Abstract
This Chapter deals with the removal of dyes from aqueous media by C₈PyDs. Like metal ion removal, effect of various parameters such as pH, amount of IL loading etc. on % dye removal from water is discussed. Due to gel kind of nature, the dye adsorption isotherm follows Langmuir model which shows that C₈PyDs has identical adsorption cites. Both cationic and anionic dyes are used for this study. The amount of dye present before and after C₈PyDs treatment is determined by using UV-Vis spectroscopy.
3b.1 Introduction

In recent years, the removal of contaminations from industrial waste water is in great demand. The industrial effluents contain dye molecules, metals, organic/inorganic compound and toxic materials. Some of them are responsible for a significant amount of water and soil pollution, which have been found to contribute to decrease environmental and economic concerns. Parallely, government legislation is becoming more stringent in most part of the world regarding the removal of pollutants from industrial effluents, which in turn becoming an increasing problem for the industries. This means that for most industries developing on-site or in-plant facilities that treat their own effluents before discharge is mandatory. Therefore, removal of pollutant from water is the crying need of the society and developing a cost effective and environmentally safe method to achieve the same is a challenging task for researcher. After all it’s the future of mankind which is at stake.

Dye is a color substance that has an affinity to the substrate to which it is being applied. Because of this, dye and dye stuffs are extensively used in various areas such as textile, plastic, food, cosmetic, carpet and paper industries. The effluents of these industries contain dye along with other toxic or nontoxic pollutants which affects aquatic environment. Charges of such wastes in environmental water bodies causes damage to ecological balance. Even small quantities of dyes can color large water sources, which not only affects aesthetic merit but also reduces light penetration and photosynthesis. This ultimately causes risks to the human health and also aquatic biota. Because of this reason several governments have established environmental restrictions with regard to the quantity of colored waste water and this obligated industries to remove dyes from their effluents before discarding. Consequently, dyes containing waste water should be treated before discharge.

Since, last two decades synthetic dyes have been increasingly used compared with natural dyes because of their ease of use in expensive cost of synthesis, stability and variety of color. These dyes are extensively use in the various industries. Today there are more than 10,000 dyes available commercially, out of these most of them are difficult to biodegrade due to their complex aromatic molecular structure and synthetic process. Azo dyes are one of the most widely used synthetic dyes (more than 70% of total) in the textile food, pharmaceutical, paper and printing, leather and cosmetic industries. They are
commonly prepared by coupling a diazotized aromatic amine with a phenol or other aromatic amine. Therefore, the degradation of azo dyes under anaerobic conditions produces aromatic amines, which have been banned because of their high toxicity and carcinogenicity.\textsuperscript{11,12} Consequently these dyes have become a major environmental concern. Many of these azo dyes find their way into the environment via waste water facilities and due to their recalcitrant nature, these dyes often pass through activated sludge facilities with little or no reduction in color.

Conventional waste water treatment methods for removing dyes included physicochemical, chemical and biological methods such as adsorption,\textsuperscript{13} coagulation and flocculation,\textsuperscript{14} oxidation and ozonation,\textsuperscript{14a,14b,15} membrane separation,\textsuperscript{14b,16} electrochemical techniques,\textsuperscript{17} fungal decolorization,\textsuperscript{18} and photocatalytic degradation.\textsuperscript{19} There is evidence that all three areas have potential for remediating dye house wastes. The fundamental principles of these techniques along with their merits and demerits are given in following parts.

3b.1.1 Adsorption methods

Adsorption is the adhesion of atoms, ions, molecules of gas, liquid or dissolved solids to a surface and as results of this it creates an accumulated layer in form of thin film. As it is a surface phenomenon, affects surface energy. The atoms on the surface of the adsorbent are not solely surrounded by other atoms and because of this it can attracts adsorbates. The real nature of the bonding depends on the nature of adsorbent as well as atoms or species involved in it. The adsorption is mainly classified as follows:

(i) \textit{Physisorption}: here adsorption of adsorbate on surface through van der walls interactions.

(ii) \textit{Chemisorption}: here adsorption through a chemical bond between molecules of adsorbate and surface.

