Removal of Reactive Black 5 from Aqueous Solution using Polyethylenimine-Crosslinked Chitin: Batch and Fixed-bed Column Studies

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Chitin is a natural polymer material that is abundant and easy to use at a low cost. In this research, a chitin-based adsorbent, polyethylenimine (PEI)-crosslinked chitin (PEI-chitin), was prepared by crosslinking PEI after binding glutaraldehyde to the specific functional groups of chitin surface. Its adsorption performance on Reactive Black 5 (RB5) was evaluated by batch and fixed-bed column studies. Regeneration study was also conducted to assess the reusability of PEI-chitin. The main results were as follows: pH 2 was optimal for the removal of RB5 from aqueous solution. Langmuir model was better fitted with the isotherm experimental data and the maximum adsorption capacity of RB5 was calculated to be 321.6 mg/g at pH 2. Pseudo-second-order model was better for depicting the kinetic data. The Thomas model can be well adapted to the breakthrough curves. The consecutive adsorption-desorption experiments were performed up to 3 cycles in batch and fixed-bed column systems. The sorption and desorption efficiencies in the batch system were at least 89.1 % and 92.2 %, while the column experiments showed 94.7 % and 97.6 %, indicating high potential in practical large-scale applications.

1. Introduction

Reactive dyes have been widely used in textile industries due to their various advantages (Li et al., 2019). A large amount of dyeing wastewater occurs with the dyeing process. Reactive dyes existed in textile industries have been regarded as one of the most efficient techniques for the treatment of wastewater containing reactive dyes (Li et al., 2019). Chitin, the second most abundant natural polysaccharide, is derived from renewable biological resources including fungi, diatoms, molluscs, annelids and arthropods (El Knidri et al., 2018). Chitin is a non-toxic, biodegradable, biocompatible natural polymer with large amounts of amino and hydroxyl groups on the surface and has the potential as an adsorbent to remove various pollutants (Cao et al., 2018). But it is not easy to regenerate the dye-loaded chitin, making it difficult to reuse the exhausted chitin adsorbent (Dolphen et al., 2007). Chitin is insoluble in common organic and inorganic solvents (El Knidri et al., 2018) and is hard to process, limiting its commercial application in wastewater treatment. Nevertheless, the insoluble property of chitin makes itself stable in a wide variety of wastewaters. Therefore, this work focused on the development of the chitin-based adsorbent with good adsorption property, reusability, and solvent resistance. The surface of chitin has a lot of amino and hydroxyl groups, a commonly used crosslinking agent is glutaraldehyde (GA) that reacts with amino/hydroxyl groups at room temperature, and polyethylenimine (PEI)
is an amino-rich polymer material. By using them, PEI-crosslinked chitin (PEI-chitin) was developed in this study. PEI-chitin was characterized by FTIR analysis, and it was evaluated on the sorption/desorption properties of PEI-chitin for a model reactive dye, Reactive Black 5 (RB5) through batch and fixed-bed column experiments.

2. Materials and method
2.1 Materials
Chitin flake was obtained from Young Puk Chemical Co., Ltd. (Sokcho, Korea) and only chitin particles crushed into 180 to 300 μm were used in this work. PEI (Mw = 70,000, 50 % purity) and GA (25 % solution) were obtained from Habjung Moolsan Co., Ltd. (Seoul, Korea) and Junsei Chemical Co., Ltd. (Tokyo, Japan). RB5 was supplied by Sigma-Aldrich US Ltd. (St. Louis, US) and its general characteristics are as follows: C.I. number 20505, empirical formula C20H24N6NaO13S6, Mw= 991.82, dye content 55 % and the λmax = 597 nm. All of the other reagents used in this study were of analytical grade.

2.2 Preparation of PEI-crosslinked chitin
5 g of chitin powder was added into 100 mL of 3 % GA solution, stirred at 25 °C and 160 rpm for 2 h, and then washed several times with distilled water. The chitin particles were again mixed with 100 mL of 10 % PEI solution for 30 min. Finally, PEI-chitin was washed with water and lyophilized for 24 h.

2.3 FTIR analysis
Infrared spectra of raw chitin and PEI-chitin were analyzed by FTIR spectrometer (DE/Vertex 80V, Bruker, Germany) in the range of 4,000 - 400 cm⁻¹. Samples for FTIR analysis were prepared as KBr pellets and tested to compare the chitin surface before and after PEI crosslinking.

