Grafting of coconut coir adsorbent with ionic liquid and its effect on the adsorption of reactive dye, Drimarene Red

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Abstract

Dye-loaded wastewater is a threatening environmental problem that has subsequently received enormous scientific attention especially in the form of adsorption studies. Considering the adsorption technique, numerous ideas have been presented for the modification of the adsorbents to enhance their adsorption efficiency. In the present study, a new modification process has been proposed in the form of grafting of the adsorbent with an ionic liquid and its effect on adsorption efficiency has been investigated. The adsorbent used in the study is coconut coir to remove Drimarene Red dye from the water after grafting with the ionic liquid, 1-hexyl-3-methylimidazolium hexafluorophosphate (HMI)[PF\textsubscript{6}]. The results are highly encouraging and have shown that grafting greatly enhances the adsorbent efficiency of coconut coir. The percentage removal efficiency increased from 67.8\% to 96.1\% as well as adsorption capacity which increased from 6.78 to a 9.61 mg g\textsuperscript{-1}. The kinetic studies have shown that adsorption follows the rapid kinetics and equilibrium is achieved within 6 min with a percentage removal of around 96.1\%. The process follows pseudo-second-order kinetics and the data is highly compatible with the Langmuir isotherm model. The scanning electron microscopy analysis and IR spectroscopy have confirmed the process of grafting. The encouraging result of the study presents a novel technique of the modification of the adsorption for the enhancement of adsorption efficiency.

Keywords: Dimarene red; Ionic liquid; Grafting; Coconut coir; Adsorption

1. Introduction

Approximately, $7 \times 10^5$ tons of dyes are produced globally and half of it is used in the textile industries [1]. Around 70\% of all the dyes used in the world are contributed by the azo dyes and because of their poor exhaustion properties, almost 30\% of the dye becomes part of the textile waste which eventually finds its way to the rivers and oceans [2]. Once in the water, these dyes prove extremely lethal to the aquatic species by blocking the sunlight penetrating the water bodies to be useful for the oceanic life [3]. Similarly, it also interferes with the oxygen transfer mechanism at the air-water interphase causing the depletion of the dissolved oxygen in the water which itself is a serious threat to the survival of the marine life [4]. In Pakistan textile is the largest manufacturing industry which contributes 57\% to the country’s export [5]. Karachi is one of the industrial hubs of the country where several dye-related industries are located. Consequently, they produce a huge amount of wastewater that often goes without treatment to the Arabian Sea through Lyari and Malir rivers. The situation is quite grave as such a huge amount of waste has reportedly posed serious threats to the environment and the marine life of the city. Removing these harmful dyes from industrial effluent is consequently of great importance. Several methods have been employed for the removal of dyes from the aqueous
medium, including adsorption, coagulation, electrodialysis, filtration, membrane separation, oxidation, and precipitation [6]. However, removal by adsorption is of the most efficient methods as adsorbents themselves being the waste products of other industrial/commercial processes. Agricultural wastes and biomass are highly effective at dye removal owing to their high lignocellulose content and also cheaply and readily available [7–9]. Recently, new adsorbents are being created by grafting existing natural fibers with monomers to increase both hydrophobicity and oleophilic of the resultant adsorbent, to provide better and more efficient adsorbent [10,11]. On the same idea, this study has been conducted to compare the adsorption efficiency of raw coconut choir and ionic liquid grafted coconut choir for the removal of Drimarene Red dye, a reactive dye which is widely used in textile industries, and kinetics and thermodynamic parameters have been studied. Several studies have demonstrated the suitability of coconut coir for the adsorption of dyes from aqueous media with percentage adsorption of more than 99% [12–14]. Similarly, studies have also shown the potential benefits of immobilizing the ionic liquids on a natural adsorbent in terms of an increased adsorption efficiency [15–17]. However, those studies have been predominantly aimed at removing metal ions from the aqueous media. This study is, therefore, an initiative in highlighting the potential of ionic liquid immobilized natural adsorbent for the removal of textile dyes from aqueous media. Fig. 1 shows the structure of the Drimarene Red dye.

2. Materials and methods

The adsorbent, coconut (Cocos nucifera L.) coir dust, and Drimarene Red were purchased from the local market and subsequently used without further purification. Before the experiments, coconut coir dust was soaked in de-ionized water for 3 d and washed several times with water until all the colored extract was removed and clean water was obtained. It was then oven-dried at 60°C for 24 h and ground using mortar and pestle to get the powdered form of the coir. The powdered adsorbent was then sieved to obtain particles in the range of 50–100 mm and then stored in a plastic container before use for adsorption studies.