Generally adsorption takes place on the wall or at specific sites of the adsorbents. As the pores are normally small, the internal surface area is greater than the external surface area, separation occurs due to the differences in molecular weight, shape or polarity cause some molecules to be held more strongly on the surface than others.\textsuperscript{20} As a consequence adsorption techniques have been found to be one of the most prominent and economic methods for the treatment of dyes from waste water.\textsuperscript{1,21} Adsorption produces a high
Chapter 3(b)

quality product and is a process which is economically feasible.\textsuperscript{22} Decoloration using adsorption is a result of two mechanism, adsorption and ion exchange.\textsuperscript{23} Therefore it is influence by many physicochemical factors, such as dye/sorbent interaction, sorbent surface area, particle size, temperature, pH and contact time.\textsuperscript{24}

Adsorption using activated carbon is the most commonly used method for dye removal and is very effective for adsorbing cationic, mordant and acid dyes and to a slightly lesser extent dispersed, direct, vat, pigment and reactive dyes.\textsuperscript{25} However, its high cost and difficulty of regeneration restrict its utilization. Moreover, like activated carbon many other dye removal treatments is well suited for one particular waste system and ineffective in another. Recently, many studies have been conducted to investigate the adsorption capacities of some low cost bio-adsorbents sugar cane bagasse,\textsuperscript{26} modified cellulose and lignin,\textsuperscript{27} orange peel,\textsuperscript{28} apple porname,\textsuperscript{29} coconut husk,\textsuperscript{30} lorfia egyptiaca,\textsuperscript{31} peanut hull,\textsuperscript{32} and bio polymers like chitosan.\textsuperscript{33} These bio-adsorbents other than biocopolymer like chitosan were found to have greater affinity for cationic dyes than anionic dyes in both single and binary system.\textsuperscript{34} Despite of extensive use, adsorption methods have main drawback of production of solid polluted waste. Because the regeneration of dyes from the super adsorber like activated carbon is quite difficult or tedious. Therefore, recently researchers are now concentrating on a super adsorbent which is biodegradable as well as easy in re-collection of dye from their surface.

3b.1.1.1 Chemical method

Coagulation or flocculation combined with floatation and filtration, electro floatation, electro kinetic coagulation, conventional oxidation methods by oxidizing agents (ozone), irradiation or electrochemical processes are examples of chemical methods. Therein, flocculation or coagulation is normally used in combination with other methods. Therefore, flocculation is regarded as one of the most successful and widely used purification techniques to produce better purification owing to its low cost and high efficiency.\textsuperscript{35,36} Recently, extensive attention has been given to flocculation method based on natural polymer, owing to their eco-friendliness, biodegradability and free of secondary pollution risk.\textsuperscript{35b,37,38} Among all natural polymer, chitosan based flocculants have attracted great interest and been widely applied in many field.\textsuperscript{14a,35a,39} Due to cationic nature, chitosan is suitable for eliminating anionic dyes\textsuperscript{14a} and because of this their use is very limited as most of the textile colorant effluents are mixture of cationic,
anionic or metal complex dyes. Apart from this, the chemical techniques including membrane separation and flocculation are often expensive and there is possibility that a secondary pollution problems will arise because of excessive chemical use. Therefore, now a day chemical methods are less industrially viable methods.

3b.1.1.2 Biological method

Dyestuffs are generally difficult to biodegrade and many substances are unsuitable for conventional biological treatment. Recently, biological substrates were used in decoloration or degradation by adsorption process. Since, last one decade, there are reports in which white rot fungi and other microbial cultures were employed for decoloration of dye effluents from industries.

The white-rot fungi use a highly non specific free radical mediated process which requires enzymes to degrade lignin and structurally related compounds. These enzymes are able to catalyze a variety of oxidation and reductions reactions as well as also produce highly Reactive Oxygen Species (ROS). The non specific mechanisms used by these fungi allow them to degrade a wide array of pollutant substances resembling lignin or its derivatives.\(^1\)\(^,\)\(^4\)\(0\) The ability of wood rotting fungi to degrade a wide range of synthetic chemicals, including dyes has been reported. They can mineralize xenobiotic materials to \(\text{CO}_2\) and \(\text{H}_2\text{O}\) through their highly oxidative and non specific ligninolytic system.\(^4\)\(1\) Kirby et. al. have shown that \(P.\ Chrysosporium\) had the ability to decolorise artificial textile effluents by up to 99% within 7 days.\(^4\)\(2\) Moreover, white-rot fungi are able to degrade dyes using enzymes such as lignin peroxidises. Other enzymes used for this purpose include \(\text{H}_2\text{O}_2\)-producing enzymes such as glucose-1-oxidase and glucose-2-oxidase along with laccase and a phenoloxidase enzyme.\(^4\)\(2,\)\(^4\)\(3\)

In case of azo dye, microorganisms cleave the azo bonds of the respective azo dye and produce decolorized products.\(^4\)\(4\) Bacterial degradation of azo dyes is carried out mostly anaerobically with only a few strains being capable of degradation under aerobic conditions. In both cases colorless and possibly toxic aromatic amines are formed.\(^4\)\(4,\)\(^4\)\(5\) The white-rot fungi have been reported to efficiently degrade azo dyes without the formation of aromatic amines.\(^4\)\(6\) The main drawback of this white-rot fungi root is the use of enzyme during decoloration process because enzymes are only active under specific environment. While the industrial effluents have variable nature in terms of pH, acidity,
metal content etc. therefore, the utilization of these fungi in their natural environment means that they are more effective in solid state fermentation only.\(^1\)