2.4 Batch and column adsorption experiments
1,000 mg/L of hydrolyzed RB5 stock solution was prepared by hydrolysis at pH 11 and 85 °C for 3 h and diluted to use for all experiments. Batch adsorption experiments were carried out by mixing 30 mL of RB5 solution and 0.2 g of PEI-chitin in 50 mL polypropylene conical tubes. The mixture was stirred at 160 rpm and 25 °C for 24 h in a multi-shaking incubator. HCl and NaOH solutions were used to adjust the pH. The adsorption performance of PEI-chitin for RB5 was examined on several parameters such as pH (2 – 12), initial RB5 concentration (20 – 300 mg/L), and time (0 – 960 min). For column experiments, a glass column with 7 mm inner diameter was packed with 0.6 g of PEI-chitin to yield a bed height of 85 mm. A 50 mg/L RB5 solution was then fed to the column in a down-flow mode at a flow rate of 0.57 mL/min using a peristaltic pump. The samples were collected in a regular interval from the eluent. The breakthrough point and saturation point were determined when the concentration of the effluent reached 1 % and 95 % of the inlet concentration. The RB5 concentration of samples was measured at 597 nm by UV-Vis spectrophotometer (X-ma 3000 pc, Human, Korea) after appropriate dilution. The dye uptake q (mg/g) was calculated using the mass balance equation as shown in Eq(1).

\[
q = \frac{V_{f}C_{I} - V_{f}C_{f}}{m} \tag{1}
\]

where C_i and C_f represent the initial and final dye concentrations (mg/L). V_i and V_f stand for the initial and final volume of dye solution (L). m is the weight of sorbent (g).

2.5 Regeneration studies
In batch desorption experiment, The RB5-sorbed PEI-chitin was put in 30 mL of eluent at 25 °C and stirred under 160 rpm for 24 h. For the column desorption experiment, the dye-loaded sorbent was regenerated by eluent (0.01 M NaOH) in the down-flow mode at the flow rate of 2.33 mL/min. The released dye concentration was measured at 597 nm and desorption efficiency was calculated. The adsorption and desorption experiments were repeated 3 times in order to evaluate the reusability of PEI-chitin.

3. Results and discussion
3.1 Comparison of raw chitin and PEI-chitin
The PEI-chitin should have a higher adsorption capacity to RB5 than chitin after PEI was crosslinked with chitin. To verify this hypothesis, a simple adsorption experiment was performed at 200 mg/L RB5 solution and the result showed in Figure 1a. The dye uptake of PEI-chitin (283.7 mg/g) was 2.9-fold more than that of the raw chitin (98.5 mg/g). This may be due to an increase in the number of RB5 binding sites (amine group). To further confirm this, a FTIR analysis was performed for raw chitin and PEI-chitin, and several characteristic
peaks were observed as seen in Figure 1b. The peaks of 1,650 and 1,560 cm\(^{-1}\) are the original peaks of raw chitin (Dolphen et al., 2007). The band at 3,440 cm\(^{-1}\) is attributed to the -NH and -OH stretching vibration (Kumari et al., 2015). The intensity of this peak in PEI-chitin was stronger than raw chitin, indicating that primary amine groups were added on the chitin surface after modification. It was also observed that the peak at 1,650 cm\(^{-1}\) in raw chitin shifted to 1,635 cm\(^{-1}\) in PEI-chitin and its intensity was increased. It can be derived from the conjugation effect between C=N and C=O and imply that the -CHO group of GA bond with the -NH\(_2\) group of chitin and PEI during the crosslinking process (Won et al., 2014). In addition, the peak intensity of 1,075 cm\(^{-1}\) (C-O-C bond vibration) in PEI-chitin was stronger that of raw chitin, which is seen as a result of the reaction between -CHO group of GA and -OH group of chitin following the formation of a new C-O-C bonding (Cao et al., 2018). The crosslinking reaction between chitin and PEI may be by Schiff base reaction and acetalization reaction according to the mechanism for glyoxal crosslinking to chitosan fiber reported by Yang et al. (2005).

![Figure 1: (a) Comparison of RB5 uptakes and (b) FTIR spectra of raw chitin and PEI-chitin](image)

### 3.2 Evaluation of PEI-chitin performance in a batch system

The solution pH is one of the major factors that affect the adsorption process and adsorption capacity. The effect of pH on RB5 adsorption by PEI-chitin was evaluated in the pH range of 2 to 12 at 200 mg/L RB5 solution. As shown in Figure 2a, the RB5 uptake was the highest (270.2 mg/g) at pH 2. The dye uptake was decreased with the increasing of pH. When the pH was increased from 2.0 to 8.0, the dye uptake decreased rapidly from 270.2 to 137.0 mg/g. With the pH continued to increase to 12, the adsorption amount dropped sharply to 8.0 mg/g. Therefore, pH 2 was selected as the optimal pH for further adsorption experiments.