Grafting of the coconut coir was achieved with 1-hexyl-3-methylimidazolium hexafluorophosphate ([HMI][PF₆]) ionic liquid. 10 ml of ([HMI][PF₆]) was mixed with 5 g of coconut coir and then heated gently at a temperature of 60°C for 2 min. The mixture was then cooled and dried in the oven.

A scanning electron microscope (SEM) was used for the surface characterization of the adsorbent before and after the adsorption experiment. The same was also done after the grafting of coconut coir. SEM analysis was conducted in the Centralized Science Laboratory (CSL) of the University of Karachi using the JEOL (Japan) SEM instrument with a model number JSM-6380A equipped with a target of gold and containing energy-dispersive X-ray spectroscopy (EDS) detector model #EX-54175JMU. Fourier-transform infrared spectroscopy (FTIR) spectra of the raw coconut coir and ionic liquid treated coconut coir were recorded on a Shimadzu FTIR spectrometer. UV/Vis spectrophotometer (CE 7400) was used to determine the dye concentration in the aqueous solutions at a wavelength of 532 nm.

The batch adsorption experiments were carried out in a 100 ml conical flask containing the required volume of dye solution along with the specific amount of the adsorbent. The mixture was then shaken using the orbital shaker at constant rpm and then filtered to find the final dye concentration in the filtrate. Eqs. (1) and (2) were used to determine the percentage adsorption and adsorption capacity respectively.

\[
\%\text{Adsorption} = \left( \frac{C_i - C_f}{C_i} \right) \times 100
\]

\[
Q_e = \left( \frac{C_i - C_f}{m} \right) V
\]

where \(C_i\) (mg L\(^{-1}\)) is the initial dye concentration, \(C_f\) (mg L\(^{-1}\)) is the dye concentration after adsorption, \(Q_e\) (mg g\(^{-1}\)) is the equilibrium adsorption capacity while \(V\) (L) is the volume of adsorbate solution and \(m\) is the mass of the adsorbent respectively.

Desorption of the dye for the regeneration of adsorbent was carried out using 0.01 M of three different desorbing
agents including \( \text{H}_2\text{SO}_4 \), \( \text{NaOH} \) and \( \text{NaCl} \). Methodologically, 0.03 g of the adsorbent was shaken with 100 mL of 10 mg L\(^{-1}\) dye solution with each of the desorbing agent. The dye-loaded adsorbent was then filtered and subsequently dried overnight. The dried adsorbent was then shaken with 100 mL of each adsorbent and the dye concentration in the solution was measured. The desorption efficiency was calculated by the following equation [18].

\[
\%D = \frac{C_{ed}}{C_i - C_f} \times 100
\]

where \( \%D \) is the desorption efficiency (%), \( C_i \) is the initial dye concentration before adsorption (mg L\(^{-1}\)), \( C_f \) is the equilibrium dye concentration after adsorption (mg L\(^{-1}\)) and \( C_{ed} \) is the dye concentration at equilibrium after desorption (mg L\(^{-1}\)).

3. Results and discussion

3.1. Adsorbent characterization

The SEM micrographs from the experiments are shown in Figs. 2a–c. The SEM of coconut coir before the grafting shows the porous nature of the coconut coir surface and it is quite evident in the figure that the surface is completely covered with ionic liquid molecules after the grafting. The morphology of the grafted adsorbent post adsorption differs from the one before the adsorption process indicating the coverage of the grafted surface with the dye molecules. The smoothness of the surface in the grafted adsorbent also indicates the chemisorption mechanism as well as monolayer coverage as supported by the compatibility of the adsorption with the Langmuir isotherm. Table 1 presents the elemental profiles which understandably shows high Carbon content of the coconut coir. Additionally, it also shows high sodium in the EDS spectrum of the adsorbent after the adsorption which could be originating from the dye which contains sodium in its structure. Similarly, high fluorine in

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Elemental profile from SEM EDS analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw coconut coir</td>
<td>C = 58.1%, O = 35.5%</td>
</tr>
<tr>
<td>Ionic liquid grafted coir before adsorption</td>
<td>C = 49.9%, O = 19.2%, F = 24.6%</td>
</tr>
<tr>
<td>Ionic liquid grafted coir after adsorption</td>
<td>C = 55.4%, O = 34.5%, Na = 3.5%</td>
</tr>
</tbody>
</table>