Other biological method is the use of microbial cultures from wide variety habitats to decolorise the dye molecules. Knapp et. al. reported decolorisation of the diazo linked chromophore of dye molecules in 15 days.\(^47\) The anaerobic bacteria as a free growing cells or in the form of biofilms on various support used to decolorized a mixture of dyes in 24-30 hrs.\(^48\) Ogawa and Yatome also demonstrated the use of bacteria for azo dye biodegradation.\(^49\) Similarly, there are numerous reports on utilization of various microbial culture including yeasts, for decoloration of dyes.\(^50\) But the main drawback of these microbial systems is requiring a fermentation process, and therefore, they are unable to cope with larger volume of textile effluents. Biosorption is a another kind of biological method, where living/dead microbial mass has been used for adsorption of dyes.\(^51\) Their basic mechanism is the same as physic-adsorption method except the utilization of biological substrate instead of activated carbon or nanoparticles.

Apart from these conventional approach for dye degradation/decoloration from industrial effluents, liquid-liquid extraction has often been a good choice for the process engineer in the development of separation process.\(^52\) However, one drawback of traditional solvent extraction is employing organic solvents, which evaporate into the atmosphere and has marked effect on the environment and human health.\(^53\) In order to protect environment, much emphasis is given on the development of clean manufacturing process and environmentally benign technologies. These ultimately make solvent extraction process less popular because of their use of toxic, flammable, volatile organic compounds (VOCs).\(^54\)

In recent years, room temperature ionic liquid (RTIL) and Task specific ionic liquid (TSIL) have received great attention in different areas of chemistry due to their novel chemical and physical properties such as non flammability, non volatility, thermal stability, wide liquid range, and electrochemical window.\(^55\) RTIL/TSILs have shown significant potential as media for organic synthesis,\(^56,57\) biphasic catalyst,\(^58\) separation,\(^59\) synthesis of nanoparticle,\(^60\) biodiesel preparation\(^61\) etc. RTILs have exhibited significant promise as media for a wide range of industrially important chemical processes to replace traditional solvent as they have no detectable vapour pressure and therefore, relatively thermally stable.\(^54\)
During past few years, several research groups investigated applications of ILs in separation and their mechanism have been extensively investigated. Rogers and co-workers have done some pioneer work using ILs in the extraction of metal ions. They incorporated thiourea, thioether, and urea into derivatized imidazolium cations and used their functionalized ILs as the extractants in liquid-liquid extraction of Pb\textsuperscript{2+} and Cd\textsuperscript{2+}. 

Apart from metal extraction, there are reports in which ILs were used in the liquid-liquid extraction or separation of organic dyes with high efficiency. In this context, Vijayaraghavan et al. used a hydrophobic IL, N-butyl, N-methyl pyrrolidinium bis(trifluoromethanesulfonyl)amide to extract and recover acid blue and acid red dyes. Pei et. al. investigated the removal of anionic dyes, such as methyl orange, eosin yellow and orange G from effluent water by means of a series of imidazolium based ILs. Fan et al. and Li et al. reported use of hexafluorophosphate based imidazolium ILs for the extraction of set of dyes and various azo dye from an aqueous phase. Apart from pure IL, recently IL with ultrasonic environment, bird feather (Keratins), temperature mediated, nanoparticles, polymer, dye extraction processes have been reported. Despite the progress made in field, the extraction/separation processes have not been well understood. Moreover, the use of PF\textsubscript{6} or BF\textsubscript{4} hydrophobic anion based ILs are expensive and undergo oxidation in presence of water, which hampered the implementation of these IL based dye separation protocols in industry.

In view of this, this chapter covers the use of economically viable and environmentally benign as well as fluoride free TSIL based processes for effectively removal of dyes (both cationic and anionic) from the aqueous media.

3b.2. Experimental

3b.2.1 Materials and methods

Water soluble dyes orange-II (OR-II) and reactive blue-21 (RB-21) that is obtained from Sigma-Aldrich and Suyog dye Chemie Pvt. Ltd. were used without any improvisation or further purification. The characteristics of the dyes are shown in Table 3b.1.

