle, to cellulosic textiles.

Table1.2.3: Different dye classes with respective fibers

Dye class	**Fibers**
Acid	Wool and nylon
Azoic	Cotton and other cellulosic
Basic	Acrylic
Direct	Cotton and other cellulosic
Dispersive	Polyester, other synthetics
Reactive	Cotton and other cellulosic
Mordant	Natural fibers after pretreating with metals
Sulphur	Cotton and other cellulosic
Vat	Cotton and other cellulosic

1.2.4 Wastewater generated in textile operations

Parameters such as Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), Suspended Solids (SS) and pH exhibit varying levels throughout the dyeing and washing processes, resulting in wastewater generation from several points.**Table 1.2.4** presents sources and nature of textile effluents at various stages of processing in India [10].

Table1.2.4: Sources and nature of textile effluents at various stages of processing in India

Process	Possible Pollutants	Nature of Effluent
Fiber preparation	-	Little or no wastewater generated
Desizing	Starch, glucose, PVA, resins, fats and waxes do not exert a high BOD.	Very small volume, high BOD and (30-50% of total), PVA.
Kiering	Caustic soda, waxes, soda ash, sodium silicate and fragments of cloth.	Very small, strongly alkaline, dark color, high BODvalues (30% of total).
Bleaching	Hypochlorite, chlorine, caustic soda, hydrogen peroxide, acids.	Small volume, strongly alkaline, low BOD (5% of total).
Mercerizing	Caustic soda	Small volume, strongly alkaline, low BOD (Less than 1% of total).
Dyeing	Dye stuff, mordant and reducing agents like sulphides, acetic acids and soap.	Large volume, strongly colored, fairly high BOD (6% of total).
Printing	Dye, starch, gum oil, china clay, mordants, acids and metallic salts.	Very small volume, oily appearances, fairly high BOD.
Finishing	Traces of starch, tallow, salts, special finishes, etc.	Very small volume, less alkaline, low BOD and COD.
Product fabrication	-	Little or no wastewater generated

PVA – Poly Vinyl Alcohol
BOD – Biological Oxygen Demand
COD – Chemical Oxygen Demand

1.3 Problem Statement

Since only a 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, Ionic Liquids technology for the removal of such effluent still remains unrecognized by many dyeconsuming industries which are presently applying the numerous available technologies for dye removal.

In the present work, Ionic Liquid–based Dispersive Liquid–Liquid extraction (IL–DLLE) method will be used to determine its effectiveness in removal of Indicator dyes from aqueous solutions.In this research work, several parameters such as initial dye concentration, amount and type of Ionic Liquid, salt concentration, dispersing agent concentration, type of stripping solution and pH have been selected to observe their effects on percentage dye extraction efficiency.

Since the recovered Ionic Liquids can be again reused for dye removal purpose, studies on their regeneration after dye removal will also be taken into account so that the process can be economically viable for many dye consuming industries.

1.4 Aim and Objectives

The aim of this research work is to investigate the performance of Imidazolium based Ionic Liquids for removal of indicator dyes by taking various important parametersinto consideration, and regenerate the used Ionic Liquid for further use to make the process economical.

Objectives: The main objectives in this study are as follows:

1. To extract the indicator dyes; Crystal violet, Methyl orange, Eriochrome black T and Malachite green from aqueous solutions using Ionic Liquid–based Dispersive Liquid–Liquid Extraction (IL–DLLE) method.
2. To study the effects of initial dye concentration, amount and type of Ionic Liquid, salt concentration, dispersing agent concentration, type of stripping solution and pHon the extraction efficiency of these dyes.
3. Toregenerate the Ionic Liquid by applying a Reverse Dispersive Liquid–Liquid Extraction method using acid stripping solutions.
4. To compare the performance of different acid stripping solutions in IL regeneration.

1.5 Scope of study

The scope of this study is based on the objectives mentioned above and is further elaborated as follows:

1. Since the Indicator dyes are sensitive towards pH and temperature variation, therefore Ionic Liquid–Based Dispersive Liquid–Liquid Extraction (IL–DLLE) is performed at a neutral pH i.e. 7 and at room temperature($25\pm2^{\circ}$C) [11].
2. The concentration of dye to be investigated in this research is between 30–250 ppm which is the average range of dye concentration found in the wastewater effluent ofcurrent dye consuming industries [12, 13]. The linear calibration curve is also obtained by preparing stock solution lying within the above range.
3. The method employed is Ionic Liquid–based Dispersive Liquid–Liquid Extraction (IL–DLLE) [11]. Its principle and details of experimental setup is explained further. In this

method, Ionic Liquid works as an “Extraction solvent” and plays the key role in dye extraction. The literature survey of thisroom temperature, highly viscous and environmentally benign “Designer organic solvents” has been detailed further.

4. The Buffer solution employed in the experiments, serves the purpose of keeping the pH neutral. On the other hand, Acetone plays an important role in separating out the dye molecules from aqueous solution by acting as a “Disperser solvent” thus allowing their easy extraction by Ionic Liquid.
5. Since the indicator dyes are frequently present along with different salts in the actual textile dye bath effluent streams, therefore thesalt concentration is varied, so that its effect on the extraction efficiency of these dyes can be studied.
6. As explained earlier regarding the pH sensitivity of indicator dyes, to investigate its effects on the extraction efficiency, a pH range from 2 to 12 is selected for this study.
7. The process is madeeconomical by regenerating Ionic Liquid through Reverse Dispersive Liquid–Liquid Extraction methodby using acid stripping solutionsto ensure its reuse.
8. Lastly, the performance of different acid stripping solutions is compared to check their regenerating ability.

CHAPTER 2: LITERATURE REVIEW

2.1 Prevalence and hazards of dyes in wastewater

The production of dye-containing wastewater is increasing rapidly with the increase in size of textile mills, so as to meet the demands of growing population. As per the survey done in 2012, about 100,000 different dyes showed worldwide existence, and between 700,000 and 1,000,000 tons were produced annually [14]. Reports suggest that only 10% of all dyes are utilized in food, printing and plastics, while the rest (90%) is consumed by the textile industries. On an annual basis, approximately 2,80,000 tons of textile dyes are discharged through wastewater worldwide.Asia generates its greatest amounts, with China being the largest producer [14].

Dyes are the organic compounds, that include two important groups chromophore and auxochrome as depicted in **Fig. 2.1**. The structure of chromophore provides color to the dye. It is composed of a delocalized electron cloud and conjugated double bonds. Azo groups (double-bonded nitrogen's), cyano groups, double-bonded carbons and carbonyl groups are some of its typical structures. The dye gets its color intensityfrom the second group; auxochrome. Sulfates, amines, hydroxyl group and carboxylic acid are some of the examples of this electron-donating group. Among all dyes, Azo dyes accounts for about 65-70% of the total production and a wide majority of these dyes are employed in textile industries [15]. Due to their poor biodegradability and ability to form carcinogenic aromatic amines under certain conditions, these dyes are coming in limelight of many research studies from the past few years.

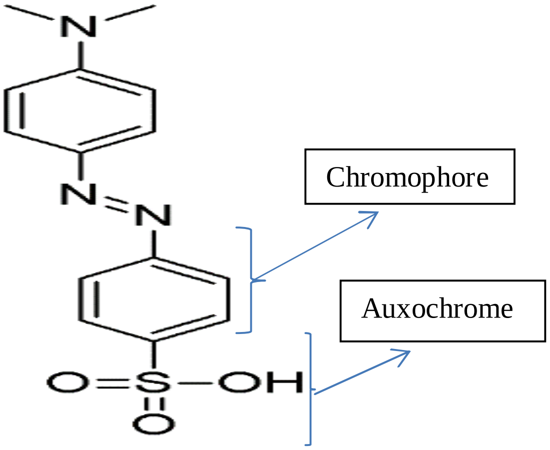


Fig.2.1: Chromophore and Auxochrome structures in Methyl orange

Textile wastewater if left untreated, leads to the increase in Total Organic Carbon (TOC), Suspended Solids (SS), Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand, Toxicity and Turbidity content. The first four factors are usually used for wastewater characterization and establishing regulatory levels. The presence of turbidity directly affects the aquatic ecosystem by making the water cloudy, thus blocking the sunlight, thereby inhibiting the photosynthetic activity of aquatic flora [14]. Along with the aquatic ecosystem, a wide range of organisms from bacteria to humans are also affected due to the toxicity caused by the maximum number of dyes. For instance, in 1998, the dyes used in synthetic food colors in India were carefully inspected by researchers Bhat and Mathur [16]. They were not only shocked to expose the potentially hazardous nature of the "safe" dyes, but also got stunned while revealing the fact that many food producing factories used the dyes reserved for textiles. These so-called "safe" textile dyes can seriously cause a large range of allergic reactions and thyroid tumors, thus infecting nearly all systems and organs including liver, kidneys, stomach, heart, spleen, lungs, red blood cells, bones, ovaries, and testes. Since natural colors are inconsistent, readily decomposable, costly, difficult to obtain and possess diverse unpleasant odors, the use of synthetic dyes has become an unfortunate necessity [16]. Thus, some important rules and regulations were put into practice for the companies which continued using these cheap and readily available synthetic dyes.

The wastewater standards and regulations set by the government vary to a great extent among different countries and regions. A research, which compared regulations from China, Germany, and the United States, stated that, among all three, China possessed the strictest and numerous norms, including setting up of limits for existing as well as new factories [4].Also, while United States has three sets of standards (one for printing, second for fabric printing and third for yarn printing), Germany possesses only a single set of it. Moreover, the limits for regulation also vary. For instance, the maximum allowable COD (chemical oxygen demand) limit in China is 80 mg/L, while in Germany it is 160 mg/L regardless of a factory, and in United States it is1.63×10^{-4}mg/ton of fabric. Such fluctuations in standards and regulations often cause hindrance in the work of people involved in research and import export of goods [4]. Nevertheless, these regulations indicate the need for treating wastewater before it is discharged into the ecosystem. The acceptable dyes or colors standard allowed in the water resources of Malaysia is less than 150 TCU (True Unit Color) according to the Interim National Water Quality Standards. **Table 2.1** below shows the Characteristics of typical untreated Textile Wastewater of Tirupur, Tamil Naduprovided by CPCB (Central Pollution Control Board), Ministry of Environment and Forests, (Govt. of India) [10].

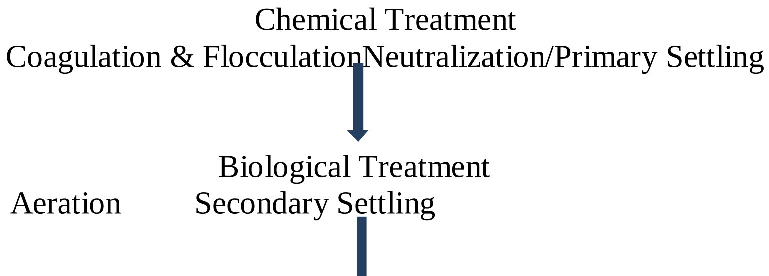
Table 2.1: Characteristics of typical untreated textile wastewater of Tirupur, Tamil Nadu

Parameter	**Range**
pH	6–10
Temperature (°C)	35–45
BOD (mg/L)	80–6,000
COD (mg/L)	150–12,000
Total dissolved solids (mg/L)	8,000–12,000
Total suspended solids (mg/L)	15–8,000
Total Dissolved Solids (mg/L)	2,900–3,100
Chlorine (mg/L)	1,000–6,000
Free chlorine (mg/L)	<10
Sodium (mg/L)	70%
Trace elements (mg/L)	–
Fe	<10
Zn	<10
Cu	<10

As	<10
Ni	<10
B	<10
F	<10
Mn	<10
V	<10
Hg	<10
PO_4	<10
Cn	<10
Oil & grease (mg/L)	10–30
TNK (mg/L)	10–30
NO_3 -N (mg/L)	<5
Free ammonia (mg/L)	<10
SO_4 (mg/L)	600–1000
Silica (mg/L)	<15
Total Kjeldahl Nitrogen (mg/L)	70–80
Color (Pt-Co)	50–2,500

2.2 Current Technologies involved in the Treatment of Textile Wastewater

Most researchers and manufacturers agree with the fact that a combination of various treatment processes is necessary for satisfactory removal of effluents. These processes are categorized as Physical, Biological and Chemical. According to a recent research, an ideal combination would imply a chemical treatment coupled with a physical treatment, followed by a biological treatment, and finally a physical treatment as a “polishing” step (**Fig.2.2.1**)[14].



Physical Treatment
Neutralization Activated Carbon Filter

Fig. 2.2.1: Schematic overview of a Wastewater Treatment Plant

2.2.1 Physical Treatment

Physical treatments are mainly responsible for the separation of components such as dyes, solids and charged particles in textile wastewater. Filtration, Adsorption and Ion-exchange are the three most important physical modes of separation. Adsorption implies adherence of soluble substances on an interface (e.g., Activated carbon). Despite having high abrasion resistance, thermal stability, small pore-diameters, capacity to produce a high quality treated effluent, high flexibility & design simplicity, ease of operation, insensitivity towards toxic pollutants and high energy efficiency in removing a wide variety of dyes, this process proves to be costly in regenerating the adsorbent thus resulting in its loss and also shows ineffectiveness in removing Vat and Disperse dyes[14, 17, 18, 19].

Ion-Exchange is a process in which the hazardous ionic materials (cations/anions) being exchanged is reversibly removed from wastewater and are further passed to the Ion–Exchange column, which releases ions of same polarity and thus the hazardous ions are replaced by the non-hazardous ones. However, this process is practically of no use in removing neutral dyes because it is only applicable in case of charged dyes. In addition to this, no loss of adsorbent is seen during the process; nevertheless, it requires regeneration [14].

Membrane separation technique employs a barrier through which the wastewater is passed to separate out Suspended Solids (SS). This technique has the ability to clarify, concentrate and most importantly, separate the dye continuously from wastewater effluent. Microfiltration, Nanofiltration and Reverse Osmosis are the three categories of membrane separation techniques. These techniques prove to be very quick and efficient in removing a vast variety of dyes, and are less energy intensive as compared to conventional thermal treatment processes. This technique leads to the production of a high-quality treated effluent and usually take place after coagulation or flocculation. However, high capital cost, incapability in treating large volumes of wastewater, pressure fluctuations, lack of efficiency, chronic toxicity, production of sludge (which demands processing too), short membrane life due to clogging are some of the drawbacks from which these processes suffer [20, 21].

2.2.2 Chemical Treatment

Chemical Unit Processes refer to an array of treatments involving chemical reactions that accelerate the progress of disinfecting the textile wastewater and thus help in achieving various water standards. The various prominent chemical unit processes that can be applied to improve the textile wastewater quality include Coagulation and Flocculation, Chemical Precipitation, Chemical Oxidation and Advanced Oxidation Process (Ozonation,Electrochemical methods such as Electrocoagulationand HeterogenousPhotocatalysis), Chemical Neutralization and Stabilization [22].

Coagulation and Flocculation refers to the technique employed for the separation of colloidal dye particles from the textile wastewater. Although coagulation and flocculation are always used in place of each other, but both are addressed as two different processes(**Fig. 2.2.2**). Colloidsmay be referred to as the particles smaller than approximately 10^{-5}mm and solutions as the particles smaller than 10^{-6}mm [23]. Smaller is the size of dye particle in wastewater, greater is the time required for its settling, which may be up to several years for certain varieties of dyes. Hence, to make settling easier and allow further dye separation, an infinite number of contacts are made so as to form larger size particles.

The first step of the process is particle charge destabilization. When added into water, the oppositely charged coagulants along with suspended solids begin neutralizing these particle charges. Once the neutralization process is over, the small colloidal particles link together to form microflocs which are still invisible to the naked eye. The process, at this stage, is made highly energy-intensive and rapid mixing is established to elevate the dispersion phenomenon as well as the contact between these particles. Thereafter, the flocculation step takes place as soon as the first step is complete. During this stage, slow mixing brings a large number of microflocs formed in the previous stage together. This stage brings out the conversion of microfloc to a macrofloc due to the growth in floc size. Macrofloc formation requires the sedimentation process for further removal. During this time, the generated macrofloc tends to settle down at the bottom of the basin, thus resulting in the formation of sludge containing clear wastewater after sedimentation, which can be separated out by the process of Filtration.

The coagulation and flocculation process suffers from few disadvantages like pH regulation of coagulants and dyed wastewater mixture before and after the treatment, which thereby consumes more amount of acids and caustics [23], insufficient charge neutralization leading to the demand for higher dosages, sensitivity towards temperature changes and dye specific characteristics and composition, as well as production of large volumes of sludge leading to the swift depletion and frequent replacement of filters.

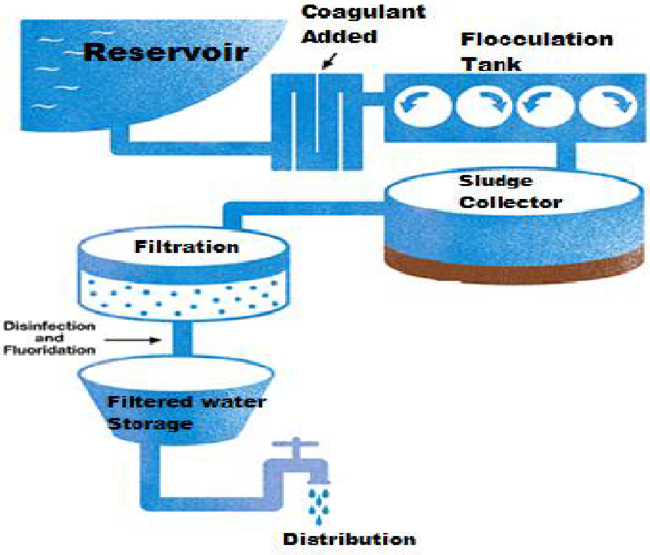


Fig. 2.2.2: Schematic overview of Coagulation and Flocculation process

Advanced Oxidation Processes (AOP's) refer to an array of chemical treatment techniques involving hydroxyl radicals (•OH), ozone (O_3), hydrogen peroxide (H_2O_2) and/or UV light that are used to remove organic (and sometimes inorganic) dye components and other hazardous effluents from textile wastewater through the process of oxidation. In situ chemical oxidation is one such type of a process [24].The set of chemical treatment techniques categorized under AOP's include electrochemical methods such as electrocoagulation, ozonation and heterogenousphotocatalysis. AOP's are considered as a viable option for dyed wastewater treatment because of their capacity to break down the aromatic structures and ability to decolorize and mineralize the textile effluents in short reaction time followed by almost zero sludge volume generation. Moreover, the rate of formation of hydroxyl radicals is correspondingly increased if UV light is imposed to accelerate the rate of H_2O_2 photolysis. When compared to the system in which only O_3 is used, the amount of ozone required is substantially reduced when combined with UV. H_2O_2/UV treatment generates •OH radicals of very high oxidation potential, therefore, no additional post-treatment disposal problems arise, because the refractory organics almost get completely destroyed during color removal from textile wastewater. AOP's prove to be an integrated solution to some of the textile wastewater quality issues, as disinfection can also be achieved in some of their designs. Theoretically, AOP's do not add any new toxic substances into the wastewater since the •OH radicals undergo complete reduction to form H_2O [25]. Besides these advantages, AOP's also suffer from certain disadvantages like byproduct formation, demanding a great deal of technical attention and continuous input of costly chemical reagents. For example, scavenging processes that yield H_2O and CO_3^-in the presence of bicarbonate ion (HCO_3^-) can reduce the concentration of •OH radicals. Therefore challenge is to throw out bicarbonate from the system [26]. Another disadvantage is unselective Peroxide Oxidation. The process of destruction rather than oxidation may result if the molecules exposed to hydrogen peroxide come across free radicals. Also, a successful H_2O_2 oxidation demands higher temperatures, pressures and longer reaction durations, thus making the process expensive in terms of energy, labor and equipment. Hence, to overcome these shortcomings, TAML®(Tetra–amido macrocyclic ligands)oxidant activatorswere designed to avoid the uncontrolled molecule destruction, thus contributing towards huge energy savings by just lowering down the temperature of the process [27].