Adsorption isotherm can provide some information such as maximum adsorption capacity, adsorbate affinity and favorability of the adsorption process. Isotherm experiments were conducted at pH 2 and 8 to investigate the maximum dye uptake depending on pH values and the results are presented in Figure 2b. The maximum adsorption capacity of PEI-chitin for RB5 sharply decreased with increasing pH from 2 to 8. The Langmuir and Freundlich models, as shown in Eq(2) and Eq(3), were applied to fit the isotherm experimental data.

- **Langmuir model**:
  \[ q_e = \frac{q_{\text{max}}KLC_e}{1 + KLC_e} \]  
  \[ q_e = \frac{q_{\text{max}}K}{1 + K/L} \]

where \( q_e \) is the dye uptake equilibrium (mg/g), \( C_e \) the dye concentration at equilibrium (mg/L), \( q_{\text{max}} \) the maximum dye uptake (mg/g), \( K_L \) the Langmuir constant (L/mg), \( K \) the Freundlich constant (L/g) and \( n \) the Freundlich exponent. These models’ parameters were obtained from non-linear regression analysis and summarized in Table 1. At both of pHs, the maximum sorption capacity, \( q_{\text{max}} \) values were close to the experimental results. Also, the coefficient of determination, \( R^2 \) values of the Langmuir model were higher than those of the Freundlich model. It indicates that the Langmuir model is suitable for describing the isotherm experimental data. At pH 8, some N-functional groups on the PEI-chitin surface are deprotonated due to their low pK\(_a\) values, which can lead to unfavourable adsorption inhibition by reducing the electrostatic attraction between PEI-chitin and dye molecules. The adsorption capacity of PEI-chitin was still as high as 141.8 mg/g at pH 8, indicating that the adsorption process was predominated by chemisorption, such as ionic bonding by electrostatic attraction (Zhou, et al., 2018). As given in Table 1, the 1/n values were 0.159 and 0.220 for pH 2.
and 8, indicating good adsorption (Rafeek et al., 2019) and chemisorption process (Wawrzkiewicz et al., 2017).

![Figure 2: (a) Effect of pH on RB5 uptake by PEI-chitin, (b) adsorption isotherms at pH 2 and 8, (c) adsorption kinetics at the initial 50 and 200 mg/L RB5 concentrations, and (d) repeated adsorption-desorption cycles.](image)

### Table 1: Model parameters for isotherms and kinetics

<table>
<thead>
<tr>
<th>pH</th>
<th>Langmuir model</th>
<th>Freundlich model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_m$ (mg/g)</td>
<td>$K_L$ (L/mg)</td>
</tr>
<tr>
<td>2</td>
<td>321.6</td>
<td>0.818</td>
</tr>
<tr>
<td>8</td>
<td>141.8</td>
<td>1.447</td>
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</table>

<table>
<thead>
<tr>
<th>RBS (mg/L)</th>
<th>Pseudo-first-order model</th>
<th>Pseudo-second-order model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_1$ (mg/g)</td>
<td>$k_1$ (L/min)</td>
</tr>
<tr>
<td>50</td>
<td>72.5</td>
<td>0.820</td>
</tr>
<tr>
<td>200</td>
<td>260.1</td>
<td>0.031</td>
</tr>
</tbody>
</table>

Kinetic experiments were carried out at two different initial RBS concentrations (50 and 200 mg/L) and adsorption equilibrium reached at 20 and 400 min for the 50 and 200 mg/L dye solutions (Figure 2c). The pseudo-first-order and pseudo-second-order kinetic models were applied to describe the kinetic experimental data and the model parameters were listed in Table 1. The pseudo-first-order and pseudo-second-order models are demonstrated in Eq(4) and Eq(5).

**Pseudo-first-order kinetic model:**

$$q_t = q_1(1 - \exp(-k_1t)) \quad (4)$$

**Pseudo-second-order kinetic model:**

$$q_t = \frac{q_2^2t}{1 + q_2k_2t} \quad (5)$$

where $q_t$ is the dye uptake at time, $t$ (mg/g), $q_1$ and $q_2$ the dye uptake at equilibrium (mg/g), $k_1$ the pseudo-first-order rate constant (L/min) and $k_2$ the pseudo-second-order rate constant (g/ (mg min)). The $R^2$ value of pseudo-second-order model was higher than that of pseudo-first-order model at all initial dye concentrations.
Furthermore, compared with the pseudo-first model, the \( q_e \) values (76.0 and 273.8 mg/g) calculated from the pseudo-second-order model were close to the experimental ones (75.5 and 279.4 mg/g). This indicates that the pseudo-second-order model is better for depicting the kinetic performance of RB5 adsorption by PEI-chitin, suggesting that chemisorption is dominant during the adsorption process (Wawrzikiewicz et al., 2017). For the regeneration and reuse of adsorbent, the reusability of PEI-chitin was examined through repeated sorption and desorption experiments. 0.01 M NaOH was used as the eluent based on a previous report (Jesus et al., 2010). As can be seen in Figure 2d, during three repeated sorption-desorption cycles, the adsorption efficiency decreased from 100 % to 89.1 %, while desorption efficiency increased from 87.2 % to 92.2 %. Although the adsorption amount for RB5 is slightly reduced as the adsorbent is repeatedly used, this result shows good reusability of PEI-chitin.

