FIXED BED COLUMN STUDIES FOR THE SORPTION OF PARA-NITROPHENOL FROM AQUEOUS SOLUTIONS USING CROSS-LINKED STARCH BASED POLYMER

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ABSTRACT

In this work, fixed bed column experiments were carried out to investigate the adsorption characteristics of para-nitrophenol (pNP) by cross-linked starch based polymers using hexamethylene diisocyanate (HMDI) as a cross-linking agent. The native and cross-linked starch polymer was characterized using Fourier Transform Infrared Spectroscopy (FT-IR). Effect of design parameters, such as influent concentration, bed height and flow rate on the breakthrough characteristics of the adsorption system were determined. The column experiments on cross-linked starch showed that the adsorption efficiency increased with increase in the influent concentration, bed height and decreased with increasing flow rate. Yoon-Nelson model was used to analyse the column performance and it was observed that the experimental data was well fitted with Yoon-Nelson model.

Key Words: Fixed bed column, Adsorption, Cross-linked starch, Breakthrough curves, Yoon-Nelson model

INTRODUCTION

Now-a-days, one of the major environmental problems facing by humanity is the increasing worldwide contamination of fresh water systems from various industrial chemical compounds. Out of all contaminants contained in industrial waste water, phenolic compounds are the most un-desired ones. The major industries that contribute to chemical compound and waste production are petrochemical, chemicals, agro-chemical, textile and pharmaceutical. Since these chemicals could cause adverse affect on digestive system, nervous system and respiratory system.¹ Particularly, nitrophenols are listed as a priority toxic pollutant and used to produce pharmaceutical drugs and pesticides such as nitrofan and parathion². Various techniques have been employed for the removal of phenolic compounds from waste water such as electrochemical treatment³, membrane⁴, adsorption⁵,⁶ and biological treatment.¹ Despite the availability of above mentioned processes for the removal of phenolic compounds, adsorption is efficient, effective and extensively adopted.⁷

Recently, many low cost adsorbents such as bagasse fly ash⁸, zeolite⁹, activated carbon¹⁰ and modified starch¹¹ have been used as adsorbents to adsorb phenolic compounds from waste water. Among them, starch have been considered as one of the best choice because starch is abundantly available, renewable, cheap, biodegradable and can be used for the removal of pollutants from waste water⁵. However, the hydrophilic nature of starch is a major drawback that limits the development of starch based materials. Chemical derivatization of starch can be one of the methods to solve the problem and to produce water resistant materials. Different methods available for the modification of starch are acid hydrolysis, oxidation, and cross-linking.¹² Among these methods cross-linking has been commonly used to modify native starch with various cross-linking agents.¹³-¹⁷

Different batch and column studies were performed by various researchers for the adsorption processes.⁷,¹⁸ However, the data obtained under batch conditions are generally not applicable to most treatment systems, such
as column operations where contact time is not sufficiently long for the attainment of equilibrium. Hence there is a need to perform equilibrium studies using columns. In order to describe the fixed bed column behaviour and to scale up it for industrial applications an accurate model has to be used. Yoon-Nelson model is often adopted to predict the adsorptive curve of breakthrough in fixed bed mode. In this study, cross-linked starch based polymers using hexamethylene diisocyanate (HMDI) were prepared for the sorption of pNP.

AIMS AND OBJECTIVES

Breakthrough studies were carried out to evaluate the performance of cross linked starch polymer for the sorption of pNP in continuous fixed bed column by varying the operating conditions such as flow rate, bed height and initial concentrations. Yoon-Nelson model has been used to analyse the breakthrough curve for the adsorption of para-nitrophenol (pNP).

MATERIAL AND METHODS

Materials

Para-nitrophenol (pNP) was purchased from Loba chemicals Limited, Mumbai (India). Corn starch was purchased from Sukhjit Starch and Chemicals Limited, Phagwara (India). Hexamethylene diisocyanate (HMDI) and dimethyl formamide (DMF) were purchased from Merck Chemicals Limited, Mumbai (India).

Adsorbent and adsorbate preparation

The cross-linked starch based polymers (CLS1, CLS2) were prepared with different amount of HMDI (25 mL for CLS1 and 45 mL for CLS2) as cross linking agent and DMF as solvent by one step reaction. The procedure introduced was used with some minor modifications. 20 g starch was dissolved in 100 mL of DMF in three necked round bottom flask. Then calculated amount of HMDI were added drop wise. The solution was stirred at 70°C for 4 h. After precipitating the content of reaction mixture was filtered and washed with double distilled water and ethanol. The product was dried at 50°C for 12 h. Cross-linked starch based polymer (CLS2) will be used for the present study.

A stock solution of pNP (1000 mg/L) was also prepared in double distilled water. All working solutions were prepared by diluting the stock solution with double distilled water to the desired concentrations. The structures of pNP is shown in Fig. 1.