Electrocoagulation involves the use of soluble anodes (made of iron or aluminium) which perform the process of electro-dissolution to create metallic hydroxide flocs within the wastewater. Since it is a powerful method of controlling pollution and offers high extraction efficiencies, therefore it has been proposed as an efficient technique for the removal of dyes and other harmful effluents from textile wastewater. This process offers some advantages like breakdown of recalcitrant pollutants (e.g., Polyaromatic organic compounds like Anthraquinone), no sludge formation and little/no utilization of chemicals because of which it turns out to be an effective method for color removal [28]. In short, this method provides a simple, reliable and cost-effective means for textile wastewater remediation by offering merits like: environmental compatibility and ease of operation[29].

Ozonationin terms of textile wastewater treatment is referred to as a process in which the chromophores undergo oxidative cleavage leading to the loss in color of the dye [25]. This process particularly proves useful for the treatment of dyed wastewater because, ozone readily decomposes to form several free $OH^{\bullet}$, $HO_3^{\bullet}$, $HO_4^{\bullet}$ and O^{2-}radicals on account of its high solubility in water. Being readily available, such free radicals immediately react with any organic component present in wastewater, including the dyes and hence render them harmless[29].Since H_2O_2 is an abundant source of highly reactive free$OH^{\bullet}$ radicals, therefore it assists in the overall oxidation phenomenon (minor effect), by making the pollutant more susceptible to ozone attack. As a result of UV addition, the rate of$OH^{\bullet}$ radical formation is equivalently increased with the increase in the rate of H_2O_2photolysis[25].

If compared with chlorine and hydrogen, Ozone shows better oxidizing properties, since it is an unstable compound. Ozonation has been skillfully applied in the degradation processes of phenols, pesticides and chlorinated hydrocarbons etc. [8].Ozonation makes the dyed wastewater suitable for discharge into the environmental watercourse by making it colorless with low BOD[30].One major application of this method is; ozone, in its gaseous state, minimizes the wastewater filtration load by reducing the volume of sludge generated. Apart from that, ozonation is sometimes coupled with a physical method to prevent any carcinogenic or toxic attacks to the textile wastewater [21].One major demerit of ozonation is, the dye extraction efficiency significantly decreases due to the short half-life (20 minutes) of the process which allows only a short contact time between the two (i.e., dye and ozone). The presence of temperature, pH, dye and salts further leads to the reduction in half-life. Ozone decomposes at a rapid rate, when the dyed wastewater is in an alkaline state. Hence, to preserve the half-life of ozone without its degradation, careful and accurate monitoring of the dyed wastewater characteristics (i.e., pH, dye concentration and temperature) is carried out.**Fig. 2.2.3** below shows the schematic overview of ozonation process.

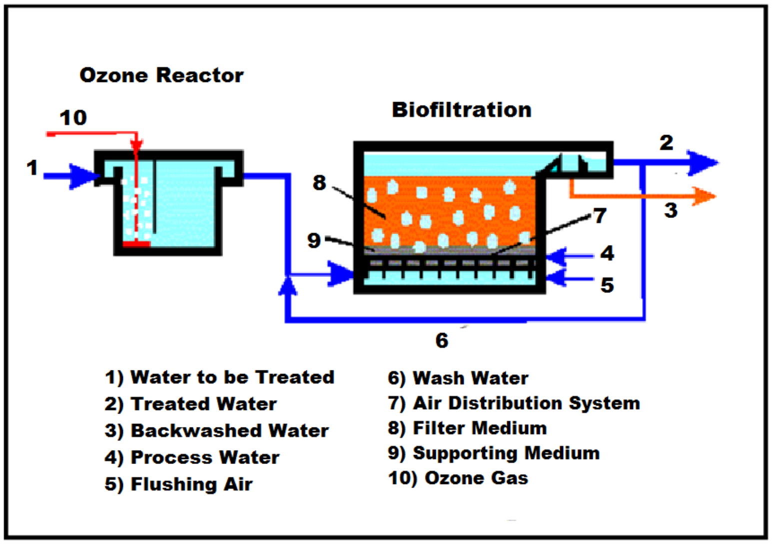


Fig.2.2.3: Schematic overview of ozonation process

HeterogeneousPhotocatalysisis considered as one of the efficient methods for dye removal. The reason behind this statement is; the process employs the most commonly used photocatalyst, TiO_2 which is well known for its high stability, significant photocatalytic activity, eco-friendly nature and low cost. Furthermore, the above process can be modified by coupling it with membrane separation techniques so that the problems encountered during dye removal are solved. This coupling is altogether known as Photocatalysis Membrane Reactor, which is a very promising technique for resolving the dye removal issues. The process involves the use of a membrane which plays a twin role of a simple barrier (for the photocatalyst) and a selective barrier (for the molecules to be degraded).

Other types of possible chemical treatments include Liquid–Liquid Extraction (LLE), in which the dye burdened wastewater is contacted with an immiscible organic solvent into which the dyes get separated. In 2004, Pandit and Basu used reverse micelles, “nanometer-sized aggregates of surfactant molecules surrounding a microscopic water core in nonpolar solvents”, to extract a wide variety of dyes[31]. Since these micelles specifically possess a hydrophobic core rather than a hydrophilic one, that’s why they are of reverse nature. The dye is extracted from aqueous solutions into the core of the micelles, which then make the dye dispersible. The dye-containing phase can then be separated by gravity, when the water layer is removed (the layer containing the dye-burdened reverse micelles is less dense than water). The dyes examined showed 70% and higherextraction efficiencies. Generally, the extraction tended to be higher at lower dye concentrations and at higher surfactant concentrations. While this method is efficient in dye removal, proper disposal methods of the extracted dye need to be established[31].

In 2010, Muthuraman and Teng proposed another LLE method, which involved the use of a xylene solution of salicylic acid to extract Methyl Violet (a cationic dye) from an aqueous solution[32]. A mixture of salicylic acid and xylene was added to an aqueous dye solution, the resulting combination was mixed and transferred to a separator funnel, and the aqueous solution was removed for analysis. Upon observation, a pH level of 6.0 (i.e. the highest pH level tested), showed the most efficient extraction. A higher salicylic acid concentration also showed the better extraction efficiencies. This technique offers one benefit, i.e., recycling of salicylic acid using other stronger acids like phosphoric, nitric or acetic acid after the dye has been stripped from it. The tests clearly showed that the salicylic acid could be used ten more times before the extraction efficiency dropped noticeably (from 96% to 90%). Unlike reverse micelles, this technique has no such stripped dye disposal problems due to salicylic acidrecycling[32].

In 2007, Mahmoud et al. observed a variety of more eco-friendly solvents for LLE[33]. An anionic dye, Remazol Brilliant Blue was extracted in a specific manner using cooking oil and variety of plant oils like cottonseed, olive, canola and sunflower. Maximum extraction efficiencies were recorded for cooking and olive oil and much poorer extraction efficiencies were found out for other oils being used as solvents. When correlated with solvent viscosity, it was observed that the liquids of higher viscosity may be an excellent media for dye extraction, but the reason behind this was not justified[33].

2.2.3 Biological Treatment

The purpose of Biological treatment in dye removalis BOD reduction by ensuring proper contact between the biological life form (bacteria, yeast, algae or fungi) and textile wastewater to be treated. Thebiological life forms feed on the organic materials (dyes and other effluents) in the wastewater, therebydegrading them into less toxic compounds [34].

Both Biosorption (adsorption on cell’s surface) and Biodegradation (exploitation of cell’s enzymes) can be utilized for the extraction of textile dyes from wastewater. The process of biodegradation may be aerobic, anaerobic or include a fusion of the two. Interactions between dyes and Microorganisms depend upon the chemical characteristics of all the reacting speciesinvolved in the process. Some of the promising adsorbents for a wide variety of xenobiotics present in the water sources are Magnetically Labelled cells, which are formed as a result of an interaction between some types of water based Ferrofluids and Yeast cells[28].

This method offers several benefits like, less deposition of relatively harmless sludge, ecofriendly and economical treatment of dye bath effluents and adequate mineralization of dyes to less complex inorganic components which are not fatal to life forms. The major advantage of this method is, total waste treatment can be accomplished through it, making it the most simplest and efficient method[35].

Like any other technique, biological treatment also suffers from certain drawbacks like, requirement of a specialized equipment for efficient dye removal as these processes are quite energy demanding and generate a considerable amount of byproducts.These processes are unable to degrade recalcitrant azo dyes completely due to their xenobiotic nature, complicated chemical structures and synthetic organic origin[18]. If biomass is used in the process, then sensitivity towards chemical toxicity and diurnal variation, requirement of a large land area, less flexibility in design and operation, optimal favorable environment including nutrition and maintenance requirements need to be satisfied, because its performance depends upon pH value and presence of salts. Lastly, being a non-destructive process, it demands chemical modification if selective bioadsorbents are employed for the purpose.

Decolorisation by White Rot Fungi

The microorganism White-Rot Fungi is generally employed in biological treatment to degrade Lignin, Dioxins and Chloroorganics present in wastewater (**Fig. 2.2.4**) [36].With respect to textile wastewater treatment, the white rot fungi exploit the lignin peroxidase enzyme, thus causing dye degradation [8].P. chrysosporium is a specific species of fungus that has the capability to degrade the largest class of conventional dyes i.e., Azo dyes which cannot be degraded by other organisms[37].In spite of the capability of fungus to decolorize dyes in liquid fermentations, the quantitative value of dye removal efficiency is consequently reduced followed by an unreliable enzyme production. The main reason behind this is;unsuitable environment of liquid fermentations for enzyme production [8]. Instead, the enzyme production was found to be more effective under the natural environment provided by the natural fermentation of fungi and therefore, yielded greater amount of enzymes than liquid fermentation.

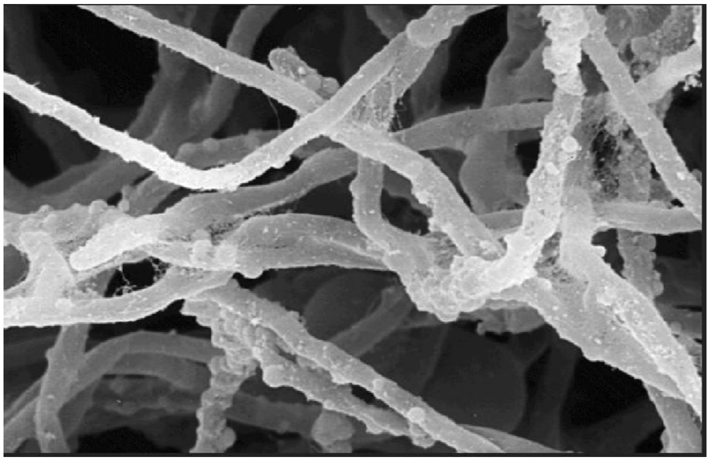


Fig. 2.2.4: White Rot Fungi, *Phanerochetechrysosporium*

2.3 Introduction to Ionic Liquids (ILs)

A new category of organic solvents having the ability to dissolve both polar and nonpolar specieshave emerged in the recent years,to meet the challenges of efficient and environmentally benign chemical processing. In fact, they have been discovered to perform much efficiently than commonly used solvents in many cases. The most striking feature of these compounds is, they can be used under unique processing conditions due to their negligible vapor pressure and behave as liquids in their pure state at room temperature. Most of these compounds behave as liquids over an incredibly large temperature range, from below ambient to well over 300 to 400°C, which clearly shows that they cannot lead to fugitive emissions. These fused organic salts with melting points as low as –96°Cand possessing significant number of potential cation/anion combinations (up to 10^{18}possibilities) are known as Room Temperature Ionic Liquids (RTIL) or simply “Ionic Liquids” (ILs) [38].**Fig. 2.3.1** illustrates some common cations and anions used in Ionic Liquid synthesis. These “Designer Solvents” possess bulky and asymmetric cations which prevent a tight crystal packing, thus lowering down the melting point, as can be seen in the case ofImidazolium, Pyridinium, and Pyrrolidinium structures. In order to reduce any interionic interactions, ILs tend to have a delocalized electron cloud and can be either bulky (*e.g.*, tosylate or *bis*[(trifluoromethyl)sulfonyl] imide) or simple (*e.g.*, Cl^-). The library of known ILs continues to grow at a rapid pace with novel combinations of a wide variety of substituted “R” groups on cation/anion being synthesized each day [11, 39].**Table 2.3** shows some characteristic properties of Ionic Liquid[40].

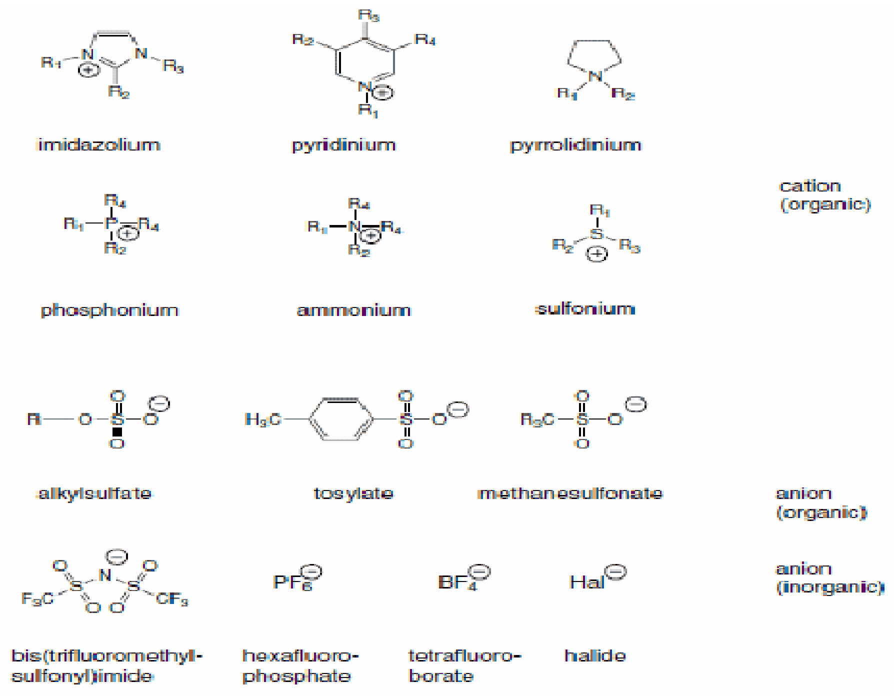


Fig. 2.3.1: Structures of common cation and anion components of Ionic Liquids

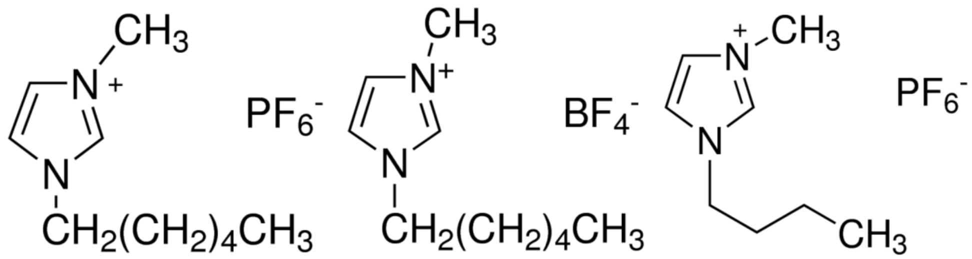
Table 2.3: Characteristics of Ionic Liquid

Salt	Cation and or anion quite large
Freezing point	Preferably below 100°C
Liquidus range	Often > 200°C
Thermal stability	Usually high
Viscosity	Normally < 100 cP, workable
Dielectric constant	< 30
Polarity	Moderate
Specific conductivity	Usually < 10 mS^{cm-1}, “Good”
Molar conductivity	< 10 Scm^{2} mol^{-1}
Electrochemical window	> 2V, even 4.5 V, except for Bronsted acidic systems
Solvent and/or catalyst	Excellent for many organic reactions
Vapor pressure	Usually negligible

As compared to conventional solvents, ILs offer better selectivity, greater reaction rates, and a much better catalyst or enzyme stability. All these properties have been thoroughly studied and applied in the processes like organometallic catalysis, organocatalysis and biocatalysis

[41].Apart from these processes, other areas like fuel cells, solar cells, sensors, nano-chemistry and electrochemical transformation also demand the application of ILs. According to Siedlecka et al., 2011 and Kowsari et al., 2011, ILs can be an ideal substitute for conventional organic solvents due to their non-measurable vapor pressure [41, 42]. The simplicity in structural modifications ofcation-anion combinations and readily available range of room-temperature Ionic Liquids to choose from provides a breakthrough to design an Ionic Liquid-solvent system, which can be well utilized for specific type of processes like textile waste water treatment [42].The ILs can possess a wide spectrum of physical and chemical properties like solubility, polarity, viscosity or solvent miscibility because of their ability to form a large number of cation and anion combinations. This is the main reason why they are referred to as, "Designer Solvents". In addition to this, the ILs also offer some environmental as well as economic benefits like IL regeneration and reuse, which indirectly minimizes the amount of waste generated [41]. Since the synthesis of ILs turns out to be highly expensive, the only option left to make the process cost effective is to recycle them after they have been regenerated. Hence, in terms of economy, it is always advisable to recycle the ILs rather than synthesizing them for the same application.