Synthesis of adsorbent (Ionic Liquid)

Detail synthesis procedure along with characterization of C\textsubscript{8}PyDs was well described in Chapter 2.
Table 3b.1 General characteristic of dyes selected for the study

<table>
<thead>
<tr>
<th>Dyes</th>
<th>$\lambda_{\text{max}}$</th>
<th>Nature</th>
<th>Mol. wt.</th>
<th>State</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orange-II (OR-II)</td>
<td>485</td>
<td>Cationic</td>
<td>350.3</td>
<td>Powder</td>
<td></td>
</tr>
<tr>
<td>Reactive Blue-21 (RB-21)</td>
<td>621</td>
<td>Anionic</td>
<td>377.4</td>
<td>Powder</td>
<td></td>
</tr>
</tbody>
</table>

Analytical methods and instrument

Uv-vis spectrophotometer (Shimadzu, Japan (UV-160A) is selected as an analytical tool to determine the concentration of dye solutions before and after extraction. This selection is made based on the fact that most dyes absorb electromagnetic radiation in the Uv-vis region. The spectrophotometer that operates in the Uv-vis range was used to determine the wave length of maximum absorbance ($\lambda_{\text{max}}$) and measure all samples. Concentration of dye solution was calculated from the absorbance measurements using Lambert Beer’s law. (equation (1))

$$A = \epsilon_0 C l$$

Where, $A =$ absorbance, $\epsilon_0 =$ molar absorptivity, $C =$ concentrations of dyes (mg/L), $l =$ path length (cm)

The dye removal capacity of the adsorbent is expressed as follows:

Amount of dye adsorbed, $q = \frac{(C_0-C_f)}{m} \times V$  

where, $C_0$ is the concentration of dyes in aqueous media (mg/L), $C_f$ is the dye concentration at equilibrium (mg/L), $V$ is the volume of experimental solution (L) and $m$ is the mass of adsorbent (mg).
The percentage of dye removal was calculated using equation (3),

\[
\% \text{ adsorption} = \frac{C_i - C_f}{C_i} \times 100
\]

(3)

\(C_i\) is the initial concentration of dye solution (mg/L) and \(C_f\) is the concentration of dye after removal.

### 3b.2.2 Maximum absorbance wavelength (\(\lambda_{\text{max}}\)) and calibration curves

Dye concentrations were estimated spectrophotometrically at the wavelength corresponding to maximum absorbance, \(\lambda_{\text{max}}\). To determine the wavelength of maximum absorbance for the two dyes having different concentrations, were prepared depending on the characteristic intensity of the dye color and sensitivity of the instrument. The wavelengths of maximum absorbance (\(\lambda_{\text{max}}\)) for the solutions were determined for the dyes and calibration curves were constructed to determine the initial and final concentration. To this end a calibration curve was prepared by dissolving desire amount of the dye to make 25 mg/L of dye solution for OR-ΙΙ and 70 mg/L for RB-21. Then the other series of solutions are made by taking the corresponding volume of the previously concentrated dye solutions using distilled water and measuring their absorbance at their respective \(\lambda_{\text{max}}\). The concentration and measured absorbance for each dye solution is used to construct the calibration curve.

### 3b.2.3 Batch adsorption studies for industrial effluent

The sample of waste water (effluent) was collected from dyeing industry at G. I. D. C., Ankleshwar (INDIA). This effluent (10 ml) was treated with media (100 mg) to see adsorption of dye molecules onto modified IL. Experimental solutions were prepared by pipetting a known amount of effluent into a 50 ml conical flask and diluting it with a known amount of distilled water. Batch experiments for decolorisation were conducted in 50 ml conical flask containing 10 ml of this solution at room temperature (30 °C), to evaluate dye removal efficiency and capacity of the IL. The IL was placed in the flask and then stirred continuously at a constant slow mixing rate with magnetic stirrer during the experiment. The initial dye concentration selected for batch experiments is within the range recommended in the actual textile effluent. The batch process for dye extraction by IL is Schematically represented in **Scheme 3b.1**. The dyes solutions for the studies were prepared by dissolving 100 mg of each dye in distilled water.
Chapter 3(b)

The effect of dose of the adsorbent, contact time, system pH and initial concentration of the dye were investigated by varying any one of the process parameters and keeping the other parameters constant. All the experiments were performed in triplicate and the mean values were reported.

Scheme 3b.1 Schematics showing the batch process of dye adsorbed on modified IL

Effect of adsorbent dose

To investigate the effect of adsorbent dose, the experiments were conducted by varying adsorbent doses (50 mg to 300 mg) for the 10 ml of the working solution of dyes at constant initial dye concentration of 100 mg/L was put in different conical flask. All the flasks were kept inside the shaker at 100 rpm and 30 °C. After 30 min, the flasks were withdrawn from the shaker and the dye solutions were separated from adsorbent with the help of filtration. The remaining concentration was determined spectrophotometrically at its corresponding \( \lambda_{\text{max}} \). A graph was plotted with percent removal (%) vs. adsorbent dose is expressed as equation (3).