### 3.3 Adsorption and desorption studies in a fixed-bed column

Accurate prediction of breakthrough curves for adsorbate materials in fixed-bed columns is important in further industrial scale applications. The breakthrough curves are shown in Figure 3a. The total adsorbed dye amount \( (m_{\text{ads}}) \) and the equilibrium dye uptake \( (q_e) \) are calculated using Eq(6) and Eq(7).

\[
m_{\text{ads}} = Q \int_0^{t_{\text{total}}} C_{\text{ads}} \, dt
\]

\[
q_e = \frac{m_{\text{ads}}}{M}
\]

where \( C_{\text{ads}} \) is the adsorbed dye concentration = inlet dye concentration \( (C_0) \) - outlet dye concentration \( (C_t) \) (mg/L), \( Q \) the volumetric flow rate \( (L/h) \), \( t_{\text{total}} \) the total elution time \( (h) \), and \( M \) the adsorbent amount in the column (g). As seen in Figure 3a, the PEI-chitin in the column process performed well RB5 adsorption even after 3 adsorption-desorption cycles. In the first, second and third cycles, the appearance of the breakthrough point \( (C/C_0 = 0.01) \) was 90, 86 and 84 h and the saturation point \( (C/C_0 = 0.95) \) occurred within 114 h in all cycles. It indicates that PEI-chitin can be regarded as a promising adsorbent for industrial applications due to its slow breakthrough and fast saturation characteristics. To better understanding the column data, Thomas model, as displayed in Eq(8), was applied to analysis the experimental data (Thomas, 1944).

\[
\frac{C_t}{C_0} = \frac{1}{1 + \exp \left( \frac{k_t q_T M}{Q} - k_t C_0 t \right)}
\]

where \( k_t \) is Thomas rate constant \( (L/(h \ mg)) \) and \( q_T \) is predicted maximum adsorption capacity \( (mg/g) \). The parameters obtained from Thomas model are shown in Table 2. The \( R^2 \) values were at least 0.996 and the predicted dye uptakes were slightly greater than the experimental results. This indicates that Thomas model is well adapted to the breakthrough curves.

<table>
<thead>
<tr>
<th># of cycle</th>
<th>( k_t ) (L/h mg)</th>
<th>( q_T ) (mg/g)</th>
<th>( q_e ) (mg/g)</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.9 \times 10^{-4}</td>
<td>299.5</td>
<td>295.5</td>
<td>0.999</td>
</tr>
<tr>
<td>2</td>
<td>4.7 \times 10^{-3}</td>
<td>286.6</td>
<td>282.4</td>
<td>0.998</td>
</tr>
<tr>
<td>3</td>
<td>3.9 \times 10^{-3}</td>
<td>283.8</td>
<td>279.8</td>
<td>0.996</td>
</tr>
</tbody>
</table>

Figure 3b shows the RB5 desorption curves in the fixed-bed column. Extremely high concentrated RB5 solutions were obtained by desorption using 0.01 M NaOH eluent.

Figure 3: Adsorption (a) and elution (b) curves of RB5 on PEI-chitin
In the first, second and third cycles, the maximum dye concentrations at the effluent volume of 23.3 mL reached 6,823.1, 6,949.7 and 6,696.5 mg/L, and concentration factors were 136.0, 139.0 and 134.0 times. A high concentration factor is preferred when the final recovery of dye is more feasible. In conclusion, it was confirmed that PEI-chitin could be reused repeatedly while maintaining excellent adsorption performance in the column.

4. Conclusions

In this study, a powerful chitin-based adsorbent, PEI-chitin was successfully fabricated. The sorption capacity of PEI-chitin for RB5 was 2.9-fold higher than that of raw chitin. Isotherm and kinetic data were well fitted by the Langmuir model and pseudo-second-order model. The maximum RB5 uptake at pH 2 was predicted to be 321.6 mg/g by the Langmuir model. Adsorption equilibrium time was dependent on the initial dye concentration and increased with increasing initial dye concentration. The column adsorption experimental data were successfully described using the Thomas model. Through reusability studies in batch and column, it was found that PEI-chitin is easily regenerated using 0.01 M NaOH and can be reused without significant performance degradation. In addition, PEI-chitin showed higher sorption and desorption efficiencies in the column process than batch process.

Acknowledgments

This work supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (NRF-2017R1A1A1A05000741).

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