Ionic Liquids are not only employed as solvents, electrolytes or catalysts, but are also being used as additives, including plasticizers, polymer electrolyte components, porogenic agents and polymers. Recently, the properties of Polymers with chemically bound Ionic Liquid have been explored for its application in some processes [42]. In this research, Ionic Liquids namely 1-Hexyl-3-methylimidazolium hexafluorophosphate($[C_6mim][PF_6]$), 1-Hexyl-3-methylimidazolium tetrafluoroborate ($[C_6mim][BF_4]$) and 1-Butyl-3-methylimidazoliumhexafluorophosphate ($[C_4mim][PF_6]$) will be utilized as extraction solvents for the removal of Indicator dyes (Crystal violet, Methyl orange, Eriochrome black T and Malachite green) from aqueous solutions.**Fig. 2.3.2** shows the chemical structure of ILs employed in the current study.



(a) (b)(c)

Fig. 2.3.2: Chemical Structures of (a) [C_6mim][PF_6], (b) [C_6mim][BF_4] and (c) [C_4mim][PF_6]

The statement, “Ionic Liquids are green solvents” is not always correct in every situation. While they possess a negligible vapor pressure, their cationic and/or anionic components often cause toxicity. In fact, some researches have also proved the non-biodegradable nature of IL cations, specifically those with long alkyl chains[39, 43, 44]. Subsequent research has also discovered that the “greenness” of cation is greatly affected by the ring planarity and the least hazardous cations possess a non-planar ring and short alkyl chains. Moreover, the toxicity of cationic alkyl chain decreases as a result of an addition of a heteroatom or a functional group, such as a nitrile or ester[39, 45].

Although anion of an Ionic Liquid does not seem to be hazardous to the same extent as thecation, but as described above, there are some anions that are definitelyharmful to the aquatic ecosystem. Any ion having one or more fluorine atoms, (e.g., Bis[(trifluoromethyl) sulfonyl] imide), is specifically problematic. Other halogens that are not nearly as hazardous but may still cause reactions in aquatic ecosystems and be injurious to organisms include Bromine and Chlorine [39]. Research studies have proved that, more hydrophilic the anion, the less hazardous it tends to be [45]. When paired with a cation having short alkyl chains, the biodegradability of the overall Ionic Liquid increases due to the presence of several sitesavailable for enzymatic hydrolysis on Acesulfamate and Saccharinate anions (**Fig.2.3.3**)Therefore, from greenness point of view, an “ideal” Ionic Liquid would be one, that possesses a hydrophilic anion and a cation incorporating a non-planar ring with short alkyl chains [39].

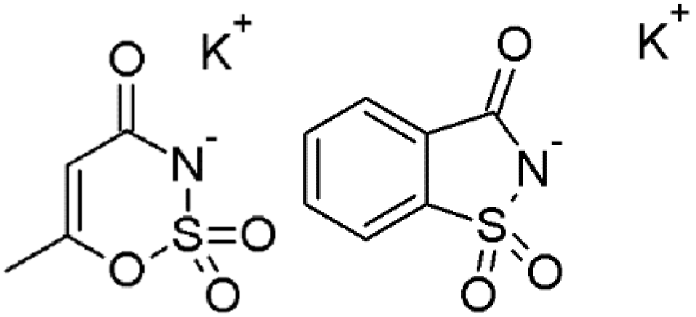


Fig. 2.3.3: Acesulfamate (left) and Saccharinate (right) structures

2.4 Applications of Ionic Liquids in Dye extraction from Aqueous Solutions

A number of researches have been carried out to examine the application of Ionic Liquids in the extraction of various dyes [46–51]. The dye constituents obviously must partition into the Ionic Liquid, or organic layer, thus leaving behind the wastewater (aqueous layer), for these extractions to be possible. The wastewater left behind can then be subjected to further treatments or directly fed to the ecosystem. To avoid the introduction of any detrimental cation or anion into the environment, the Ionic Liquid itself must not partition into the aqueous layer in any noticeable quantities. If, in any particular case, loss and capture of cation or anion occur, then they both need to be environment friendly.

Dye extraction is quantified by calculating the distribution ratio “D” (expressed as a unit–less number), defined according to the Equation 1, in which the dye concentration in the organic (IL) phase is divided by the dye concentration in the aqueous phase:

$$D = \frac{[dye]_{org}}{[dye]_{aq}} \qquad (1)$$

When $D > 10$, then extraction process is said to be efficient and when $D < 1.0$, then extraction process is said to be inefficient [52].

Several studies have been successfully carried out to extract a wide variety of dyes from aqueous solutions using ILs and each of them showed varying levels of extraction efficiencies. In year 2000, Visser et al. [46] extracted an anionic dye Thymol Blue from aqueous solutions using three Imidazolium-based IL’s namely, 1-Butyl-3-methylimidazolium hexafluorophosphate, 1-Hexyl-3-methylimidazolium hexafluorophosphate and 1-Octyl-3-methylimidazolium hexafluorophosphate at various pH levels, ranging from 1.5 to 13. They observed that, for acidic pH, the distribution ratio (D_{dye}) followed a steep incline from approximately 100 to 1000 and for a pH of 12 or above, D_{dye} followed a steep decline to a value less than 1 [46].

To attain the need for efficient dye extraction over a wide pH range (to adapt the properties of textile wastewater), pH dependency of extraction is of great concern [14]. But, the noticeable variations in D with pH provides a way out by which the extracted dye can be recovered (i.e., stripped) from the IL, thus enhancing the dye extraction efficiencies.

In year 2005, Vijayaraghavan et al. employed a Pyrrolic Ionic Liquid, mainly N-Butyl-N-methyl pyrrolidinium bis [(trifluoromethyl)sulfonyl] imide, abbreviated as $[P_{14}][Tf_2N]$ to observe the extraction of the anionic (i.e., as a sodium salt) forms of Acid Blue and Acid Red dyes [47]. This specific IL possesses a stable and hydrophobic nature. Upon observation, it was found that the IL phase was slightly favored when the distribution ratios D attained the values close to 2.0. Moreover, the extraction efficiency for the dyes as high as 95% could be achieved, if fresh aliquots of IL were repeatedly added. Although this method achieves the higher extraction efficiencies, yet it suffers from some significant drawbacks too, i.e. the need for continuously adding the IL because of which some of the IL is lost to the wastewater, thus requiring the use of Ion exchange resins to recover it prior to discharge of the water into the ecosystem [47].

In year 2006, Ali et al. employed several ILs such as 1-Butyl-3-methylimidazolium hexafluorophosphate ($[C_4mim][PF_6]$), 1-Butyl-3-methylimidazolium tetrafluoroborate ($[C_4mim][BF_4]$), 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_4mim][Tf_2N]$) and 1-Hexyl-3-methylimidazolium bromide ($[C_6mim][Br]$) to extract a wide variety of cationic dyes like Acridine orange, Nile blue A, Neutral red, Methylene blue, Safranin O and Pinacyanol chloride with extraction efficiencies as high as 99% [48]. With no extraction mechanism formally established, the researchers inquisitively came to a conclusion that the extraction efficiency is not at all affected by the hydrophobicity of an Ionic Liquid. Hence, at least one succeeding study is required to challenge this claim [48].

With reference to the claim mentioned earlier, the above study was contradicted by Pei et al. in 2007 [49]. They basically extracted three anionic dyes namely Eosin yellow, Orange G and

Methyl orange using four different Ionic Liquids i.e., 1-Hexyl-3-methylimidazolium hexafluorophosphate ($[C_6mim][PF_6]$), 1-Butyl-3-methylimidazolium hexafluorophosphate ($[C_4mim][PF_6]$), 1-Hexyl-3-methylimidazolium tetrafluoroborate ($[C_6mim][BF_4]$) and 1-Octyl-3-methylimidazolium hexafluorophosphate ($[C_8mim][PF_6]$) over a wide range of pH values [49]. Upon observation, it was concluded that, longer the IL alkyl chain, more efficient is the extraction. Thus, the highest D values were recorded for $[C_8mim][PF_6]$, which continued to decrease as the alkyl chain size decreased, suggesting that, more hydrophobic the IL, more efficient it is as an extraction solvent. The data also pointed out that below an acid dissociation constant (pKa value) of 3.46, the neutral form of Methyl orange preferably shows a poor partitioning (i.e., low D 's). However, the extraction efficiency quickly elevates when the anionic form of IL predominates at pH levels above 4.0. On the contrary, a steep drop at an increasing pH level was observed in case of Eosin yellow, which attained high D values at pH levels below 4. Orange G showed a crucially constant D value till very basic pH's were attained, at which the point D_{dye} declined. In additionto this, the authors made an inference that the fluorine atoms of the PF_6^- anion were unable to bond with the hydrogen atoms due to the incapability of the dye at a high pH range [49].

In 2008, Li and Xin employed an IL, 1-Butyl-3-methylimidazolium hexafluorophosphate ($[C_4mim][PF_6]$) and a conventional solvent, Octanol to extract the anionic dyes Acid yellow RN and Acid brilliant red B [50]. The dye partitioning into the IL was found to be much more efficient as compared to that of octanol. For Acid red dye, the D values in the IL and octanol systems were found out to be 424.8 and 3.0, respectively and for Acid yellow dye, the same values obtained were 130.25 and 13.6 respectively, clearly indicating the higher distribution ratio in case of ILs. The researchers implied that the ions from which the Ionic Liquids are composed of, behave as counter ions, thereby enhancing their extraction capacities.It was also proved that the hexafluorophosphate (PF_6^-) anion exchanges its anion with Acid yellowforming a $[C_4mim]org^+[Dye]org^-$ complex, as shown by comparing NMR spectra of the IL before and after the dye contact, thus making it difficult for the IL to recover itself after being repeatedly used for incorporating dye into it. In case of Acid red dye, it is possible to recover the IL after its several uses, because the structure of the IL phase contained in the $[C_4mim]$ org^+ $[Dye]$ org^- ion pair remains unaltered. Although both cases described above, suffer the loss ofhexafluorophosphate anionPF_6^-(a part of an IL) to the aqueous phase, still it may be introduced into the ecosystem through other ways, thus barring the dedicated IL regeneration steps (the remaining pair after combination would be $[Dye]aq^+[PF_6]aq$), which is just contrary to the definition of ILs that describe them as "Green" solvents. Therefore, this problem needs to be tackled and an alternative solutionshould be proposed before this methodology can be considered viable [50].

In 2011, Fan et al. examined the role of several Ionic Liquids like $[C_4mim][PF_6]$, $[C_6mim][PF_6]$, $[C_8mim][PF_6]$, $[C_6mim][BF_4]$ and $[C_8mim][BF_4]$ for the extraction of various azo dyes which included, neutral 1-(Phenylazo)-2-naphthol and 4-(Nitrophenylazo) resorcinol plus some cationic dyes like1-(2-Pyridylazo)-2-naphthol, 4-(2-Pyridylazo) resorcinol and Methyl red [51]. A cation exchange involving the transfer of the cationic dye into the IL phase accompanied by the movement of the imidazolium cation into the aqueous phase was observed. The loss of cation to the aqueous phase may not be very detrimental as long as the alkyl chain is adequately short. Nevertheless, the economy of the process would be greatly affected by this cation loss. The larger hydrogen bonding ability of tetrafluoroborate ion and the constitution of hydrogen bonds between the dye and the IL was investigated as the main reason behind the higher D_{dye}values with the tetrafluoroborate ion than for thehexafluorophosphate ion. Ultimately, the researchers were able to recover only one dye i.e., (1-(Phenylazo)-2-naphthol) successfully [51].

In 2012, Gharehbaghi and Shemirani applied Ionic Liquid-Based Dispersive Liquid–Liquid extraction (IL-DLLE) method to extract and remove a carcinogenic textile dye, Congo Red (CR) from aqueous solutions [11]. The method employed a suitable binary solution of a "Disperser solvent" (Acetone) and an "Extraction solvent" (1-Hexyl-3-methylimidazolium bis(trifluormethylsulfonyl) imid) for the removal of CR dye from aqueous phase. They also examined the effects of different parameters like pH, type and volume of the dispersant, type and amount of IL and salt concentrations on the extraction of the dye. They also conducted several surveys and established a reverse dispersive liquid–liquid extraction method employing acidic stripping solutions for the regeneration of IL. Despite the presence of a rather high salt content and water soluble organic solvents, this method turned out to be a successful one in the partitioning of this commercial dyeing pollutant. After noticing the effect of different parameters on the dye extraction, they concluded that, for ionizable (but hydrophobic) solutes like CR, the hydrophobic IL like [Hmim][Tf_2N] turns out to be a perfect extractant. They also added that, only the specific values of the parameters like pH (5.0), IL application (between 90-400 mg/10mL), salt concentration (0.25% w/v) and dispersant were able to bring about >95% quantitative CR dye extraction in the initial range of 40–250mg/L [11].

Because of its advantages like robustness, efficiency in dye separation and removal, fastness and simplicity in IL regeneration, IL-DLLE has proved to be a novel yet economical method and the present research involving Liquid–Liquid Extraction (LLE) of Indicator Dyes into Imidazolium-Based ILs is purely adapted from the above approach [11].

Since this method involves the use of only small quantities of the "green extraction solvent" (IL), therefore, it provides higher dye extraction efficiencies, improved IL regeneration capabilities and low toxicity. Moreover, the practical applications of IL-DLLE in biphasic industrial applications, dye determinations and analytical purposes have also been discussed by them [11].In spite of being an efficient method, it suffers from a drawback too, which includes difficulty in the complete removal of aqueous phase, which, on the other hand is easier to remove in case of cloud point extraction (CPE) method due to the high viscosity of ILs involved.

It is clear from these studies that additional work is required: (a) to define the specific features of an IL that lead to high extraction efficiency and flexible recovery, (b) to clarify the processes by which dye molecules are extracted into an IL and (c) to grasp the apparently contradicting results obtained by various researches. Keeping this in mind, a planned study of the effects of initial dye concentration, amount and type of Ionic Liquid, salt concentration, dispersing agent concentrations, pH and type of stripping solutions on the dye partitioning between Imidazolium based Ionic Liquids ([C_6mim][PF_6], [C_6mim][BF_4] & [C_4mim][PF_6]) and aqueous solution (water) has been carried out. Moreover, the study also focusses on the performance of acid stripping solutions in regenerating the ILs and ability of the regenerated ILs to be re-used for subsequent dye separations. Particularly, four different dyes were used to examine the performance of the above mentioned ILs as "Extraction Solvents". These include two cationic dyes (Crystal violet and Malachite green) and two anionic dyes (Methyl orange and Eriochrome black T). These were chosen because they represent the two major families of commercial dyes, are consistent in an array of media, have well-known structures, and are easy to handle.

2.5 Characteristics of Selected Dyes

Eriochrome Black T (EBT) is an azo dye that is specifically employed in the water hardness determination process as a complexometric titration indicator. EBT is a diprotic dye with pKa values of 6.6 and 11.6 over a pH range between 2.0 to 11.0 and possesses a wine red color at a maximum wavelength $(\lambda)_{max.}$ of 526 nm (Visible range) in water. In its protonated form, the dye attains a blue color in a buffered solution of pH 10 and turns red on forming a complex with calcium, magnesium, or other metal ions. Another application of the dye is to detect the presence of rare earth metals. Being a major group of azo dyestuffs, it has been extensively used in textile, printing and leather industries and contributes for more than 50% of the global dye production. However, it has been identified as one of the problematic anionic dyes in the industrial effluents due to the resistance of its complex molecular structure towards light, water and chemicals; hence they persist in nature [53, 54].

Methyl Orange (MO)is a pH indicator dye frequently used in titrations because of its clear and distinct color change. It is a model compound of Azo reactive dyes, which are the largest class of watersoluble synthetic dyes with greatest variety of colors and structures generally resistant to aerobic biodegradation and are not amenable to conventional biological wastewater treatment due to their complex aromaticmolecularstructure and lack of requisite enzymes in the conventional biological treatment plant [55]. It gives a pKa value of 3.46 in water at 25°C over a pH range between 3.1 to 4.4 and possesses a deep orange color at a maximum wavelength $(\lambda)_{max.}$ of 464 nm (Visible range) in water. In a solution becoming less acidic (i.e., pH below 3.1), Methyl Orange shows a color transition from red to orange and finally to yellow with the reverse occurring for a solution increasing in acidity (i.e., pH above 4.4). In an acid, it is reddish and in alkali, it is yellow. The dye acts as a pH indicator when mixed in Xylene cyanol solution and undergoes a color transition from grey (i.e., below pH 3.2) to green (i.e., above pH 4.2). Despite being widely employed in paper industries, biological stain, chemical, paints, inks, plastics, textile and leather industries [56], its anaerobic transformationresults in the formationand accumulation of colorless aromatic amines, which can be highly toxic, mutagenic and carcinogenic to human being and aquatic life. Hence to combat this severe problem, it is required that, this target pollutant must undergo thorough elimination prior to its release so as to protect the fragile ecosystems [57, 58].