Effect of Initial pH

The initial dye concentrations (100 mg/L), IL (100 mg), and temperature were all kept constant during the experiment. 10 ml of the working solution was put in each different conical flask. The optimum adsorbent dose (IL) as obtained from the above study was put in each flask. The pH of each flask was adjusted at 2, 7 and 10 with dilute HCl and ammonia solution by the use of pH meter. Then, all the flasks were kept inside the shaker at 100 rpm and 30 °C for 30 min. After that, flasks were withdrawn, solutions were filtered and absorbance of the solutions were measured. The residual dye concentration was determined after 30 min of contact time. A graph was plotted with % adsorption vs. initial pH.

84


Chapter 3(b)

Effect of Contact Time

10 ml of the working solution was put in each different conical flask. The results obtained from above two studies of optimum adsorbent dose and initial pH was used here. All the flasks were put in the shaker at 100 rpm and 30 °C for a predetermined time period ranging from 10 min. to 180 min. Then, flasks were withdrawn from the shaker, solution was filtered and absorbance of the solutions was measured. A graph was plotted with % adsorption vs. contact time.

Effect of initial dye concentration

To investigate the effect of initial dye concentration, experiments were conducted by varying dye concentrations of 5 mg/L to 100 mg/L and at constant untreated adsorbent dose of 100 mg/10 ml, system pH = 7 and equilibrium time is 30 min. The final dye concentration was analyzed from the absorbance of the supernatant.

Isotherm studies

All adsorption measurements carried out through batch technique at room temperature and desired pH. In each measurement, 10 ml of the dye solution of desired concentration and appropriate amount of the media were taken in a 50 ml graduated airtight conical flask and mechanically agitated for about 1 hr to achieve equilibrium. The adsorbent were now removed from the solution after carefully filtering by filter paper and the concentration of the dye was determined spectrophotometrically by recording the absorbance at corresponding λ\(_{max}\).

3b.3. Results and Discussions

3b.3.1 Preparation of Calibration curves

Figure 3b.1 shows the UV-vis absorbance curves for the OR-II and RB-21 dye solutions in water. The curves are obtained by preparing dye solutions for which the concentrations are within the effective concentration range of the dyes. The obtained λ\(_{max}\) values for OR-II and RB-21 are 483 nm and 621 nm respectively.
In order to construct calibration curves, UV-vis curves as a function of various concentrations of dyes were obtained. The absorbance vs concentration of dyes relationship for OR-II and RB-21 are shown in Figure 3b.2. The correlation coefficients for the dyes show strongly linear relationship between the concentration of the dye solution and the absorbance.

In Figure 3b.1 UV-vis. spectra of OR-II, (conc. 30 mg/L) and RB-21, (conc. 30 mg/L) at pH = 7.0

**Figure 3b.1** UV-vis. spectra of OR-II, (conc. 30 mg/L) and RB-21, (conc. 30 mg/L) at pH = 7.0

**Figure 3b.2** UV-vis spectra of dyes as a function of concentration (a) OR-II and (b) RB-21. Inset shows calibration curves with coefficient obtained from efficient linear fits at pH = 7.0
In order to check adsorption capacity of IL, Uv-vis absorbance spectra for both dyes (100 mg/L, 10 ml) with 100 mg absorbent (C₈PyDs) before and after extraction of dyes were measured and shown in Figure 3b.3.

![Figure 3b.3](image-url) UV-vis spectra of (a) OR-II and (b) RB-21, before and after removal from 100 mg/L dye solution using 100 mg adsorbent. Inset photographs show the color of dye solution before and after extraction process at pH = 7.0

From figure, it reveals that due to dye adsorption by C₈PyDs from aqueous dye solutions, the absorbance at corresponding $\lambda_{max}$ values of dyes decrease drastically. This ultimately confirms that C₈PyDs is able to remove dyes from aqueous solutions effectively.

3b.3.2 Effect of absorbent dose

To investigate the effect of absorbent doses experiments were conducted by varying absorbent doses (50 to 300 mg/10 ml) for both OR-II and RB-21 dyes at constant initial dye concentration of 100 mg/L. Further addition of absorbent does not provide more increment in the adsorption amount (Figure 3b.4 and Table 3b.2 for both the dyes).

The results show that the adsorption of OR-II on to the IL is relatively slow as compare to RB-21 where as the adsorption of RB-21 is very fast and reached equilibrium within 10 min. It may be due to the nature of the adsorbent and the nature of the dyes. As RB-21 is anionic dye, it prefers to interact electrostatically with pyridinium cation which is relatively smaller in size, results into a stable close packing type of arrangement. On the other side, OR-II is cationic in nature which approaches readily towards
relatively large sulphate anion which itself undergoes steric hindrance due to long alkyl chain. The other possible reason for the slow nature of the adsorption process for OR-II could be the hydrophilic nature of the dye. Reactive dyes are very soluble in water and, therefore, are poorly adsorbed. All this leads to better extraction of anionic dye by C₈PyDs compare to cationic dye.

Figure 3b.4 Effect of absorbent doses on OR-II and RB-21, conc. of dyes solution is 100 mg/L.