![Fig. 1: Structure of para-nitrophenol](image)

Fourier transform infrared spectroscopy (FT-IR)

The native and cross-linked starch based polymer (CLS2) were equilibrated at 50 °C for 24 h and FTIR spectra of native and CLS2 were recorded by FTIR instrument (Perkin Elme, Model RX-1) using potassium bromoide (KBr) pellets (Sigma Aldrich). FTIR spectra were recorded at a resolution of 4 cm⁻¹ and wave number ranged between 400 and 4000 cm⁻¹.

Experimental set-up

Column experiments were conducted in a glass column of 1cm internal diameter and 20 cm length. The column performance was studied at different initial concentration (50, 100 and 150 mg/L), bed height (2.5, 5 and 7.5 cm) and flow rates (4, 6 and 8 mL/min). The bed depths taken were 2.5 cm (1 g), 5 cm (2 g) and 7.5 cm (3 g). A known quantity of adsorbent was placed in the column to yield the desired bed height of the adsorbent with a support plate at the bottom. pNP solutions of known concentrations and pH was pumped downward through the column at a desired flow rates by a peristaltic pump. The effluent samples were collected at specified intervals and analysed for the residual concentrations using UV spectrophotometer (La Motte Company, Chestertown, USA) at 400 nm for pNP.

Analysis of column data

The loading behaviour of pNP to be removed from aqueous solution in a fixed bed was
usually expressed in terms of \((C_t/C_o)\) where \(C_t =\) effluent adsorbate concentration and \(C_o =\) influent adsorbate concentration) as a function of time or volume giving a breakthrough.\(^{22}\) The maximum column capacity \(q_{\text{total}}\) (mg), for a given feed concentration and flow rate is equal to the area under the plot of the adsorbed adsorbate concentration \(C_{\text{ad}}\) \((C_{\text{ad}} = C_o - C_t)\) (mg/L) versus volume (L) and is calculated from equation (1)

\[
q_{\text{total}} = \int_{V=0}^{V_{\text{total}}} C_{\text{ad}} \, dV \quad (1)
\]

The equilibrium uptake \((q_{\text{eq(exp)}}\)), the weight of adsorbate adsorbed per unit dry weight of adsorbent (mg/g) in the column, is calculated as follows:

\[
q_{\text{eq}} (\text{exp}) = \frac{q_{\text{total}}}{x} \quad (2)
\]

Where \(x\) is the total dry weight of adsorbent in column (g).

Total amount of adsorbate sent to column \((W_{\text{total}})\) is calculated as:

\[
W_{\text{total}} = C_o \, V_{\text{total}} \quad (3)
\]

Where \(V_{\text{total}}\) is the total volume passed through the column.

Total percentage removal \((Y)\) of adsorbate is the ratio of the maximum capacity of the column \((q_{\text{total}})\) to the total amount of adsorbate sent to column \((W_{\text{total}})\).

\[
Y = \frac{q_{\text{total}}}{W_{\text{total}}} \times 100 \quad (4)
\]

**Modeling of column data**

**Yoon-Nelson model**

Yoon and Nelson have proposed a less regress model to represent the breakthrough of gases and vapour onto activated coal. The model was proposed based on the assumption that the rate of decrease in the probability of sorption for each adsorbate molecule was proportional to the probability of adsorbate sorption and the probability of adsorbate breakthrough on the adsorbent.\(^{23,24}\) The linear form of Yoon-Nelson model is represented as:

\[
\ln \left(\frac{C_t}{C_o - C_t}\right) = K_{YN} \, t - \tau \, K_{YN} \quad (5)
\]

Where \(K_{YN}\) is the Yoon-Nelson rate constant, \(\tau\) is the time required for 50% adsorbate breakthrough and \(t\) is the sampling time. A plot of \(\ln \left(\frac{C_t}{C_o - C_t}\right)\) versus \(t\) gives a straight line with a slope of \(K_{YN}\) and intercept of \(-\tau \, K_{YN}\).

**RESULTS AND DISCUSSION**

**Adsorbent characterization**

FTIR spectroscopy was used to verify the change in chemical structure of starch molecules after cross-linking. FTIR spectra of native and CLS2 are shown in Fig. 2. In the spectra of native starch there were bands at 1156.59, 1080.07 and 1018.88 cm\(^{-1}\) which were attributed to C-O band stretching. Additional characteristic absorption bands appeared at 930.07, 861.49, 765.88 and 575 cm\(^{-1}\), which were due to anhydroglucose ring stretching vibrations. An extremely broad band because of hydrogen bonded –OH groups appeared at 3339 cm\(^{-1}\). Spectra of CLS2 also showed an intensive band for OH (and NH) groups at 3373.83 cm\(^{-1}\). However the intensity of OH/NH band decreased and the peak became narrower. Other differences of characteristic bands for CLS2 appeared at 1575 cm\(^{-1}\) (amide group) and 1622 cm\(^{-1}\) (carbonyl group).\(^{25}\) Since HMDI consists of 6 consecutive –CH\(_2\) groups the bending vibration at 773 cm\(^{-1}\) was observed.\(^{26}\)