Crystal Violet (CV)is a basic triarylmethane dye with antifungal, antibacterial and anthelmintic properties. It is soluble in water, forming a dark-purple solution. The % solubility of the dye in water and acetone is 0.2-1.7 and 0.4 respectively. Its acid dissociation constants i.e., pKa1 and pKa2 values are 5.31 and 8.64 respectively and possesses a blue-violet color at a maximum wavelength $(\lambda)_{\max.}$of 589 to 594 nm (Visible range) in water.Since the dye color depends upon the acidity of the solution, therefore, at a pH of 1.0, the dye is green with absorption maxima at 420 nm and 620 nm, while in a strongly acidic solution (pH of –1); the dye is yellow with absorption maxima at 420 nm.That’s why it is used as a pH indicator. It is used for various purposes such as a biological stain, an external skin disinfectant in humansand animals, a veterinary medicine, and anadditive to poultry feed to inhibit propagation of mold, intestinalparasites and fungus. It is also extensively used as a purple dye for dying textiles such as cotton and silk, colorant for paper and in paints and printing ink. CV is a mutagenand mitotic poison and can form a protein-dye complex and hence acts as an enhancer for bloody fingerprints. CV is carcinogenic and has been classified as arecalcitrant molecule; since it is poorly metabolized by microorganisms, it can therefore persist in a variety of environments. It is responsible for causing moderate eyeirritation, producing painful sensitization to light.It can also cause permanent injury to the cornea and conjunctiva.It is highly toxic to mammalian cells; and, ifabsorbed in harmfulamounts by the granular tissue of the skin, can cause permanent skin pigmentation and digestive tract irritations. In extreme cases, it may also lead to respiratory and kidney failures.Therefore, it is crucial to propose new environmentallyfriendly processes with low cost and high efficiency to remove CVfrom industrial effluents and water bodies [59].

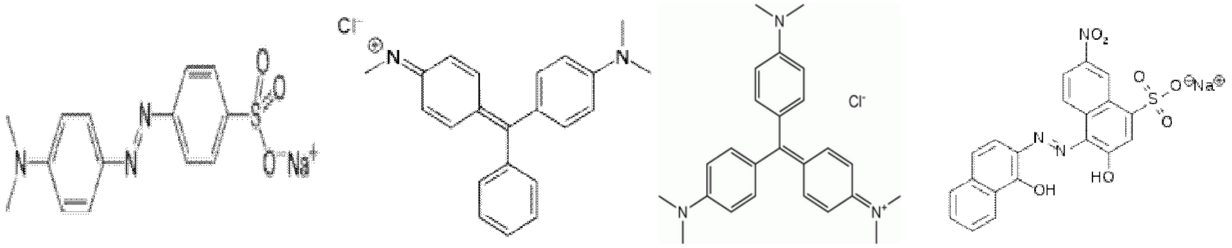
Malachite Green is a triarylmethane dye which is classified and used in the dyestuff and pigment industry for coloring materials such as leather and paper.It is most widely used as a direct dye for coloring jute, wool and silk in the textile industry.This dye on photo-oxidation via nascent oxygen break into various N-dealkylated primary and secondary amine derivatives which are similar to carcinogenic aromatic amines [60]. It is composed of green crystals (or loose colored chloride or oxalate anions) with metallic luster which are highly soluble in neutral water with solubility and bulk density being 75 mg/L and 500 kg/m^3 respectively. It has a pKa value of 6.90 over a pH range between 0 to 2 and 11.6 to 14 and possesses anintense bluish-green color at a maximum wavelength $(\lambda)_{max.}$ of 618 nm (Visible range) in water.The dye, being used as a pH indicator, undergoes first color transition from yellow (i.e., below pH 0.2) to green (i.e., above pH 1.8) and second color transition from green (i.e., below pH 11.5) to colorless (i.e., above pH 13.2). Apart from being used as a dye, it also acts as an antibacterial agent, parasiticide, biological stain for microscopic analysis of cell biology and tissue samples, endospore staining agent, saturable absorber in dye lasers, disinfectant, multi-drug resistance inhibitor, radiochemotherapist, antiseptic and antifungal agent in aquatic and fisheries industry, wound dressing material, anti-tumor agent and pulmonary tuberculosis treatment agent. In spite of these advantages, this dye suffersfrom some drawbacks too i.e., if metabolized by the aquatic animals to its principal lipophilic metabolite (Leuco Malachite Green), it can retain inside their bodies in non-polar form, thus inducing renal and hepatic tumors in mice and reproductive abnormalities in fishes, which has become the basis of controversy in government regulations.Hence, mineralization of the dye is essential before its discharge into the water bodies [60].

Table 2.5.1 and **Fig.2.5**shows the physiochemical characteristics and chemical structures of the above mentioned dyes along with the summary of other reported solvent and IL-based extraction techniques described in **Table2.5.2**.

Table2.5.1: Physicochemical characteristics of indicator dyes

Name	**Nature**	**Other name**	**Molecular Formula**	**M_w (g/mol)**	**$\lambda_{max.}$ (nm)**	**Solubility**	**Application**
Eriochrome black T	Anionic	Solochrome Black T	$C_{20}H_{12}N_3NaO_7S$	461.38	526	50 g/L at 20 °C	Complexometric titration indicator
Methyl Orange	Anionic	Gold Orange	$C_{14}H_{14}N_3NaO_3S$	327.33	464	Highly soluble in hot water at 20 °C	pH indicator, titration agent

Crystal Violet	Cationic	Gentian Violet	$C_{25}H_{30}CIN_3$	407.97	589-594	4000 mg/L at 25°C	pH indicator
Malachite Green	Cationic	Basic Green 4	$C_{52} H_{54} N_4 O_{12}$	928	618	75 mg/L at 25 °C	Biological stain



(a) (b) (c) (d)

Fig. 2.5: Chemical structures of (a) Methyl Orange, (b) Malachite Green, (c) Crystal violet and (d) Eriochrome black T [49, 61, 62, 63]

Table 2.5.2: Chronological summary showing different applications of solvent as well as Ionic Liquid based extraction techniques

Name and Year	Topic	Research Outcome	Ref.
Liu et al., (2003)	Use of Ionic Liquids (ILs) for Liquid Phase Microextraction (LPME) of Polycyclic Aromatic Hydrocarbons (PAH)	Nonvolatility and adequate viscosity allowed the IL to be conveniently adopted as extractant.	[64]
Muthuraman and Palanivelu, (2004)	Selective Extraction and Separation of Textile Anionic Dyes from Aqueous Solution by Tetrabutyl Ammonium Bromide (TBAB).	1. TBAB is able to extract more than 98% of dye ions in a short time of 15 min. 2. The dye extraction efficiency was not affected in the presence of salts like NaCl and Na_2SO_4. 3. TBAB can be regenerated by salicylic acid and Na_2CO_3 solution.	[65]

Zhou et al., (2008)	Temperature-controlled ionic liquid dispersive liquid phase micro-extraction (LPME)	Inexpensive sample pretreatment technique for trapping of pesticides.	[66]
Freire et al., (2008)	Mutual Solubilities of Water and the [Cnmim][Tf_2N] Hydrophobic Ionic Liquids	1. Mutual solubilities between water and the [C_2mim][Tf_2N] to [C_8mim][Tf_2N] series of IL's in the temperaturerange between 288.15 K and 318.15 K at atmospheric pressure were presented. 2. Hydrophobic character of the IL increases with the increase in length of cation alkyl chain. 3. To predict ecotoxicity impact of IL's, imidazolium-based salts of amphiphilic character are employed.	[67]
Baghdadi and Shemirani, (2009)	In situ solvent formation microextraction for determination of inorganic species in saline solutions	Mercury determination using TMK as complexing agent.	[68]
Zhou et al., (2009)	Ultrasound-assisted Ionic Liquid-Based Dispersive Liquid Phase Micro-Extraction (IL-DLPME) for determination of aromatic amines in water samples	Excellent enrichment performance, stability, low cost.	[69]
Pereira et al., (2010)	Ionic Liquids as Adjuvants for the Tailored Extraction of Biomolecules in Aqueous Biphasic Systems (ABS)	1. The IL's employ L-tryptophan as a model biomolecule to finely tune the phase behavior and extraction capability of ABS. 2. The characteristics of the polymer-rich phase are modified by using IL's as adjuvants.	[70]
Freire et al., (2010)	High Performance Extraction of Alkaloids using Aqueous Two-Phase Systems with Ionic Liquids	1. The extractionperformances of both alkaloids (Caffeine and Nicotine) are significantly improved with human urine samples. 2. A decrease in K was observed for the two partitioning solutes (nicotine and caffeine) in the system containing the [C_4mim][CF_3SO_3] IL.	[71]

Othman et al., (2011)	Liquid-Liquid Extraction of Black B Dye from Liquid Waste Solution Using Tridodecylamine	The % of removal of Remazol Black B dye of textile industries varies with: 1) pH values of dyed waste water 2) Concentration of dye 3) Addition of diluents.	[72]
Moattar and Hamzehzadeh, (2011)	Effect of pH on the Phase Separation in the Ternary Aqueous System Containing the Hydrophilic Ionic Liquid 1-Butyl-3-methylimidazolium bromide and the Kosmotropic Salt Potassium Citrate at T = 298.15K	1. ATPS-promoting capabilityin the investigated system increases with the increase in pH of aqueous medium. 2. Citrate ions with higher valence existing in the basic pH medium promote salting-out effects more efficiently.	[73]
Sekar et al., (2012)	Choline-Based Ionic Liquids-Biodegradation of Azo Dyes	Degradation to less toxic components, low biomass formation.	[74]
Freire et al., (2012)	Aqueous Biphasic Systems: A Boost Brought about by Using Ionic Liquids	1. Advantages shared by IL-based ABS include enriched aqueous media, no use of volatile organic solvents, low viscosity, and quick phase separation. 2. Ionic-liquid-based ABS has been formed in the presence of a large range of inorganic and organic salts and amino acids. 3. Superb liquid–liquid behaviors have been found because of the IL being used as a salting-out species.	[75]
Neves et al., (2012)	Improved Recovery of Ionic Liquids from Contaminated Aqueous Streams using Aluminium-Based Salts	1. Two aluminum-based salts ($Al_2(SO_4)_3$ and $AlK(SO_4)_2.12H_2O$) were used to treat imidazolium-, pyridinium- and phosphonium-based IL’s. 2. Above salts prove to be the novel promising agents with enhanced abilities for the removal and recovery of IL’s with a minimum efficiency of 96%.	[76]
Oplawski, (2014)	Extraction of Indicator Dyes into Imidazolium- Based IL	More efficient dye recovery with less hydrophobic IL.	[77]
Ferreiraa et al.,	Complete Removal of Textile	Better extraction efficiencies and	

(2014)	Dyes from Aqueous Media using IL-ATP’s.	partitioning coefficients with phosphonium based ATPs.	[78]

2.6 Gaps in Literature

Although various IL-based extraction methods have been applied in the recent years for the extraction of different classes of carcinogenic dyes including azoic dyes, no work as such has been carried out for the extraction of Eriochrome Black T, Malachite Green and Crystal Violet, which are equally harmful as the above mentioned ones. Moreover, to make the process inexpensive, no particular emphasis has been laid on the IL regeneration or re-using the regenerated IL for subsequent dye separation.Although Vijayaraghavan et al. (2006) [47] and Stepnowski (2005) [79] havesuccessfully recovered the lost ILs from the aqueous phaseby using ion exchange resins, but the process turned out to be an expensive one.So there is a great need to explore, improve and modify the field involving IL regeneration and re-use, in order to make the IL based extraction processes economically viable on industrial scale.To overcome the above shortcomings, Ionic Liquid-based Dispersive Liquid–Liquid Extraction process (IL-DLLE) is adapted as an efficient method for the extraction of indicator dyes (Crystal violet, Methyl orange, Eriochrome black T and Malachite green) from aqueous solutions in the current research study.Moreover, to maintain the economy of process, acid stripping solutions are used to regenerate the IL byReverse Dispersive Liquid–Liquid Extraction process to ensure its further use.

CHAPTER 3: MATERIALS AND METHODS

3.1 Experimental Procedures/Approach

In the current research, experimental procedures based upon Ionic Liquid-Based Dispersive Liquid–Liquid Extraction (IL-DLLE) have been implemented. The dyes Crystal violet, Methyl orange, Eriochrome black T and Malachite green are selected as target pollutants to be removed from aqueous saline solutions because of their complex molecular structures that are resistant towards biodegradation, thereby turning them into potential carcinogens and mutagens. The ILs employed for the removal of these dyes are[C$_6$mim][PF$_6$], [C$_6$mim][BF$_4$] and [C$_4$mim][PF$_6$]. Since this method utilizes only a small quantity of IL, is superior against high salt content and water-miscible organic solventsand is much safer compared totraditional solvent extraction (SE) methods, that's why it is considered to be a novel, reliable, potent, quick, eco-friendly and economical method for dye removal, thus offering high dye extraction efficiencies and simplicity in IL regeneration [11].

Fig. 3.1shows the general experimental procedures that will be implemented in this research project.

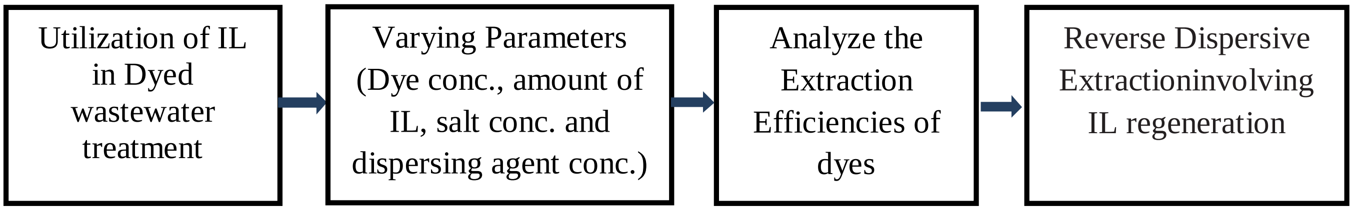


Fig. 3.1: Schematic diagram depicting the general approach in the project

3.2 Experimental

3.2.1 Instruments and Equipments

A Perkin Elmer Lambda 35UV-Vis Spectrophotometer with an absorption range between 200-700nm, a CF15RXII type Centrifuge (Hitachi Koki Co. Ltd., speed 300-15000 rpm, frequency 50/60 Hz, temperature range between–9 to 40°C, Time 5-99 min., rotor speed 31-49 Rotational Centrifugal Force), graduated measuring cylinder, beakers (1000mL), bottles (500mL & 300mL), glass cuvettes (Optiglass Ltd., T% > 80%, 10mm path length), test tubes, hot air oven, glass pipette

(10mL & 2mL), polytetrafluoroethylene (PTFE) needle,weighing balance (0.1-120 mg), pH meter. Magnetic stirrer with an adjustable rpm was purchased from Medi Lab Enterprises, Chandigarh, round-bottom centrifuge tubes (max. volume 10mL) and microlitre syringe (range 0.1-1mL) were purchased from Tarsons Product Pvt. Ltd., Kolkata.

3.2.2 Reagents and Solutions

1. Indicator dyes

The indicator dyes Crystal violet, Methyl orange and Eriochrome black Twere purchased from LobaChemie Pvt. Ltd. Mumbai, India and Malachite green was purchased from Yogesh Dyestuffs Pvt. Ltd. Mumbai, India. The physical state, appearance and purity of these dyes at room temperature (25°C) is: Crystal violet appears as a solid, dark green colored powder with 96% purity, Methyl orange appears as a solid, yellowish-orange colored powder with 95% purity, Eriochrome black T appears as a solid, brown-black colored powder with 99% purity and Malachite Green appears as a solid, dark green chloride crystals with metallic luster and 96% purity.

2. Ionic Liquids(ILs)

The Ionic Liquids[C_6mim][BF_4], [C_4mim][PF_6] and [C_6mim][PF_6], which will act as "Extraction solvents" in the current experiment, were purchased from Io-li-tec (Ionic Liquid Technologies) GmbH, Germany. At room temperature (25°C), they appear as clear; colorless to orange viscous liquids with 99% purityand no characteristic odor. The chemical names of these compounds are;1-Hexyl-3-methylimidazolium tetrafluoroborate, 1-Butyl-3-methylimidazolium hexafluorophosphate and1-Hexyl-3-methylimidazolium hexafluorophosphateare represented by the molecular formulas; $C_{10}H_{19}BF_4N_2$, $C_8H_{15}F_6N_2P$ and $C_{10}H_{19}F_6N_2P$ respectively. The molecular weight and density of theseImidazolium based hydrophobic organic compounds are:254.08 g/mol, 1.149 g/cm^3 ([C_6mim][BF_4]); 284.19 g/mol, 1.38 g/cm^3([C_4mim][PF_6]) and 312.24 g/mol, 1.3045 g/cm^3 ([C_6mim][PF_6]). It is composed of both cationic ([$C_n$mim]; alkyl chain) as well as anionic ([PF_6]; fluorine atoms) substituents which exchange themselves with the hydrogen bonds of –OH groups of the respective cation or anion dye components, thereby allowingeffective dye separation.

3. A stock solution (250 mg/L) of Crystal violet, Methyl orange, Eriochrome black T and Malachite green was prepared by dissolving the proper amount of these dyes in double distilled water. Working solutions of required concentrations were prepared by appropriate dilution of the dye stock solution.

4. Acetone (99% pure), which will be used as a “disperser solvent” was purchased from LobaChemie Pvt. Ltd. Mumbai, India.

5. An acetate buffer solution of 2 mol/500 mL concentration was prepared bymixing 118.53 g of sodium acetate and 60.05 g of acetic acid in 500 mL double distilled water at room temperature (25±2°C) and pH was adjusted to 5. The buffer solution will serve the purpose of keeping the pH neutral throughout the experiment.

Both components of acetate buffer solution were purchased from Qualigens Fine Chemicals, Mumbai, India and theircharacteristic properties are described below:

- Sodium acetate (CH_3COONa): Appears as a white,granular,deliquescent,odorless and crystalline powder with 82.03 g/mol molecular weight and 99% purity in anhydrous state.
- Acetic acid (CH_3COOH): Appears as a colorless liquid with a strong, pungent/vinegar like odor, 60.05 g/mol molecular weight and 99.8% purity in anhydrous state.

6. A salt solution of 10% w/v was prepared by dissolving 5g $NaNO_3$ in 500mL double distilled water at room temperature (25±2°C). $NaNO_3$ appears as a white crystalline powder with 84.99 g/mol molecular weight, 99% pure and was purchased from LobaChemie Pvt. Ltd. Mumbai, India.

7. For each dye, pH solutions(HCl and NaOH) of 1mol/100 mL concentration, within the range of 2–12were prepared by mixing appropriate amounts of HCl (3.09 mL) and NaOH (1.87 mL)separately in 100 mL double distilled water at room temperature (25±2°C).NaOH appears in the form of white deliquescent pellets, with 40 g/mol molecular weight, 2.13 kg/L density, 98% purity and was purchased from LobaChemie Pvt. Ltd. Mumbai, India.The characteristic features and suppliers of HClare mentioned in the next point.