Fig. 2. (a) SEM micrograph of untreated coconut coir, (b) SEM micrograph of grafted coconut coir before adsorption, and (c) SEM micrograph of grafted coconut coir after adsorption.
the grafted adsorbent before adsorption evidences the ionic liquid immobilization on the surface of coconut coir. The FTIR spectra of the raw coconut coir and the grafted coconut coir are shown in Fig. 3. The bands at 3,450 and 3,444 cm\(^{-1}\) shows the OH group stretching, before and after the interaction, respectively. The key difference between the two spectra is the peak at 2,966 cm\(^{-1}\) in the grafted adsorbent spectra which is absent on the raw coconut coir spectra which shows the asymmetric stretching of CH\(_2\) groups of the ionic liquid indicating the immobilization of ionic liquid on the surface of the coconut coir. The peak at 1,579 cm\(^{-1}\) in the grafted adsorbent spectra is due to the aromatic ring which is also absent in the raw coconut adsorbent spectra. Also, strong bands ranging from 1,112 to 1,067 cm\(^{-1}\) and 1,109 to 1,055 cm\(^{-1}\) before and after grafting, respectively, confirmed the presence of a C–O bond [19].

3.2. Adsorption experiments

3.2.1. Equilibrium time

Fig. 4a shows a plot of percentage removal against time which is useful in predicting the time it takes for the adsorbent to achieve the equilibrium at a particular initial concentration. It is apparent that as the time increases, the percentage removal also increases until at the time of approximately 6 min the percentage removal becomes almost constant which corresponds to the highest percentage removal of 96.1%. Similarly, Fig. 4b gives the plot of adsorption capacity against time which can be used to find the equilibrium adsorption capacity and as apparent, the adsorption capacity increases with time and equilibrium capacity (Q) of 9.6 mg g\(^{-1}\) is achieved in 6 min. The effect of grafting of the adsorbent with ionic liquid is also quite evident and promising as can be seen in Figs. 4a and b, wherein, the percentage removal is greatly enhanced from 67.8% to 96.1% as well as adsorption capacity which increased from 6.78 to a 9.61 mg g\(^{-1}\). These results are encouraging and represent better adsorption removal of dyes compared to other reported results with different untreated adsorbents. A 75% percentage removal dye at an initial concentration of 10 mg L\(^{-1}\) was reported onto immobilized fungus Aspergillus niger SA1 h [20]. Similarly, less than 90% adsorption of Drimarene Red onto untreated agricultural residues like orange peel, banana peel and rice husk [21] while 80% removal on white clay has been reported [22].

3.2.2. Initial concentration and adsorbent dose

Considering the practical applicability of the adsorbents for the removal of contaminants from water, it is always meaningful to optimize the parameters like adsorbent dose and initial concentration of the adsorbate. Figs. 5 and 6 show the plots of percentage removal for initial concentration and adsorbent dose respectively. The optimized concentration of the dye is 10 mg L\(^{-1}\) after which the percentage removal starts declining while the optimized dose of the adsorbent is 0.02 g. The effect of grafting is also quite conspicuous as in both the graphs, the percentage removal is comparatively higher in the case of the ungrafted adsorbent.

3.2.3. Equilibrium pH

pH is an important factor effecting the adsorption processes as pH of the medium controls the magnitude of the electrostatic charge [12]. Effect of pH of initial dye solution on removal efficiency is presented in Fig. 7 which suggests that adsorption is maximum at a pH of 6 and it decreases on both sides of this pH value. The same pattern of the plots has been observed for the grafted as well as ungrafted adsorbent and the only difference is higher adsorption removal with the grafted adsorbent. The lower adsorption in the acidic pH could be due to the competition between the large number of H\(^+\) present at lower pH and the cationic dye molecules. As the pH is increased, the number of H\(^+\) depletes in the
solution making the adsorbent sites more available for the dye molecules to occupy. The reported value of pH of zero charge for the coconut coir is 6.3 [23] which shows that the main mode of adsorption of dye molecules is the functional group interaction at the surface of the adsorbent and dye molecules rather than electrostatic attraction alone. In the grafted adsorbent, as SEM micrographs have shown the surface is fully covered with ionic liquid and adsorption is maximum at near neutral pH, therefore it could be suggested that the functional group interaction is the dominant mechanism of adsorption.