In general the decolorization efficiency was increased with dose as reflected by the measured residual dye concentration. Furthermore it was found that by increasing the amount of the adsorbent from 50 mg to 300 mg, the adsorption increases, from 91% to 99.9% for OR-II and 98 to 99.9 for RB-21 (see Figure 3b.4 and Table 3b.2).

The increase in the dye adsorption was due to increased availability of dye binding sites resulting from an increase in adsorbent dosage. Higher dose of the media (greater than 300 mg) for both the dyes are not required because almost ~ 99.9% dyes were removed with the maximum 300 mg/10 ml absorbent used. To maintain maximum capacity and high removal efficiency, the surface loading (i.e. the mass ratio of the dye to adsorbent dose) should be lower than the optimum value. These experimental results suggest that modification of the surface chemistry of the adsorbent may enhance its capacity.

Although percentage adsorption increases with increase in adsorbent dose, amount adsorbed per unit mass decreases. Thus, increase in adsorption is there with respect to
Chapter 3(b)

increase in dose, but the trend of amount adsorbed per unit mass is decreasing with increasing dose.

**Table 3b.2 Effect of IL dose and pH on % removal of dyes**

<table>
<thead>
<tr>
<th>IL dose (mg/10 ml)</th>
<th>OR-ΙΙ</th>
<th>2.0</th>
<th>91.80</th>
<th>99.47</th>
<th>99.75</th>
<th>99.90</th>
<th>99.95</th>
<th>99.99</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 7.0</td>
<td></td>
<td>90.65</td>
<td>99.07</td>
<td>99.40</td>
<td>99.45</td>
<td>99.75</td>
<td>99.99</td>
<td></td>
</tr>
<tr>
<td>pH 10.0</td>
<td></td>
<td>86.58</td>
<td>98.17</td>
<td>98.80</td>
<td>99.28</td>
<td>99.56</td>
<td>99.60</td>
<td></td>
</tr>
</tbody>
</table>

**RB-21**

| pH 2.0           | 97.86 | 99.97 | 99.99 | 100.0 | -     | -     |
| pH 7.0           | 98.70 | 99.98 | 99.99 | 99.99 | -     | -     |
| pH 10.0          | 98.19 | 98.51 | 99.00 | 99.75 | -     | -     |

The decrease in adsorption capacity with increase in adsorbent dose is mainly because of unsaturation of adsorption sites through the adsorption process. From the above figure, we can infer that the optimum adsorbent dose is 100 mg/10 ml solution. Though, there is an increase in % removal of dyes on further addition of adsorbent but this increase is marginal and from an economic point of view, it might not be a wise step to use adsorbent more than 100 mg/10 ml solution.

3b.3.3 Effect of contact time

It can be seen from the Figure 3b.5, that adsorption increases more rapidly at the initial time period and rate of adsorption decreases as we proceed to the saturation limit. The equilibrium can be assumed to have achieved after 15 min as the final dye concentration does not seem to increase much after this limit. The reason might be the saturation of the active sites which do not allow further adsorption to take place.

3b.3.4 Effect of pH on adsorption

The pH of initial solution has significant effect on the adsorption process, since it determines the surface charge of the adsorbent and the degree of ionization and separation of the adsorbates. The effect of initial pH on the dye removal was studied at the pH
values 2, 7 and 10 with the initial dye concentration of 100 mg/L at room temperature and adsorbent dose 100 mg.

![Figure 3b.5](image)

**Figure 3b.5** Effect of contact time (OR-II and RB-21 on adsorbent) with 100 mg/L dye concentration and pH = 7.0

The respective results are shown in **Table 3b.2** as well as in **Figure 3b.6**, which reflects that the initial pH negligibly affects the extent of adsorption of both the dyes OR-II and RB-21 over the IL and the removal percentages are decreased slightly at higher pH values. It was seen that maximum uptake of the dyes were obtained at pH = 2.

![Figure 3b.6](image)

**Figure 3b.6** Effect of pH on percentage of dyes removal at fixed dye concentration (100 mg/L) and adsorbent dose (100 mg).
Therefore all subsequent studies were carried out at pH = 2. Slight lower adsorption of dyes (both anionic and cationic) at high pH is related to the electrostatic repulsion between dye molecule and cationic/anionic moiety of the adsorbent, C₈PyDs. Hence, the removal of the dyes can be due to either hydrogen bonding or electrostatic forces between the dye and the amphoteric groups of the adsorbent. At lower pH, (acidic condition) the functional groups on the adsorbent polarizes thereby creating electrostatic interaction along side with hydrogen bonding.