8. Lastly, for each dye, two series of 0.5 mL acid stripping solutions (HCl and HNO_3) of 5 mol/100 mL concentration will be prepared by mixing appropriate amounts of HCl (15.44 mL)and HNO_3 (20.86 mL) separately in 100 mL double distilled water at room temperature (25±2°C). The performance of both acid stripping solutions will then be compared so as to check their ability in regenerating the settled IL phase containing the respective dye.

The characteristic features of the acid stripping solutions (HCl and HNO_3) are as follows:

- Hydrochloric acid (HCl): Appears as a colorless, transparent, highly pungent liquid with36.46 g/mol molecular weight, 1.18 kg/L density,35.4% purity and was purchased from Sd Fine Chemicals, Ltd. (SDFCL), Mumbai, India.
- Nitric acid (HNO_3): Appears as a Colorless, yellow, or red fuming liquid with acrid or suffocating odor, 63.01 g/molmolecular weight, 1.51 kg/L density, 69-70% purity and was purchased from Thermofisher Scientific India Pvt. Ltd., Mumbai.

3.2.3 Ionic Liquid-Based Dispersive Liquid–Liquid Extraction (IL-DLLE)

Mechanism

When dissolved in the aqueous solution of double distilled water containing acetate buffer, $NaNO_3$ salt, acetone and IL of different concentrations, the dye molecules ionize and are dispersed by the disperser solvent, acetone. After getting dispersed, hydrogen bonds in the –OH group of cationic/anionic dye substituents interact with the respective cation ([$C_n$mim]) or anion ([PF_6]) component of IL, thereby forming an IL-dye complex which settles at the bottom leaving the clear aqueous solution above.

Procedure

The schematic view of IL-DLLE experimental setup is shown in **Fig.3.2.3** [11]. The extraction process was performed at room temperature (25±2°C) as follows:A total of 200μL of Acetate buffer (pH 5.0, 2.0 mol/500 mL conc.) and 250μL $NaNO_3$of 10% w/v (2 g/200 mL) were added into a 10mL round-bottom plastic centrifuge tube containing different dye concentrations(up to 250mg/L) and the total volume of 5.0mL was adjusted with double distilled water.Afterwards, a binary solution containing 200μL of IL and 500μL of acetone was rapidly injected into each sample using a syringe, thereupon, a cloudy solution was obtained.Thedyes were extracted into fine droplets of IL.The mixture was then centrifuged for 5 min at 4000 rpm to decrease the sedimentation time. To allow proper partitioning of the dye and aqueous phase, the mixture was kept overnight. Upon observation, fine droplets of IL along with the extracted dyeswere found to be settled at the bottom of centrifuge tube, leaving the clear aqueous solution above them. Thus, two phases of IL+Extracted dye and clear aqueous solution were distinctly visible (**Fig. 3.2.4**).

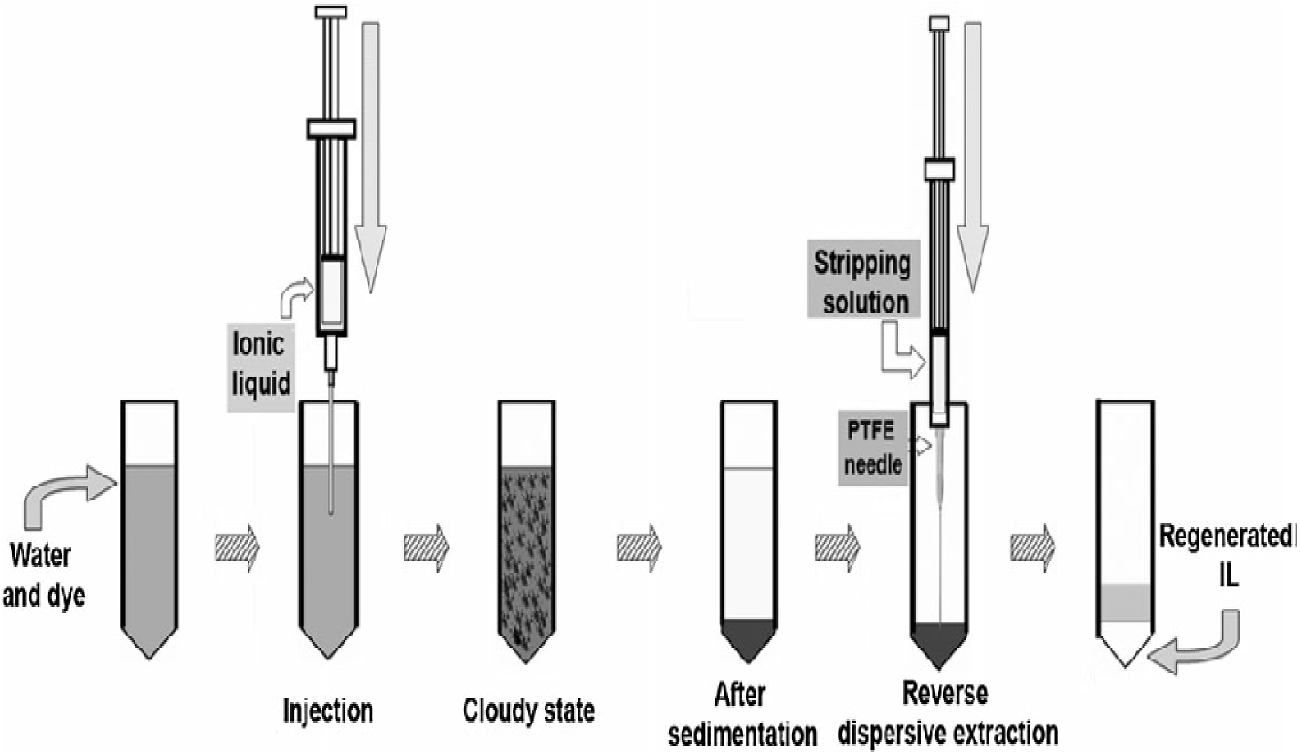
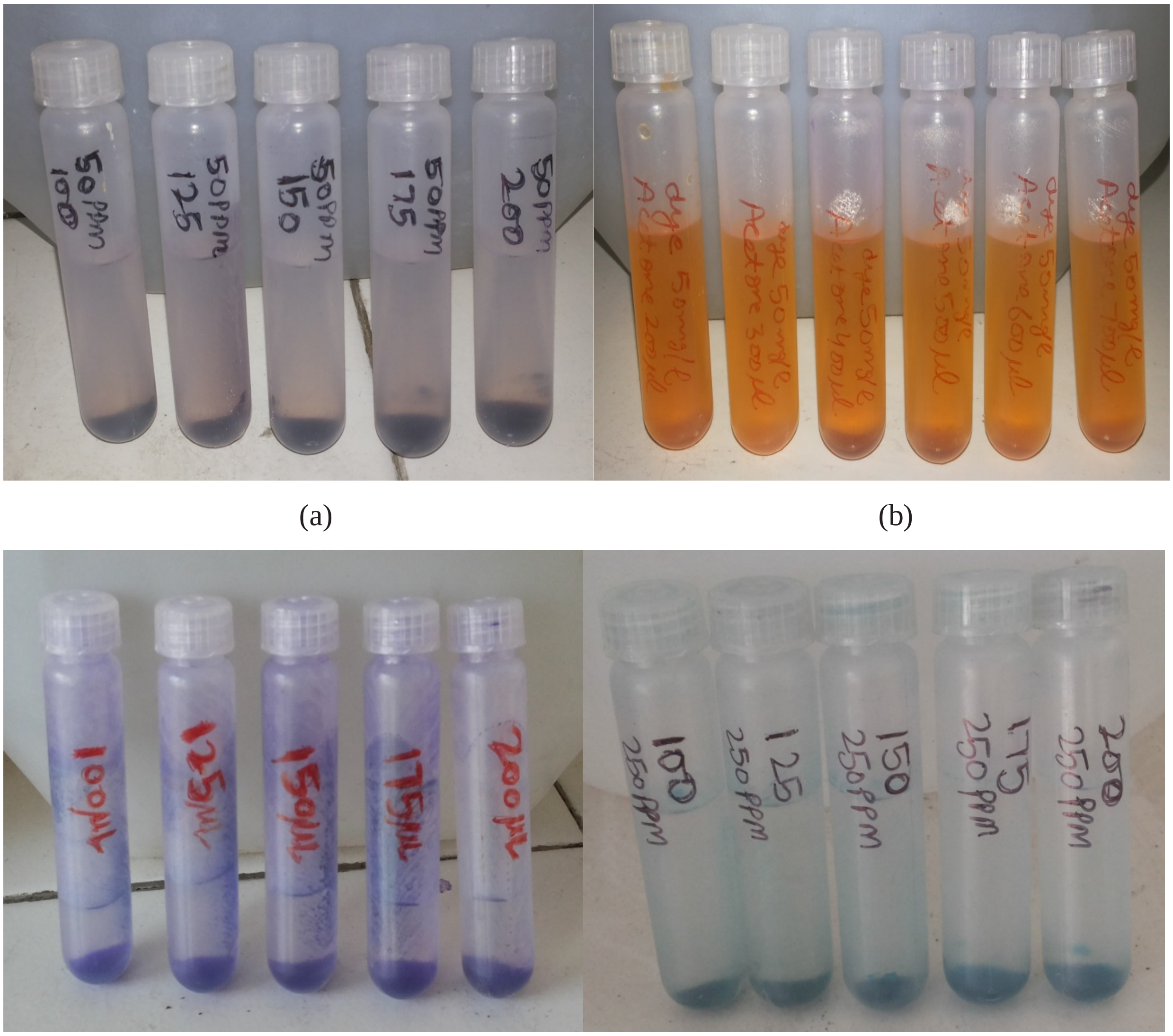


Fig. 3.2.3: Schematic view of IL-DLLE experimental setup



(a) (b)

(c) (d)

Fig.3.2.4: Formation of two phases of IL+ extracted dyes (bottom) and aqueous sol. (top) in, (a) EBT, (b) MO, (c) CV and (d) MG

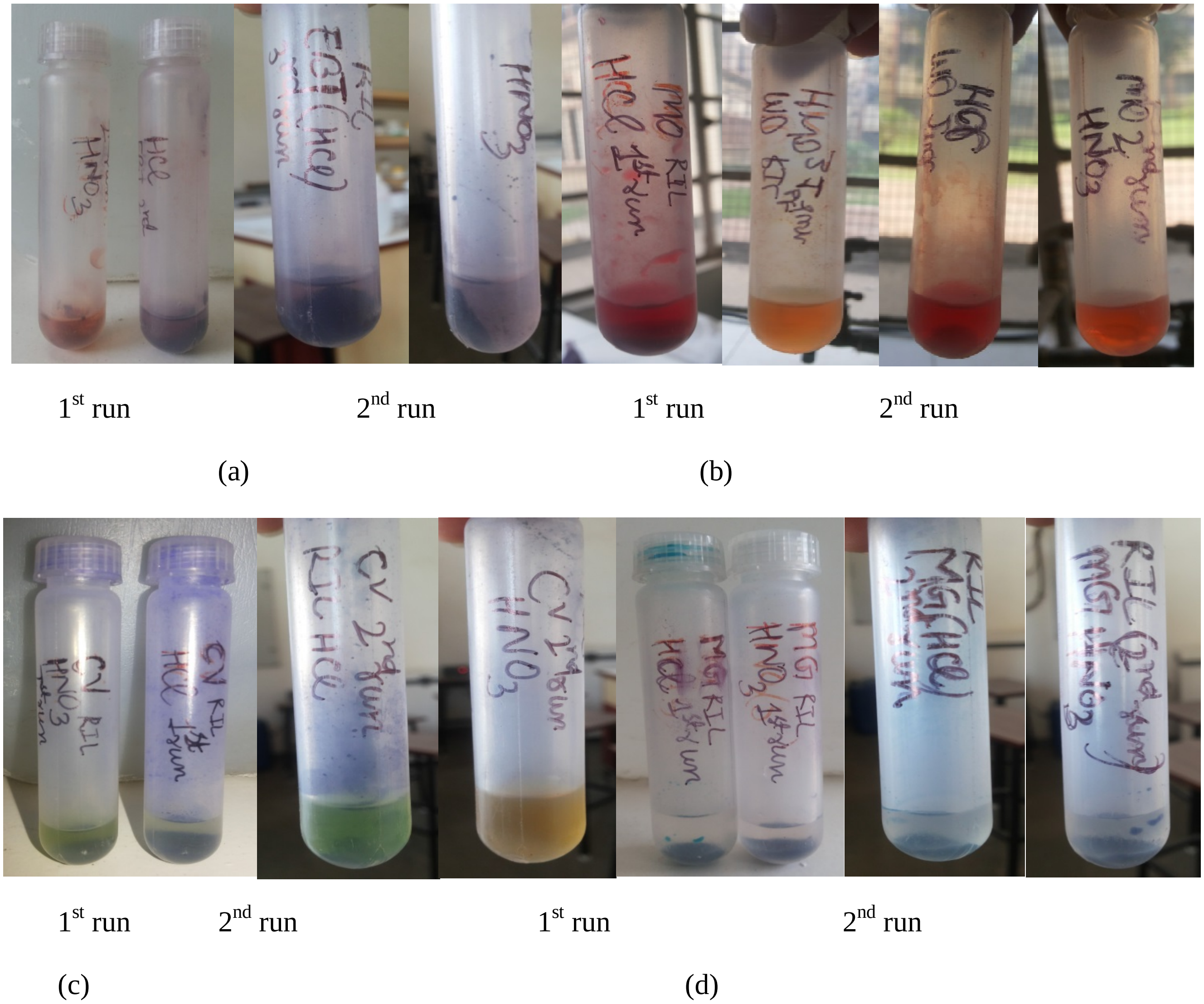
The remaining concentration (in mg) of each dye left in the aqueous phase after the extraction process was determined by measuring the absorbance of aqueous phase in a UV-Vis Spectrophotometer with a wavelength range between 200-700nm. Also, the absorbance of aqueous phase was measured thrice to maintain the accuracy. After that, the percentage extraction efficiency for each dye was calculated by using Equation 2. Pure solutionsof each dye in different concentrations(0-250mg/L) were initially calibrated in terms of absorbance values, which were recorded at the maximum wavelength $(\lambda)_{max.}$= 589 nm (Crystal violet), $(\lambda)_{max.}$ = 464 nm (Methyl orange), $(\lambda)_{max.}$ = 526nm (Eriochrome black T) and $(\lambda)_{max.}$ = 618nm (Malachite green).

$$E = \frac{C_i - C_f}{C_i} \times 100\,\% \quad (2)$$

Where C_i and C_f represent initialand final dye concentration in the aqueous phase respectively.

3.2.4 Recovery of Ionic Liquid based on Reverse Dispersive Extraction

Using IL as a valuable extractant for the DLLE process, recovery, regeneration, and reuse of the IL is of great importance to meet the economy of the process. To regenerate these valuable extraction solvents for the subsequent DLLE process, different acid stripping solutions were investigated. After the general extraction procedure, centrifugation and removal of the upper aqueous phase, two series of 0.5 mL acid stripping solutions (HCl and HNO_3) of 5 mol/100 mL concentrationswere rapidly injected at the end of each round-bottom centrifuge tube by a syringe equipped with a PTFE needle, and a cloudy state was obtained. The mixtures were then centrifuged for 2 min at 4000 rpm. Consequently, an upper colorless layer of IL phase and an underneath aqueous solution containing a blue layer of Crystal violet, an orange layer of Methyl orange, a black layer of Eriochrome black T and a bluish-green layer of Malachite green were obtained in the respective tubes. After separation of two phases, recovery efficiency of each acid stripping solution was measured and compared in terms of IL regeneration for each dye individually.**Fig. 3.2.5** show the regenerated Ionic Liquidsalong with the stripped dyes (EBT MO, CV and MG), for both acid stripping solutions (HCl and HNO_3) till 2nd run.



1st run 2nd run 1st run 2nd run

(a) (b)

1st run 2nd run 1st run 2nd run

(c) (d)

Fig. 3.2.5: Formation of upper and lower phases of regenerated ILs and stripped dyes respectively using HCl& HNO_3 in (a) EBT, (b) MO, (c) CV and (d) MG

CHAPTER 4: RESULTS AND DISCUSSION

4.1 General

This chapter reports Ionic Liquid-Based Dispersive Liquid–Liquid Extraction (IL-DLLE) ofindicator dyes namely Eriochrome black T, Methyl orange, Crystal violet, and Malachite green from its aqueous solutions by using Imidazolium based Ionic Liquids([C_4mim][PF_6]),([C_6mim][PF_6]) and([C_6mim][BF_4]). Several experiments on the extraction of these dyes have been carried out with the above mentioned ILs for many important parameters given in**Table 4.1**. The experimental observations have been used to compute the performance of process in terms of extraction efficiency of IL.

Table 4.1: Variation of different parameters to study extraction efficiencies of indicator dyes

Parameter	Values
Dye concentration (mg/L)	31.25 - 250
Amount of Ionic Liquid (µL)	100 - 225
Volume of disperser solvent (µL)	200 - 700
Salt concentration (%)	5 - 25
pH	2-12
Ionic Liquids (µL)	[C_4mim][PF_6], [C_6mim][PF_6] and [C_6mim][BF_4]
Acid stripping solutions (5 mol/100 mL)	HCl and HNO_3

In general, the selection of an extracting agent is based on two objectives; it must extract analytesof interest efficiently as well as it should meet the process economically. To make the process economical, the selected IL has to be more immiscible in the sample solution, for reducingthe consumption of extraction solvent. The hydrophobicity of IL increases with increase in alkyl chain length on the cation. On the basis of above objectives three Imidazolium based hydrophobic ILs, [C_4mim][PF_6], [C_6mim][PF_6] and [C_6mim][BF_4] have been selected as extracting agents for this study. Since these classes of IL possess both cation as well as anion substituents, that’s why they are capable of removing almost all classes of dyes, including indicator dyes.

The results obtained from the performed experiments in relation to the extraction of selected dyes from aqueous solutions via above mentioned Ionic Liquids are presented in following sections. The presented results are also being discussed accordingly into five main sections, namely “Effect of initial dye concentrations on dye extraction efficiency” has been discussed in Section 4.3. “Effect of pH of aqueous solution on dye extraction efficiency” has been discussed in section 4.4; “Effect of Ionic Liquid (IL) type and amounton dye extraction efficiency” has been discussed in section 4.5; followed by Section 4.6 and 4.7, which are “Effect of dispersing agent concentrations on dye extraction efficiency” and “Effect of salt concentrationson dye extraction efficiency” respectively. Lastly, “Effect of acid stripping solutions on dyeextraction efficiency” has been described in Section 4.8.