3.2.4. Adsorption modeling

The adsorption data was fitted to the well-known adsorption isotherms of Langmuir and Freundlich and the plots and summary of the results obtained from the two isotherms are presented in Figs. 8 and 9 and Table 2 respectively. The linearized equations of the two isotherms have been given in the form of Eqs. (4) and (5) respectively [24]

\[
\frac{C_e}{Q_e} = \frac{1}{K_LQ_{\text{max}}} + \frac{C_e}{Q_{\text{max}}}
\]

(4)

where \( C_e \) (mg L\(^{-1}\)) is the equilibrium concentration, \( Q_e \) (mg g\(^{-1}\)) sorption capacity, \( K_L \) is Langmuir constant, \( Q_{\text{max}} \) (mg g\(^{-1}\)) is the monolayer capacity. The constants \( K_L \) and \( Q_{\text{max}} \) can be calculated from the slope and intercept of the plots of \( C/Q_e \) vs. \( C_e \).
where $n$ and $K_f$ both are Freundlich constants their values can be derived from the slope and intercept respectively of the plots of $\ln Q_e$ against $\ln C_e$. The slope of the plot is given by $1/n$ and it shows adsorption intensity and surface heterogeneity whereby a value close to zero indicates more heterogeneity and chemisorption [25].

From Table 2, based on determination coefficients $R^2$ for the two models, it is noticeable that the data fits comparatively well with the Langmuir isotherm model. The Langmuir model is conceptualized by the formation of monolayer at the surface of the adsorbent at maximum coverage. It further indicates the chemisorption mechanism of the adsorption which is based on the electrostatic attraction between the active charged sites on the surface of the adsorbent and the adsorbate molecules.

### 3.2.5. Kinetics of adsorption

Kinetics studies are useful in designing the batch adsorption systems as they could predict the adsorption mechanism as well as the rate of removal of adsorbate form the aqueous media. In this study, Lagergren’s pseudo-first-order and Ho’s pseudo-second-order models have been investigated for the kinetics of adsorption of Drimarene Red on the ionic liquid grafted coconut coir. The linear form of the two models have been given as follows:

**Lagergren’s pseudo-first-order linear equation** [26]:

$$\ln \left( 1 - \frac{Q_t}{Q_m} \right) = -\frac{kt}{Q_m}$$

where $Q_m$ (mg g$^{-1}$) is Lagergren’s maximum sorption capacity and $k$ (min$^{-1}$) is rate constant and were obtained from the slope and intercept of $\ln (1 - Q_t/Q_m)$ against time $t$.

**Ho’s pseudo-second-order linear equation** [27]:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_m^2} \frac{t}{Q_e}$$

where $Q_t$, $Q_e$, and $t$, have their usual meanings and $k_2$ is the pseudo-second-order rate constant (g mg$^{-1}$ min$^{-1}$) and was calculated from the slope and intercept of linear plot of $t/Q_t$ against time $t$. 

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**Table 2**

Values of different parameters from Langmuir and Freundlich isotherms

<table>
<thead>
<tr>
<th>Isotherms models</th>
<th>Parameters</th>
<th>Grafted</th>
<th>Ungrafted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$K_L$</td>
<td>0.60</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>$Q_{max}$</td>
<td>24.75</td>
<td>15.38</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
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<td>0.89</td>
</tr>
<tr>
<td></td>
<td>$n$</td>
<td>3.17</td>
<td>2.54</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$K_f$</td>
<td>180</td>
<td>20.63</td>
</tr>
<tr>
<td></td>
<td>$1/n$</td>
<td>0.32</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.91</td>
<td>0.48</td>
</tr>
</tbody>
</table>

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![Fig. 7. Effect of pH on percentage removal at an initial concentration of 10 mg L$^{-1}$, shaking time of 10 min and an adsorbent dose of 0.03 g.](image1)

![Fig. 8. Plot of Langmuir adsorption isotherm.](image2)

![Fig. 9. Plot of Freundlich adsorption isotherm.](image3)
3.3. Desorption studies

Results from the desorption studies indicated that 0.01 M NaOH was a suitable regenerant which resulted in a desorption efficiency of 87.5% as compared to 0.01 M H2SO4 and NaCl which showed a desorption efficiency of 23.5% and 33.3% respectively.

4. Conclusion

The effect of grafting with ionic liquid on the dye removal efficiency of coconut coir has been studied and promising results have been achieved. Grafting with ionic liquid greatly enhanced the percentage removal efficiency of the coconut coir from 67.7% to 96.1%. The process of grafting is easy to follow and repeat and it could be confirmed by SEM, and FTIR spectroscopy. The adsorption with the grafted adsorbent is generally rapid, and equilibrium is established within 6 min at a dye concentration of 10 mg L−1. The grafted adsorbent has been observed to follow pseudo-second-order kinetics and it fits well into the Langmuir isotherm model.

References