3b.3.5 Effect of dye concentration on percentage extraction

The effect of dye concentrations at a fixed quantity of the adsorbent dosage is shown in the following figure (Figure 3b.7 and Table 3b.3). The percentage of dye removal at fixed adsorbent dose increased with increasing dye concentration. This is expected because in surface adsorption reactions the equilibrium concentration of a given solute in the semi solid phase is proportional to the equilibrium concentration in the liquid phase.

![Figure 3b.7](image.png)

**Figure 3b.7** Effect of dye concentrations on percentage of dye removal at fixed adsorbent dose (100 mg) on OR-II and RB-21 (System pH = 2, 7 and 10)

From the Figure 3b.7 it is observed that increasing the dye concentration increases the removal capacity of the adsorbent. The correlation coefficients of the experiments show that there is a strong linear relationship between the initial concentration of the dye and the removal capacity of the adsorbent. This result indicates that the method is suitable for the treatment of high-strength textile effluent in terms of dye concentration.
Table 3b.3 Effect of concentration and pH on % removal of dyes with 100 mg/10 ml IL dose

<table>
<thead>
<tr>
<th>pH</th>
<th>Concentration, mg/L</th>
<th>10</th>
<th>30</th>
<th>50</th>
<th>100</th>
<th>300</th>
<th>500</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OR-II</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>99.10</td>
<td>99.33</td>
<td>99.20</td>
<td>99.45</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7.0</td>
<td>97.23</td>
<td>98.56</td>
<td>99.10</td>
<td>99.24</td>
<td>-</td>
<td>-</td>
<td>99.49</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>98.51</td>
<td>98.00</td>
<td>98.52</td>
<td>98.23</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>RB-21</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>70.40</td>
<td>-</td>
<td>96.00</td>
<td>97.86</td>
<td>99.93</td>
<td>99.85</td>
<td>99.97</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>88.33</td>
<td>-</td>
<td>99.11</td>
<td>99.67</td>
<td>99.91</td>
<td>99.98</td>
<td>98.51</td>
<td></td>
</tr>
</tbody>
</table>

3b.3.6 Effect of adsorbent on industrial effluent

The effect of C₈PyDs on industrial effluent from textile or dye industry has also been studied to see the % removal of dye from waste water. This effluent (10 ml) was treated with IL (C₈PyDs, 100 mg) to see adsorption of dye molecules onto IL (adsorbent). Figure 3b.8 shows that the UV-vis of effluent before and after treatment of IL.

Figure 3b.8 UV-vis spectrum of industrial effluent before and after treatment of 100 mg absorbent (IL) with 10 ml effluent. Inset the photograph of effluent before and after treatment of IL.
For the UV-vis spectra, we have diluted the effluent to ~ 35 times and measured absorbance in UV-vis range. But for the adsorption process, we use effluent in its original state (10 ml) as collected from industry and treated with adsorbent (100 mg). Inset of Figure 3b.8 is the photograph of industrial effluent before and after removal.

From the figure it is clear that the adsorption of dyes/pollutants from the effluent was done effectively by C₈PyDs. Therefore, we can conclude that IL, C₈PyDs is also a promising candidate even for mixture of dyes or in presence of other effluent materials.

3b.3.7 Adsorption isotherms study

Adsorption process is usually studied through adsorption isotherm. The adsorption isotherm describes the equilibrium relationship between the adsorbate, adsorbent and the equilibrium concentration of adsorbate in solution. As our IL is quasi-solid in nature (gel type), two well known adsorption isotherms, Langmuir and Freundlich models are applied to describe the adsorption isotherms. These isotherms relate the equilibrium adsorption capacity to the equilibrium concentration in the solution. The applicability of the isotherm equations is compared by judging the correlation coefficients $R^2$. As C₈PyDs has a semi solid kind of nature one can use the various adsorption models based on liquid extraction on solid surface.

3b.3.7.1 Langmuir model

Langmuir isotherm is valid for monolayer adsorption on a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption on the surface and no transmigration of adsorbate in the plane of the surface. The Langmuir equation is commonly expressed as,

$$q_e = \frac{q_m K C_e}{1 + K C_e}$$  \hspace{1cm} (4)

$$\frac{C_e}{q_e} = 1 + \frac{1}{q_m K} C_e$$ \hspace{1cm} (5)

In equation (4), $C_e$ and $q_e$ are as defined in equation (5). $K$ is a direct measure for the intensity of the adsorption process, and $q_m$ is a constant related to the area occupied by a monolayer of adsorbate, reflecting the adsorption capacity. From a plot of $C_e/q_e$ vs. $C_e$, $q_m$ and $K$ can be determined from its slope and intercept (Figure 3b.9).
Table 3b.4 presents the correlation coefficient results for Langmuir isotherm, which has not a satisfactorily good correlation between the model predictions and the experimental data, giving the correlation coefficients for Langmuir isotherm in the range of 0.969-0.999 (Table 3b.4). The essential characteristic of the Langmuir isotherm can be represented by the equilibrium parameter, $R_L$, calculated by using equation (6):

$$R_L = \frac{1}{(1 + K_L C_0)}$$

(6)

Where, $K_L$ is the Langmuir constant and $C_0$ is the initial dye concentration (mg/L). $R_L$ is dimensionless separation factor used to determine whether the adsorption process is favourable or unfavourable. The value of $R_L$ can show that the adsorption dye on C$_8$PyDs is unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable (0 < $R_L < 1$) or irreversible ($R_L = 0$). The result shown in Figure 3b.9 implies favourable adsorption of two dyes on C$_8$PyDs.