Before each extraction, standard calibration curves were drawn at themaximum absorption wavelength,$\lambda_{max.}$ = 526 nm, 464 nm,589 nm and 618 nmfor Eriochrome black T, Methyl orange, Crystal violet and Malachite green respectively to obtain a calibration equationand after each extraction, concentration of the left over dye in the aqueous solution was calculated by substituting the absorbance values obtained from Lambda 35 UV-Vis Spectrophotometer (at$\lambda_{max.}$of each dye)in the above calibrationequation. In the final step, the extraction efficiencies (E) were calculated by the following equation:

$$E = \frac{C_i - C_f}{C_i} \times 100\ \% \quad (3)$$

Where C_i and C_f represent initial and final dye concentrations in the aqueous phase respectively

4.2 Calibration Curves of studied dyes

Before the samples can be analyzed, a standard calibration plot must be produced beforehand. To produce the standard calibration plot, samples of known concentration (0 to 250 mg/L)are prepared.A particular concentration from the above working solutions is selected to determine the maximum absorption wavelength ($\lambda_{max.}$)of the respective dyes and can be easily observed from the highest peak corresponding to the absorbance of that particular concentration. The value of $\lambda_{max.}$ attained can either lie in UV/Visible wavelength region. The calibration curves for Eriochrome black T, Methyl orange, Crystal violet and Malachite green are shown in **Fig.4.2.1, 4.2.2, 4.2.3**, and **4.2.4** respectively.

By identifying the absorbance for each known concentration at$\lambda_{max.}$ of the respective dyes, a standard calibration curve of Absorbance versus Concentration can be drawn, which adheres to the Beer Lambert's Law Equation as shown below:

Absorbance, **A= ε b c**(4)

ε = Molar absorptivity

b = Path length

c = Concentration

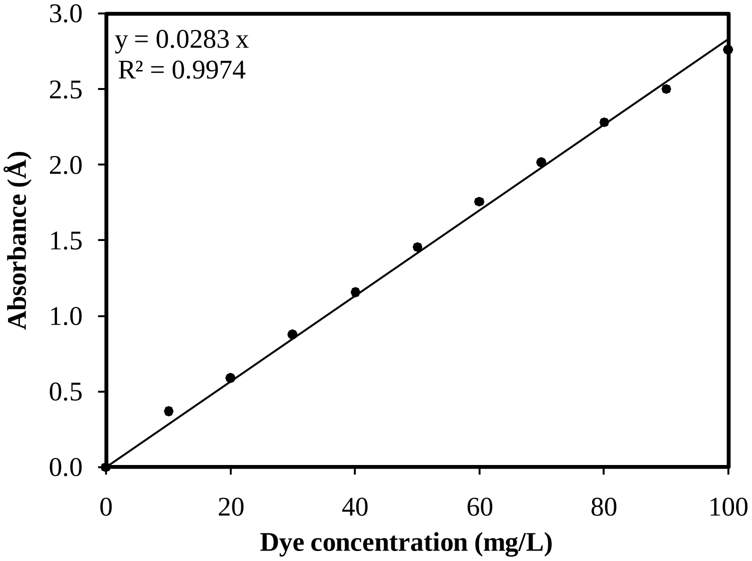


Fig. 4.2.1: Standard calibration curve for Eriochrome black T

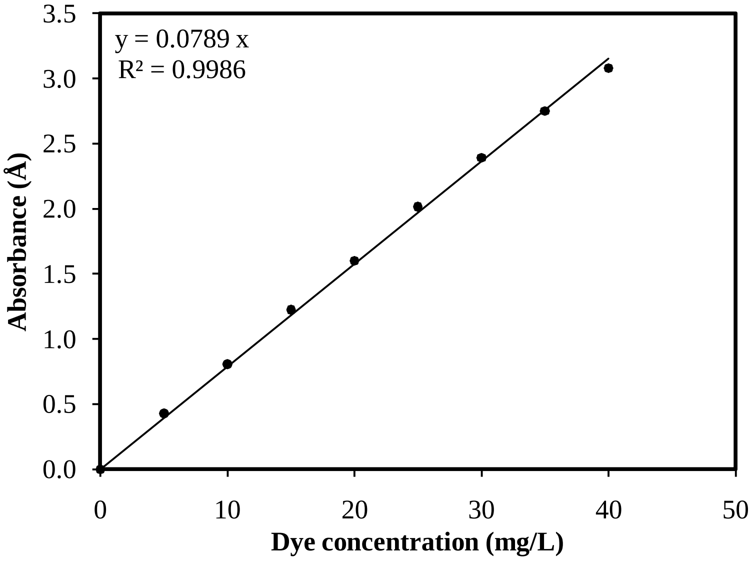


Fig. 4.2.2: Standard calibration curve for Methyl orange

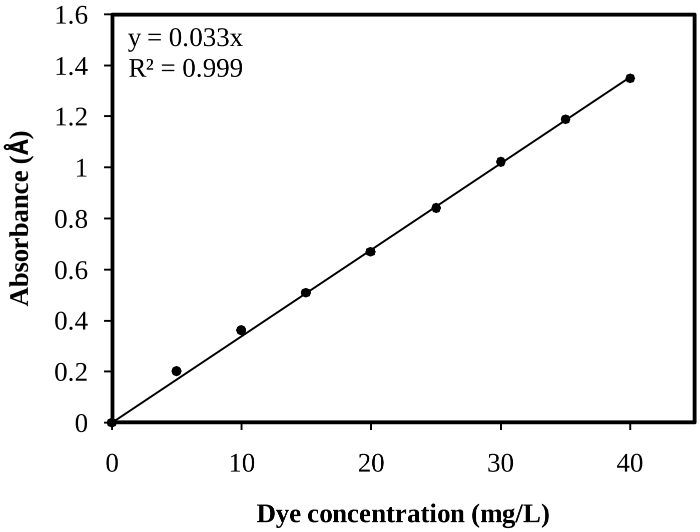


Fig. 4.2.3: Standard calibration curve for Crystal violet

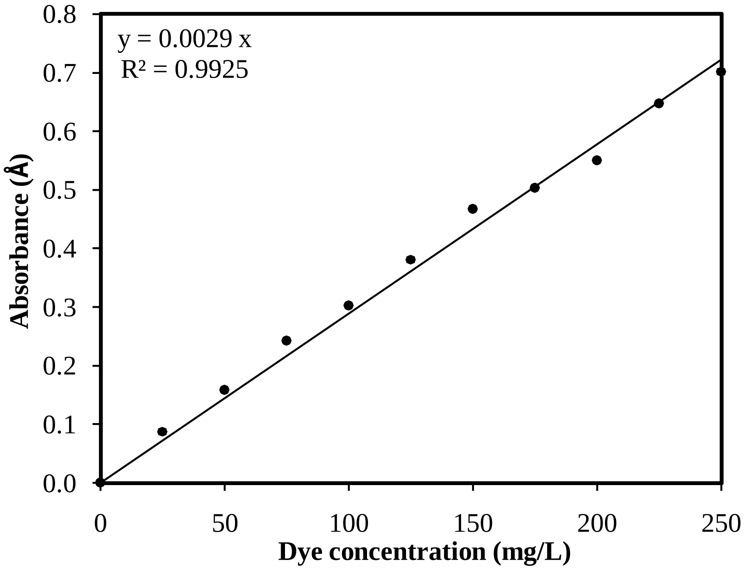


Fig. 4.2.4: Standard calibration curve for Malachite green

4.3 Effect of initial dye concentrationson dye extraction efficiency

In this section, the results retrieved from the performed experiments, which investigate the effect of initial dye concentrations on dye extraction efficiency are being presented and discussed. All dyes are extracted by following the general procedure of Ionic Liquid-Based Dispersive Liquid–Liquid Extraction (IL-DLLE) as described in the Section 3.2.3.

Fig.4.3.1, 4.3.2, 4.3.3 and **4.3.4** show the effect of initial dye concentrations on extraction efficiencies of Eriochrome black T, Methyl orange, Crystal violet, and Malachite green dyes respectively, by using ILs as extracting agents. It has been observed that, as the initial dye concentration increases, extraction efficiency for all the dyes increases till a certain concentration, after that it attains almost a constant value for all the dyes, although this increment is not large. As shown in Fig. 4.3.1 and 4.3.2 for anionic dyes,Eriochrome black T and Methyl orange,[C_6mim][BF_4] gives best results in terms of extraction efficiency as compared to rest of the two Ionic Liquids studied. Minimum extraction efficiency is achieved by using [C_4mim][PF_6]) while [C_6mim][PF_6]shows intermediate value.Equation 5 is the general equation for extraction of anionic dyes in IL.

$$C_n mim^+ X_{IL}^- + Y_{aq}^- \leftrightarrow C_n mim^+ Y_{IL}^- + X_{aq}^- \quad (5)$$

During the extraction of anionic dyes, cation of Ionic Liquid combines with the anionic dye and anion of Ionic Liquid goes in the aqueous phase, so it is required that hydrophobicity of anion of Ionic Liquid should be less and for cation it should be high. Considering the fact that, as the alkyl chain length of IL increases, its hydrophobicity increases. As a result, anionic dye combines better with the long alkyl chain length of IL cation, leaving behind the anionic component of Ionic Liquid in aqueous phase. As previously reported data, out of two anionic components of the selected ILs($[BF_4]^-$ and $[PF_6]^-$), hydrophobicity of $[BF_4]^-$is less as compared to $[PF_6]^-$ [80]. Due to this fact, IL $[C_6mim][BF_4]$ shows best result for both the anionic dyes. Comparing the performance on both the anionic dyes, larger extraction efficiency is attained in case of EBT(99.77%) as compared to MO (82.02%) for all the ILs used.

In the case of cationic dyes (Crystal violet and Malachite green), $[C_4mim][PF_6]$) works best in terms of extraction efficiency out of all the ILs used as shown in Fig.4.3.3 and 4.3.4. The lowest extraction efficiency is achieved by using $[C_6mim][BF_4]$, while $[C_6mim][PF_6]$ shows the intermediate value. The reason behind the above findings may be due to the fact that, during extraction of these dyes, the cationic dye component combines with the anionic component of IL, leaving behind the cationic component of IL in aqueous phase. Equation 6 is the general equation for extraction of cationic dyes in IL.

$$C_n mim^+ X_{IL}^- + Y_{aq}^+ \leftrightarrow Y^+ X_{IL}^- + C_n mim_{aq}^+ \qquad (6)$$

So the favorable situation for extraction of cationic dyesis that, anionic component of IL should be more hydrophobic and cationic component should be less hydrophobic. Both the above requirements are fulfilled in a best way by $[C_4mim][PF_6]$ IL out of all the ILs used. While comparing the performances of $[C_6mim][BF_4]$ and $[C_6mim][PF_6]$ ILs, $[C_6mim][PF_6]$ gives better results because, hydrophobicity of $[PF_6]^-$ is higher than $[BF_4]^-$.Comparing the performance on both the cationic dyes, larger extraction efficiency is attained in case of CV (98.45%) as compared to MG (93.79%) for all the ILs used.

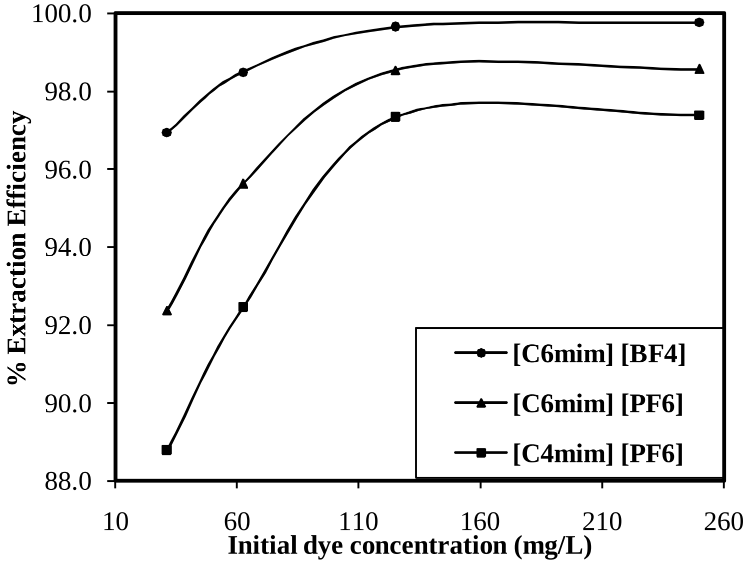


Fig. 4.3.1: Effect of initial dye concentration on the extraction efficiency of EBT

Max. Extraction Eff. = 99.77% at 250 mg/L for [C_6mim][BF_4]. Utilized conditions: IL = 200 µL, Acetate Buffer = 200 µL, Acetone = 500 µL, $NaNO_3$ = 250 µL, make up volume of dye = 5 mL

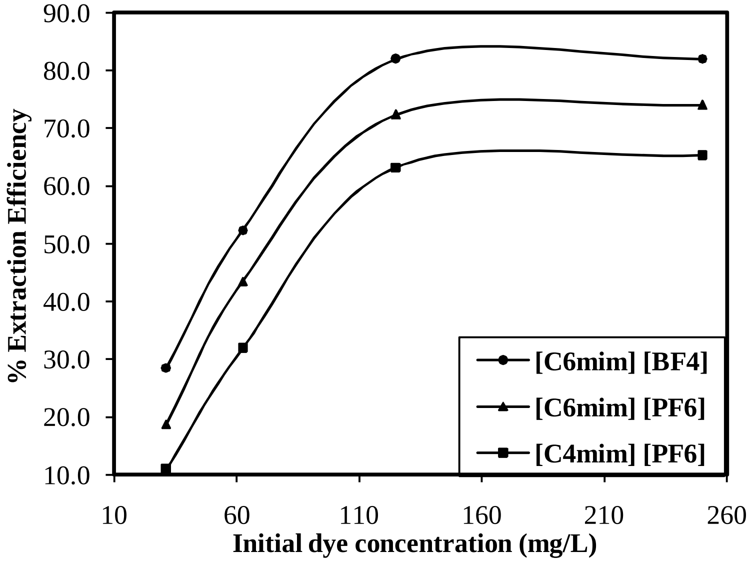


Fig. 4.3.2: Effect of initial dye concentration on the extraction efficiency of MO

Max. Extraction Eff. = 82.02% at 250 mg/L for [C_6mim][BF_4]. Utilized conditions: IL = 200 µL, Acetate Buffer = 200 µL, Acetone = 500 µL, $NaNO_3$ = 250 µL, make up volume of dye = 5 mL

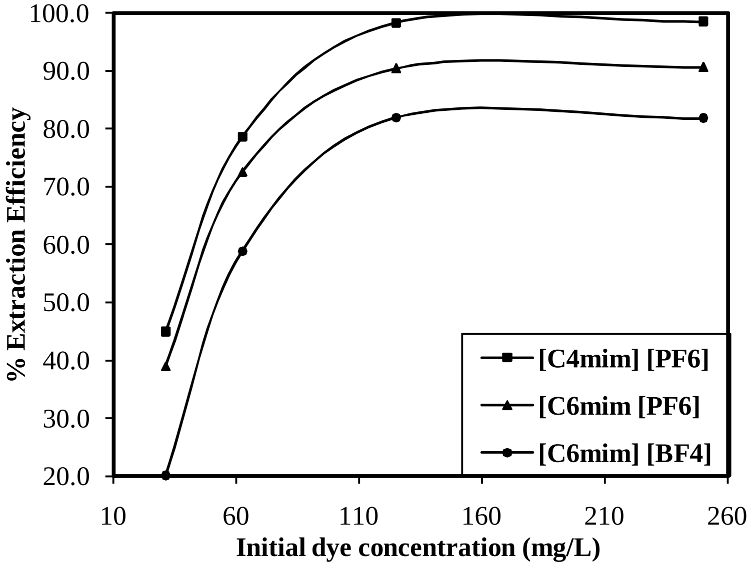


Fig. 4.3.3: Effect of initial dye concentration on the extraction efficiency of CV
Max. Extraction Eff. = 98.45% at 250 mg/L for [C_4mim][PF_6]. Utilized conditions: IL = 200 µL, Acetate Buffer = 200 µL, Acetone = 500 µL, $NaNO_3$ = 250 µL, make up volume of dye = 5 mL

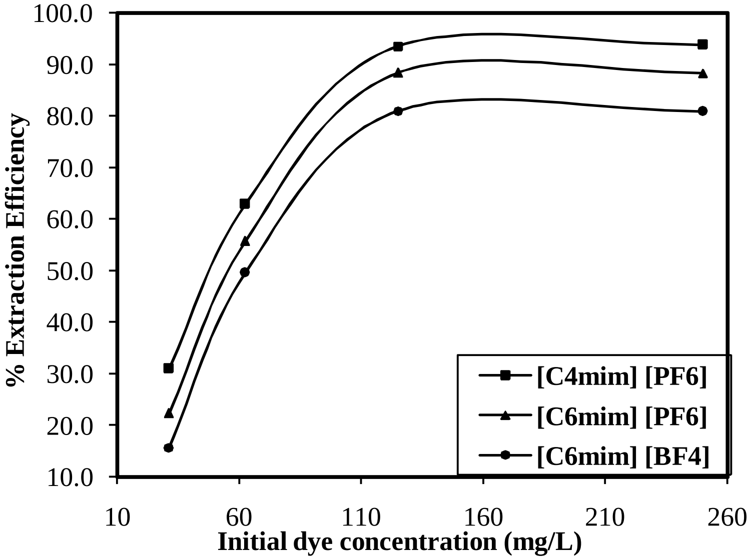


Fig. 4.3.4: Effect of initial dye concentration on the extraction efficiency of MG
Max. Extraction Eff. = 93.79% at 250 mg/L for [C_4mim][PF_6]. Utilized conditions: IL = 200 µL, Acetate Buffer = 200 µL, Acetone = 500 µL, $NaNO_3$ = 250 µL, make up volume of dye = 5 mL

4.4 Effect of pH onDye Extraction Efficiency

Since indicator dyes are sensitive towards pH variation, so the pH dependency of extraction efficiency for different dyes (EBT, MO, CV, MG) are investigated at a constant experimental condition by adding proper amounts of hydrochloric acid or sodium hydroxide solutions, for all the ILs. **Fig. 4.4.1, 4.4.2, 4.4.3** and **4.4.4**show the variation in extraction efficiency of the above dyes for pH ranging from 2-12 by using selected ILs. It is interesting to note that, by changing pH of aqueous phase extraction efficiency varies significantly for all the dyes used. Each dye attains its maximum extraction efficiency at different pH values.

For MO, extraction efficiency increases rapidly as the pH of aqueous solution increases from 2 to 4 for all the ILs used. By further increase in pH, the observed variation in extraction efficiency is not significant. For EBT, with the increase in pH, extraction efficiency increases and attains the maximum value at pH in the range of 5.2-6 for all the ILs used, by further increase in pH extraction efficiency declines for all ILs studied in this work. For CV, with the increase in pH,from 2-4 extraction efficiency increases very rapidly, and on further increase in pH from 4-8 extraction efficiency further increases but the magnitude of increment is not large. By further increasing the pH, it attains almost constant value. In case of MG also, almost similar trend to CV is obtained by increase in pH of aqueous solution.As a result it can be stated that, for cationic dyes best extraction efficiency is observed for neutral to basic aqueous solution while for anionic dyes best extraction efficiency was observed in range of acidic to neutral pH aqueous solution. Due to the above reasons, 7 pH was selected for the subsequent experiments of dye extraction.

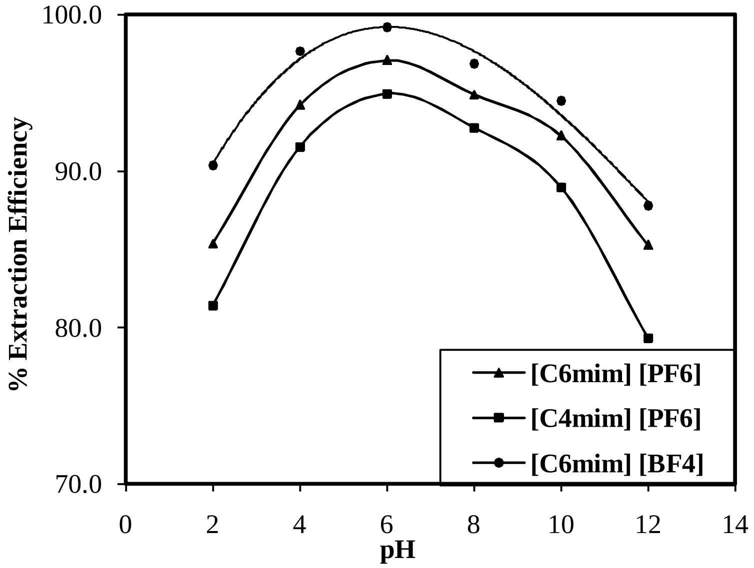


Fig. 4.4.1: Effect of pH on the efficiency of DLLE for EBT removal. Maximum extraction efficiency attained in pH range 5.2-6 for [C_6mim][BF_4]. Utilized conditions: Initial EBT conc. = 250 mg/L, ILs = 200 µL, Acetone = 500 µL,$NaNO_3$ = 250 µL, make up volume of dye = 5 mL

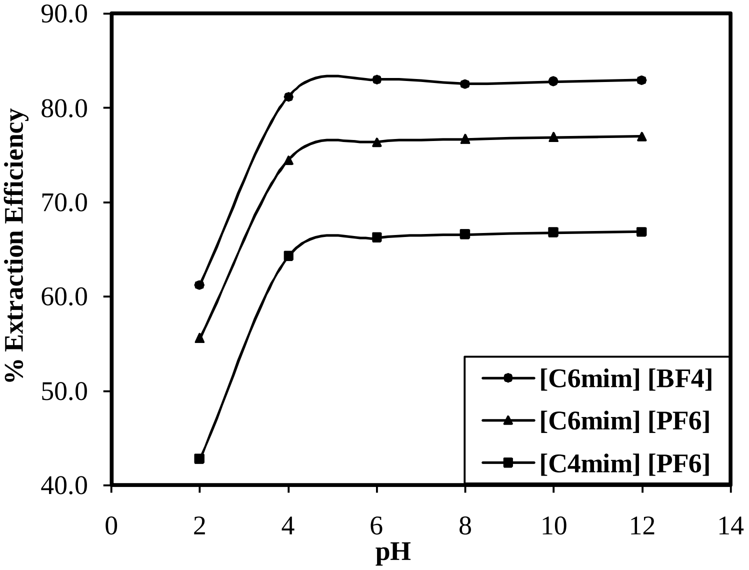


Fig. 4.4.2: Effect of pH on the efficiency of DLLE for MO removal. Maximum extraction efficiency attained in pH range 2-4 for [C_6mim][BF_4]. Utilized conditions: Initial MO conc. = 250 mg/L, ILs = 200 µL, Acetone = 500 µL, $NaNO_3$ = 250 µL, make up volume of dye = 5 mL

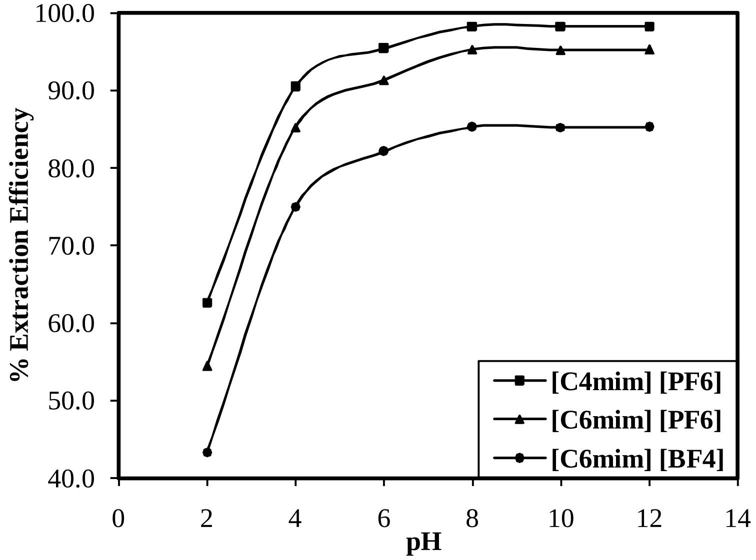


Fig. 4.4.3: Effect of pH on the efficiency of DLLE for CV removal. Maximum extraction efficiency attained in pH range 2-4 for [C_4mim][PF_6]. Utilized conditions: Initial CV conc. = 250 mg/L, ILs = 200 µL, Acetone = 500 µL, $NaNO_3$ = 250 µL, make up volume of dye = 5 mL

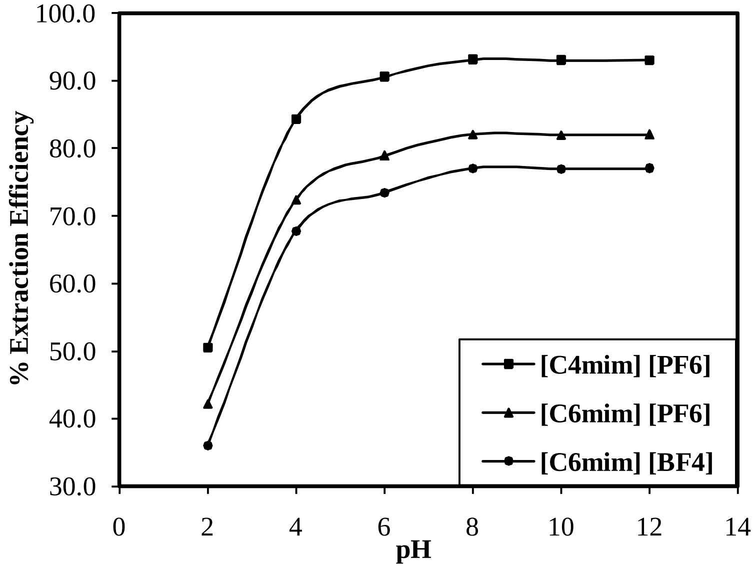


Fig. 4.4.4: Effect of pH on the efficiency of DLLE for MG removal. Maximum extraction efficiency attained in pH range 2-4 for [C_4mim][PF_6]. Utilized conditions: Initial MG conc. = 250 mg/L ILs = 200 µL, Acetone = 500 µL, $NaNO_3$ = 250 µL, make up volume of dye = 5 mL

4.5 Effect of Ionic Liquid (IL) amount on dye extraction efficiency

For successful IL-DLLE of dye, it is idealistic to have a minimum consumption of IL, as well as amaximum extraction yield in the dye removal.For observing the effect of IL amount only two Ionic Liquids [C_4mim][PF_6] and ([C_6mim][BF_4]) were selected for the study which worked best on the cationic and anionic dyes. Effect of these ILs amount is observed for both anionic as well as cationic dyes and it is shown in **Fig.4.5.1, 4.5.2, 4.5.3** and **4.5.4**for different initial dye concentrations (50, 125 and 250 mg/L) in 5.0 mL aqueous solutions.Therefore, from the figures below, it has been observed that, the extraction efficiency increases with increase in initial dye concentration for the given IL concentration range of all the studied dyes. Also, the results obtained from the following figures show that, the % extraction efficiency obtained for different initial concentrations of each studied dye is directly proportional to the amount of IL utilized. In other words, the extraction efficiency for different initial concentrations of all the studied dyes increases with increase in the amount of IL utilized.This increment is minimum in case of EBT and maximum in case of MG, while CV and MO showed intermediate increments for all range of initial dye concentrations studied.Moreover, at lower dye concentration (50 mg/L), increment in extraction efficiency with increase in IL amount is very low. It has been observed that for dye concentrations higher than 50 mg/L, extraction of all the dyes increases when the amount of the IL increases from 150 to 200 µL. Hence fromthe following figures, it may be concluded that, for quantitative extraction (> 95%) of EBT & CV; and (> 80-90%) of MO and MG at initial dye concentrations of 125 and 250 mg/L, optimum required amounts of IL are varied from about 150 to 200 µL/5 mL.

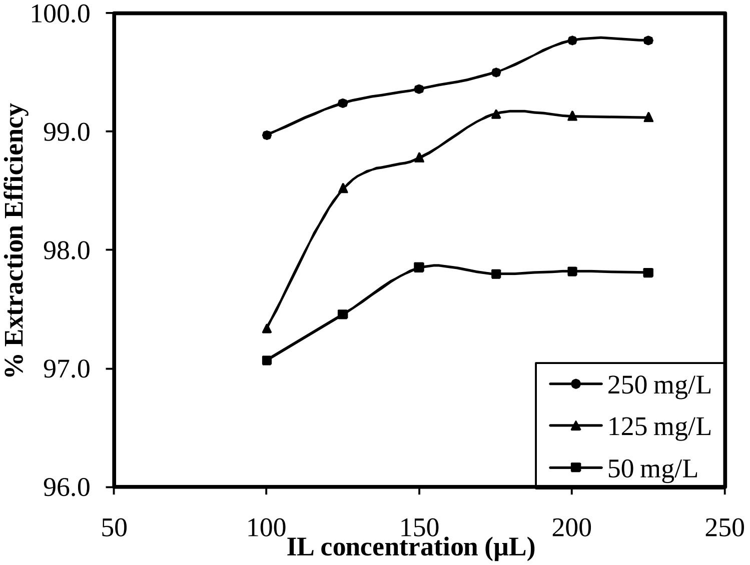


Fig. 4.5.1: Effect of amount of [C_6mim][BF_4] on the efficiency of DLLE at initial concentrations of EBT (50, 125 & 250 mg/L).Utilized conditions**:** $NaNO_3$ = 250 µL, Acetone = 500 µL, Acetate buffer = 200 µL, Make up vol. of dye = 5 mL

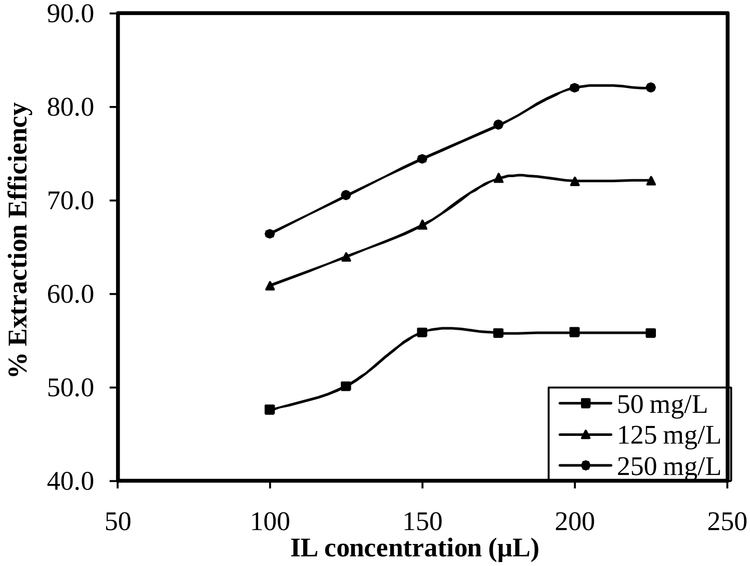


Fig. 4.5.2: Effect of amount of [C_6mim][BF_4] on the efficiency of DLLE at initial concentrations of MO (50, 125 & 250 mg/L).Utilized conditions**:** $NaNO_3$ = 250 µL, Acetone = 500 µL, Acetate buffer = 200 µL, Make up vol. of dye = 5 mL

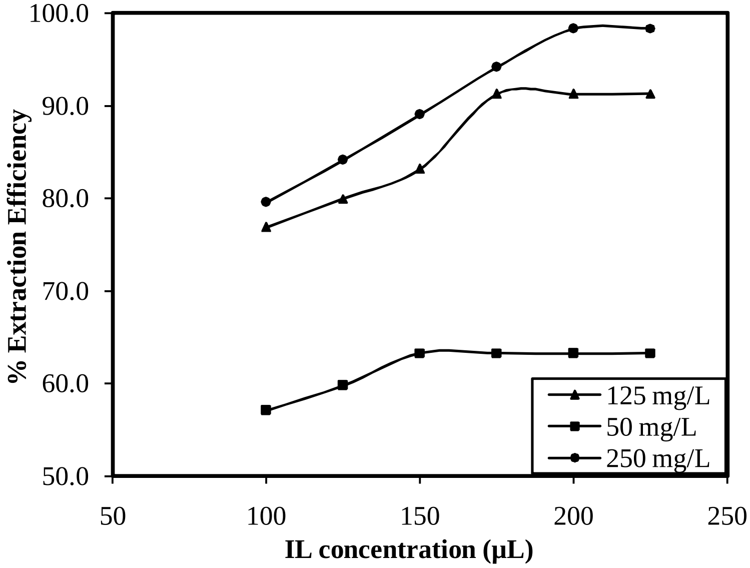


Fig. 4.5.3: Effect of amount of [C_4mim][PF_6] on the efficiency of DLLE at initial concentrations of CV (50, 125 &250 mg/L).Utilized conditions**:** $NaNO_3$ = 250 µL, Acetone = 500 µL, Acetate buffer = 200 µL, Make up vol. of dye = 5 mL

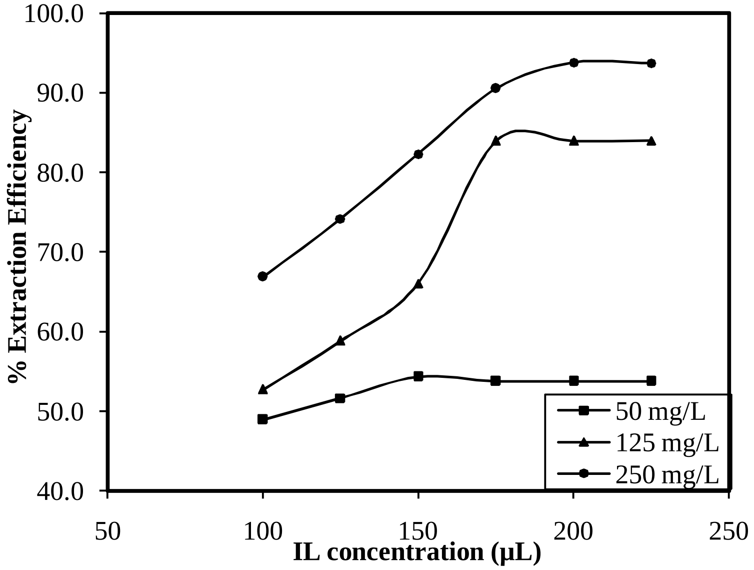


Fig. 4.5.4: Effect of amount of [C_4mim][PF_6] on the efficiency of DLLE at initial concentrations of MG (50, 125 & 250 mg/L).Utilized conditions**:** $NaNO_3$ = 250 µL, Acetone = 500 µL, Acetate buffer = 200 µL, Make up vol. of dye = 5 mL

4.6Effect of dispersing agent concentrations on dye extraction efficiency

While selecting a disperser solvent, its miscibility must be kept in mind. Generally, dispersant must be miscible with both extractant and aqueous solution.Since acetone has the ability to dissolve ILs in a better manner than any other organic solvent, therefore it has been selected as a suitable disperser solvent in the current experiment. Since [C_4mim][PF_6] IL worked best on cationic dye Crystal violet (98.45%)and [C_6mim][BF_4] IL worked best on anionic dye Eriochrome black T (99.77%), therefore for observing the effect of dispersing agent,only these combinations were adopted for subsequent experimentation.

Different volumes of this dispersant in the range of 200-700 µL with the addition of 100 µL of [C_4mim][PF_6] and [C_6mim][BF_4] were examined for the extraction of Crystal violet and Eriochrome black T respectively at the low level initial concentrations of 50 mg/L.Similar volumes with the addition of 200µL [C_4mim][PF_6] and [C_6mim][BF_4] were examined for the extraction of above dyes, atthe high level initial concentration of 250 mg/Lfrom 5.0mL aqueous samples.Although the general trend for the effect of dispersing agent concentrations on the extraction efficiencies of both high and low level initial dye concentrationscould not be predicted from the **Fig. 4.6.1** and **4.6.2**, but it can be clearly observed from these figures, that the extraction efficiencies obtained for the low level initial dye concentration (50 mg/L) are less as compared to the high level initial dye concentration (250 mg/L). As it is visible from both the figures that highest extraction efficiency is achieved at 500 µL of disperser solvent, hence 500 µL was selected as the proper volume of dispersant for both low and high level initial concentrations of CV and EBT.