3b.3.7.2 Freundlich model

The Freundlich isotherm is an empirical equation and is shown to be satisfactory for low concentrations. The equation is commonly given by

$$q_e = K_F C_e^{1/2}$$

(7)

$$\ln q_e = \ln K_F + \frac{1}{2} \ln C_e$$

(8)
where, $K_F$ is Freundlich constant for the system related to the bonding energy. $K_F$ can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbent for an unit equilibrium concentration (i.e., $C_e = 1$ mg/L). The slope $1/n$, ranging between 0 and 1, is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value for $1/n$ below one indicates that adsorption of dyes is unfavourable with this model. A plot of $\log q_e$ vs. $\log C_e$ enables the empirical constants $K_F$ and $1/n$ to be determined from the intercept and slope of the linear regression. Figure 3b.10 and Table 3b.4 presents the results of the Freundlich isotherm fit of RB-21 and OR-II to the measured adsorption capacity data for modified IL at various pH.

![Freundlich adsorption isotherms of OR-II and RB-21 dyes with IL](image)

Figure 3b.10 Freundlich adsorption isotherms of OR-II and RB-21 dyes with IL

From column 5 of Table 3b.4 the values for $1/n$ are above 1 (1.01-1.81) which indicates that adsorption of dyes is unfavourable with this model. The correlation coefficient, ($R^2$) from Freundlich isotherm fitting data are in the range of 0.825-0.894. Poor fitting coefficient of Freundlich model also confirm the failure of this model for our system. All this confirms that C₈PyDs has uniform available adsorption sites. But the other results (including visible observation) indicate that IL is able to adsorb dyes. Therefore, failure of Freundlich model suggest that our adsorbent (IL) has uniform bonding sites for dyes, which is opposite to the assumption (applied only for adsorbent with heterogeneous active sites on the surface of adsorbent).
Table 3b.4 Langmuir, Freundlich adsorption isotherm constant correlation coefficient and $q_m$ for OR-II and RB-21 adsorption onto IL

<table>
<thead>
<tr>
<th>pH</th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_m$ (mg/g)</td>
<td>$K_L$ (L/mg)</td>
</tr>
<tr>
<td>----</td>
<td>-----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>2.0</td>
<td>16.89</td>
<td>1.068</td>
</tr>
<tr>
<td>7.0</td>
<td>8.00</td>
<td>0.880</td>
</tr>
<tr>
<td>10.0</td>
<td>9.80</td>
<td>0.713</td>
</tr>
<tr>
<td></td>
<td>OR-II</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>14.16</td>
<td>11.27</td>
</tr>
<tr>
<td>7.0</td>
<td>42.46</td>
<td>3.62</td>
</tr>
<tr>
<td>10.0</td>
<td>49.28</td>
<td>0.778</td>
</tr>
<tr>
<td></td>
<td>RB-21</td>
<td></td>
</tr>
</tbody>
</table>

3b.4 Conclusions

This study confirmed that the modified ionic liquid (TSIL) was an excellent sorbent for removal of ionic dyes from aqueous solution. The optimal pH for favourable sorption was 2 or below 7. The 0.2 g/10 ml or more sorbent could almost completely remove OR-II and RB-21 from 100 mg/L of dye solution. The ratio of dyes adsorbed kept above 95% over a range from 50 to 100 mg/L of dye concentration when 0.2 g/10 ml of sorbent was used. The isothermal data fitted the Langmuir model. The sorption capacities for OR-II and RB-21 were 208.33 and 188.68 mg/g respectively. The IL, C₈PyDs also works effectively for real effluent sample from textile industry which is a mixture of multiple dyes along with other pollutants. This modified IL offers many advantages for potential industrial use such as high efficiency, sorbent savings, minimal amount of sludge formation, high quality of treated water, possibility for the potential reuse of water and also a economic feasibility since it does not require high costs for chemicals and equipment.
3b.5 References

Chapter 3(b)

31. El-Ashtoukhy, E. S. Z. *Desalination* 2011, 267, 64.
34. Mahmood, N. M.; Salehi, R.; Arami, M.; Bahrani, H. *Desalination* 2011, 267, 64.
Chapter 3(b)