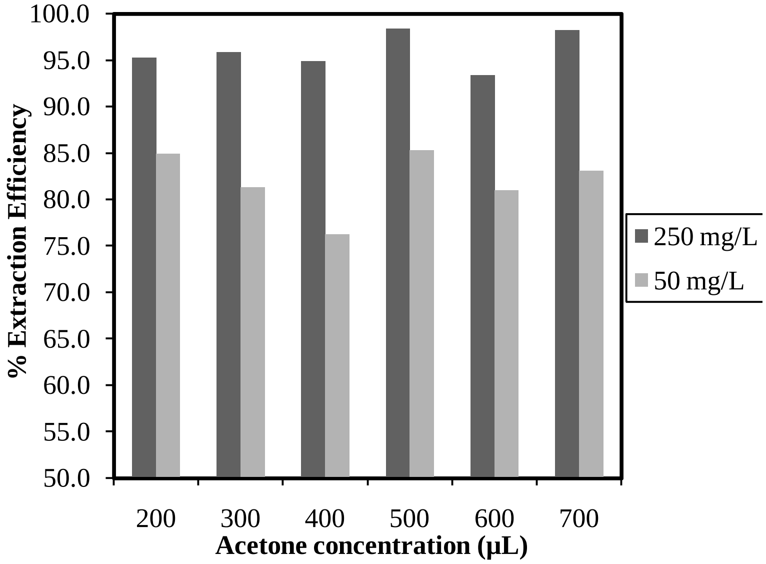


Fig. 4.6.1: Effect of dispersing agent concentrations on the efficiency of DLLE at initial low level (50 mg/L) and high level (250 mg/L) concentrations of CV.Utilized conditions**:** $NaNO_3$ = 250 µL, Acetate buffer = 200 µL, [C_4mim][PF_6] = 100 µL for 50 mg/L & 200 µL for 250 mg/L, Make up vol. of dye = 5 mL

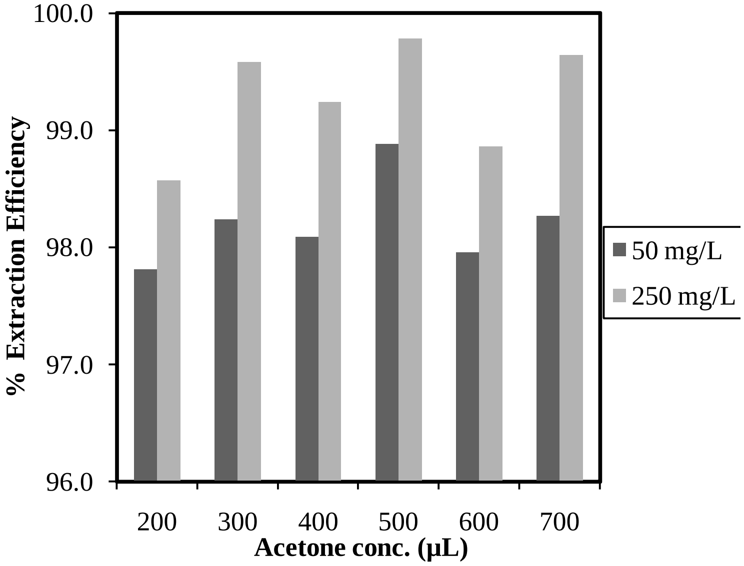


Fig. 4.6.2: Effect of dispersing agent concentrations on the efficiency of DLLE at initial low level (50 mg/L) and high level (250 mg/L) concentrations of EBT. Utilized conditions**:** $NaNO_3$ = 250 µL, Acetate buffer = 200 µL, [C_6mim][BF_4] = 100 µL for 50 mg/L & 200 µL for 250 mg/L, Make up vol. of dye = 5 mL

4.7Effect of salt concentrations on dye extraction efficiency

The effluent streams of textile industries are generally associated with different salts. To understand the effect of salt concentration on dye extraction efficiency, experiments are conducted for different salt ($NaNO_3$) concentrations ranging from 5% to 25% w/v(1 g/200 mL-5 g/200 mL) at different initial dye concentrations (50, 125 and 250 mg/L) for Crystal violet and Eriochrome black T dyes using [C_4mim][PF_6] and [C_6mim][BF_4]ILs respectively. It is observed from **Fig. 4.7.1** and **4.7.2**that, the effect of salt concentration on extraction efficiency is different for CV and EBT. For any of the dye, no significant variation in extraction efficiency is observed by change in salt concentration at any of the initial dye concentration.In case of CV, for the highest initial dye concentration (250 mg/L), maximum extraction efficiency was obtained at 10% salt concentration (2 g/200 mL), while for the intermediate and lowest initial dye concentration (125 and 50 mg/L), maximum was obtained at 20% salt concentration (4 g/200 mL).In case of EBT, for the highest initial dye concentration (250 mg/L), maximum extraction efficiency was obtained at 5%salt concentration (1 g/200 mL), while for the intermediate and lowest initial dye concentration (125 and 50 mg/L), maximum was obtained at 10% salt concentration (2 g/200 mL).

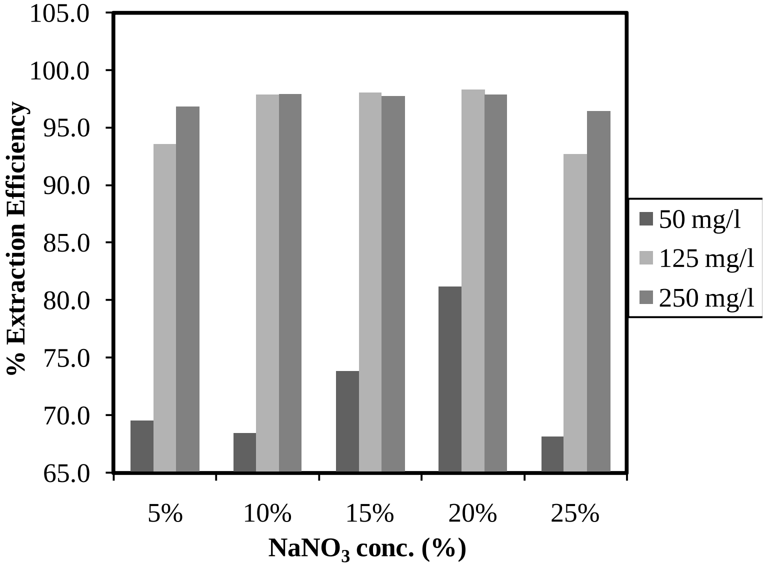


Fig. 4.7.1: Effect of salt concentrations on the efficiency of DLLE at initial concentrations of CV = 50, 125 and 250 mg/L.Utilized conditions**:** Acetate buffer = 200 µL, [C_4mim][PF_6] = 200 µL, Acetone = 500 µL, make up vol. of dye = 5 mL

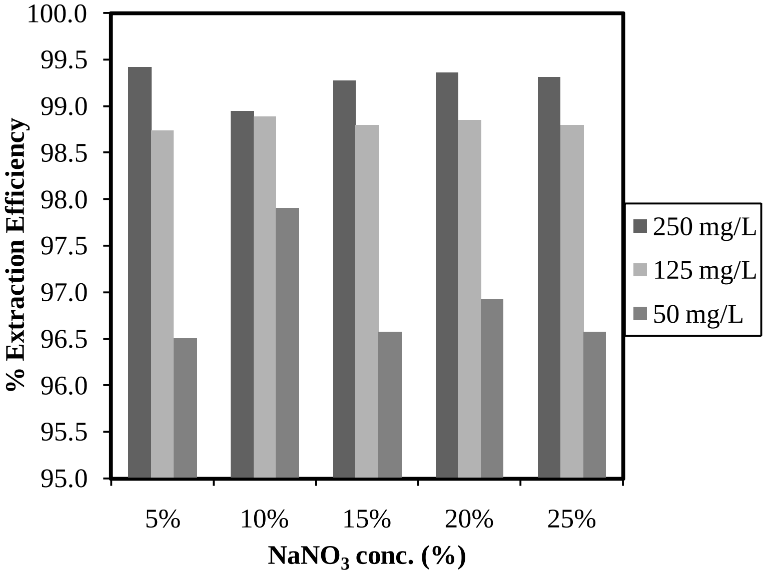


Fig 4.7.2: Effect of salt concentrations on the efficiency of DLLE at initial concentrations of EBT = 50, 125 and 250 mg/L.Utilized conditions**:** Acetate buffer = 200 µL, [C_6mim][BF_4] = 200 µL, Acetone = 500 µL, make up vol. of dye = 5 mL

4.8 Effect of Acid stripping solutionson Reverse DLLE

The effect of two acid stripping solutions (HCl and HNO_3) of 5 mol/100 mL concentration was observed individually on the mixture of extracted dyes and ILs ([C_6mim][BF_4] IL with EBT & MO; [C_4mim][PF_6] IL with CV & MG). Although both types of acid stripping solutions were found suitable for regeneration of all the ILs, HCl was observed as a better stripping agent for anionic dyes (EBT & MO) and HNO_3 for cationic dyes (CV & MG) as shown in the**Fig. 4.8.1** and **4.8.2**. The regenerated ILs were tested again for extraction of fresh dye solutions, and extraction efficiencies were estimated again. This process was repeated twice and considerable good results were observed (**Fig. 4.8.3**). It is visible from figures that very little drop in extraction efficiency is obtained while re-using the regenerated ILs in subsequent runs. On the basis of these results, it can be concluded that IL is an economical extracting agent for dye extraction.Besides presenting the results and discussing on the aforementioned six parameters, **Table 4.8**will highlight on the "Comparison between characteristic performance of IL-DLLE (Ionic Liquid-Based Dispersive Liquid–Liquid Extraction) and other IL-based methods of Dye removal".

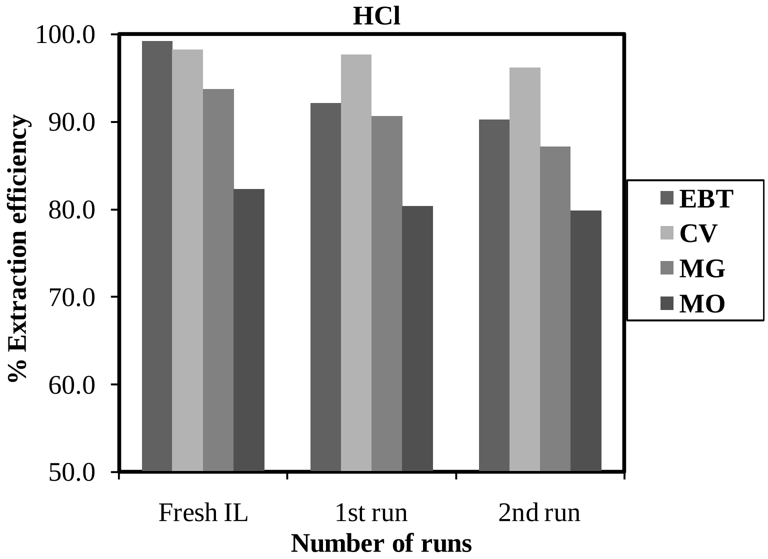


Fig. 4.8.1: Effect of Acid stripping solution (HCl) on the efficiency of reverse DLLE. Utilized conditions: HCl = 0.5 mL, Acetate buffer = 200 µL, $NaNO_3$ = 250 µL (10% w/v), Acetone = 500 µL, vol. of Regenerated IL ([C_6mim][BF_4]) reused for 1st& 2nd run = 200 µL, make up vol. of each dye = 5 mL

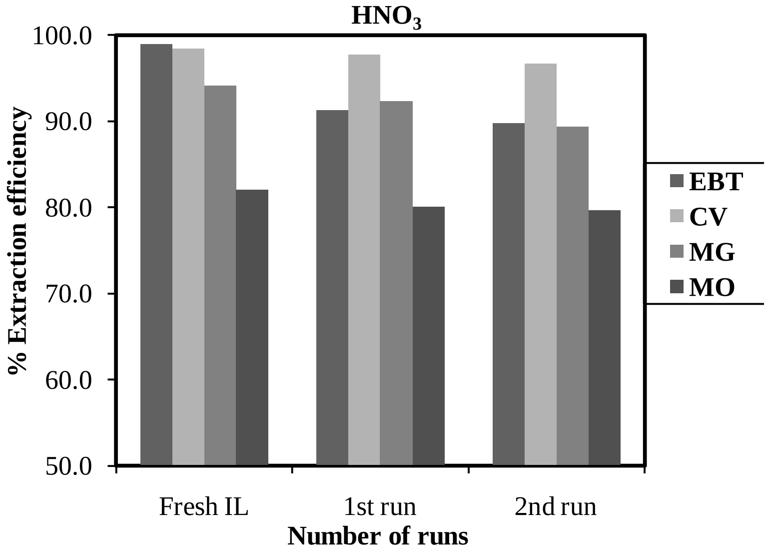


Fig. 4.8.2: Effect of Acid stripping solution (HNO_3) on the efficiency of reverse DLLE. Utilized conditions: HNO_3 = 0.5 mL, Acetate buffer = 200 µL, $NaNO_3$ = 250 µL (10% w/v), Acetone = 500 µL, vol. of Regenerated IL ([C_4mim][PF_6]) reused for 1st& 2nd run = 200 µL, make up vol. of each dye = 5 mL

Table 4.8 Characteristic performance data obtained by using IL-DLLE and other IL-based methods for dye removal

Method	**IL (extractant)**	**Dye**	**pH of aq. phase**	**Max. Ext eff (%)**	**Sample vol. (mL)**	**IL vol. used (μL)**	**Initial dye conc. (mg/L)**	**Ext time (min)**	**Re-generating method**	**Ref.**
DLLE	$[C_6mim][BF_4]$	Eriochromeblack T	7	99.77	5.0	200	250	5	Reverse-DLLE with acidic stripping solutions (5.0 mol/L of HCl or HNO_3)	This work
	$[C_6mim][PF_6]$	Methyl orange		82.02						
		Crystal violet		98.45						
	$[C_4mim][PF_6]$	Malachite green		93.79						
LLE				99						
		Methyl orange							Addition of aqueous HCl solution (1.0 mol/L), 1-pentanol or isopropyl alcohol with 0.1 mol/L	[49]
	$[C_4mim][PF_6]$									
			6	100	5.0	1000	1000	>35		
		Eosin yellow		69						
LLE	$[C_6mim][PF_6]$	Orange G	1-8	92.87						
		Acid Yellow RN	1-12	60.21	10		100	60		
						1000				
	$[C_6mim][BF_4]$	Weak acid brilliant blue	3.5-7.5	81.59						[81]
LLE	$[C_8mim][PF_6]$	Reactive black		50	1.0		0.166	30		
			3	25						
	$[C_4mim][PF_6]$	Blue dye				500				[47]
		Red dye							Washing with iso-propyl alcohol/water (1:1 v/v)	
	$[P_{14}][Tf_2N]$									

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1Conclusions

In this study, a novel separation method; IL-DLLE (Ionic Liquid based dispersive liquid-liquid extraction) was adapted for the separation of anionic as well as cationic dyes. Two anionic dyes (Eriochrome black T &Methyl Orange) and two cationic dyes (Crystal violet&Malachite Green) were selected for this study to compare the performance of different Ionic Liquids. Three imidazolium based ionic liquids- ([C_4mim][PF_6]),([C_6mim][PF_6]) and ([C_6mim][BF_4]) were used as extracting agent for this study. On the basis of performance of above mentioned Ionic Liquids on anionic and cationic dyes and other studied parameters following conclusions are drawn.

Cationic as well as anionic components of Ionic Liquids play important role in dye extraction. For the extraction of anionic dyes (EBT & MO), the hydrophobicity of anionic component of theselected Ionic Liquid should be less and for cationic component, it should be high. While the favorable situation for extraction of cationic dyes (CV & MG) is that, the anionic component of IL should be more hydrophobic and cationic component should be less hydrophobic.The extraction efficiency of dyes increases with increase in initial dye concentration and then attains almost a constant value at fixed operating conditions for both classes of dyes. Results showed that, out of all three, [C_6mim][BF_4] IL worked best for anionic dyes, [C_4mim][PF_6] IL worked best for cationic dyes while [C_6mim][PF_6] showed intermediate results.pH of the aqueous phase affects the extraction efficiency of dyes very strongly. For cationic dyes best extraction efficiency was observed for neutral to basic aqueous solution while for anionic dyes best extraction efficiency was observed in range of acidic to neutral pH aqueous solution.The type and amount of IL also produced a significant effect on the extraction efficiency of dyes. Extraction efficiency was found toincrease with increase in the amount of IL utilized and this increment wasminimum in case of EBT, maximum in case of MG, while CV and MO showed intermediate increments for all range of initial dye concentrations. The dispersing agent and salt concentrations showed no significant trend in the extraction efficiencies of CV and EBT, for all range of initial dye concentrations.

To make the process cost-effective, a Reverse Dispersive Liquid-Liquid Extraction process was adapted for the regeneration of used IL. Two acid stripping solutions were employed for this purpose. The IL was successfully regenerated from the IL+ dye mixture and re-used for the extraction of fresh dye solutions. The regenerated ILs also resulted in high extraction efficiencies for all the dyes studied. On the basis of these results, it is hereby concluded that, IL-DLLE is an efficient, simple, economical and fast method for dye extraction.

5.2 Recommendations

From the above conclusions, it is recommended to perform the operation in continuous mode and its efficiency should be evaluated. In order to check the suitability of process for industrial applications for removal of various dyes from waste streams,pilot scale study is recommended. This method holds a good future prospect on economics point of view, because appreciable IL regeneration efficiencies were obtained in the subsequent runs. The process efficiency and economics can be enhanced by employing alternative technologies that ensure complete removal of aqueous phase, thus allowing effective recovery of the lost IL for maximum number of regeneration cycles. IL regeneration by using more environmentally benign acid stripping solutions should also be tried.

As explained earlier structural differences between anionic and cationic dyes lead to differences in the way they are extracted by the Ionic Liquids. The extraction of cationic dyes is favoured by smaller IL cations and more hydrophobic anions, while extraction of anionic dyes is favoured by a larger IL cation and a less hydrophobic anion. On the basis of above conclusion it is recommended to select the best suitable IL for extraction of any dye before experimentation. Moreover, IL-DLLE process should also be used on other potentially harmful dyes and different ILs.