**Column studies**

**Effect of initial concentration**

The effect of initial concentration for the adsorption of pNP on CLS2 have been investigated at 50, 100 and 150 mg/L, respectively. The bed height was 2.5 cm. The flow rate was fixed at 4 mL/min at a pH of 5. The effect of initial concentrations on the adsorption of pNP on CLS2 is shown by breakthrough curve in Fig. 3. It was observed from the breakthrough curve that the initial concentration of organic pollutant strongly affects the volume of solution treated. The volume of solution treated decreased as the initial concentration increased and the slope of the plots from throughput volume increased as the initial concentration increased from 50 to 150 mg/L. These results indicated that the breakthrough become steeper as the initial concentration increased which was due to the increase in driving force and decrease in the adsorption zone length.\(^{27}\) The availability of the adsorbate for the adsorption site was more at higher concentration, which leads to the higher uptake of adsorbate (pNP) at higher concentration even though the breakthrough time was shorter than the breakthrough time of lower concentration.\(^{27}\) The adsorption capacity increased with increased in
initial concentration (Table 1). This was due to the high driving force between the adsorbate. It was also observed that for 2.5 cm bed height, flow rate of 4 mL/min, the maximum bed capacity obtained was 42.26 mg/g at 150 mg/l initial pNP concentration.

![FT-IR spectra of native and cross-linked starch (CLS2)](image)

**Fig. 2**: FT-IR spectra of native and cross-linked starch (CLS2)

![Breakthrough curves for pNP adsorption at different inlet concentrations](image)

**Fig. 3**: Breakthrough curves for pNP adsorption at different inlet concentrations (bed height 2.5 cm, flow rate 4 mL/min and pH 5)

**Effect of bed height**

The breakthrough curve for the adsorption of pNP on CLS2 at various bed heights by fixing the influent concentration at 100 mg/L, flow rate at 4 mL/min and pH 5 is shown in Fig. 4. In order to yield different bed heights, 1, 2 and 3 g of the adsorbent were added to produce bed heights of 2.5, 5 and 7.5 cm, respectively. The results indicated that throughput volume of pNP solution increased with increased in bed height, which was due to the more number of adsorption sites (i.e. the total surface area increases). As the bed height increased from 2.5 cm to 7.5 cm, the equilibrium capacity \( q_{\text{eq(exp)}} \) increased from 38.14 mg/g to 42.64 mg/g. This was due to the fact that, pNP had more time to contact with the CLS2, that resulted in higher equilibrium capacity \( q_{\text{eq(exp)}} \) of pNP in the column. At the same time, higher bed column results in decreasing pollutant concentration the in effluent. The column parameters are shown in Table 1.
Table 1: Column parameters obtained at different inlet (pNP) concentrations, bed heights and flow rates

<table>
<thead>
<tr>
<th>Bed height (cm)</th>
<th>$C_0$ (mg/L)</th>
<th>Flow rate (mL/min)</th>
<th>$q_{\text{total}}$ (mg)</th>
<th>$q_{\text{eq (exp)}}$ (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>50</td>
<td>4</td>
<td>25.82</td>
<td>25.82</td>
</tr>
<tr>
<td>2.5</td>
<td>100</td>
<td>4</td>
<td>38.14</td>
<td>38.14</td>
</tr>
<tr>
<td>2.5</td>
<td>150</td>
<td>4</td>
<td>42.26</td>
<td>42.26</td>
</tr>
<tr>
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<td>100</td>
<td>4</td>
<td>38.14</td>
<td>38.14</td>
</tr>
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<td>4</td>
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</tr>
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<td>4</td>
<td>127.93</td>
<td>42.64</td>
</tr>
<tr>
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<td>38.14</td>
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<td>6</td>
<td>32.27</td>
<td>32.27</td>
</tr>
<tr>
<td>2.5</td>
<td>100</td>
<td>8</td>
<td>29.29</td>
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</tr>
</tbody>
</table>

**Fig. 4**: Breakthrough curves for pNP adsorption at different bed heights ($C_0$ 100 mg/L, flow rate 4 mL/min and pH 5)

**Effect of flow rate**

The effect of flow rate for the adsorption of pNP on CLS2 was investigated by varying the flow rate from 4 to 8 mL/min and keeping the initial concentration 100 mg/L and bed height of 2.5 cm with pH 5. Results were shown in **Fig. 5**. As the flow rate increased, the breakthrough became steeper and reached the breakthrough quickly. The reason was that at higher flow rate the rate of mass transfer

**Fig. 5**: Breakthrough curves for pNP adsorption at different flow rates ($C_0$ 100 mg/L, bed height 2.5 cm and pH 5)
increased and the amount of pNP adsorbed onto unit bed height gets increased with increased in flow rate leading to faster saturation at higher flow rate. Results of Table 1 showed that, as the flow rate increased from 4 to 8 mL/min, equilibrium capacity \( q_{\text{eq(exp)}} \) decreased from 38.14 mg/g to 29.29 mg/g, this was due to the insufficient contact time of the solute in the column and solute \( \text{pNP} \) left the column before equilibrium occurred.²⁹

**Application of Yoon-Nelson model**

The column data were fitted to the Yoon-Nelson model to determine the rate constant \( K_{YN} \) and 50 % breakthrough time \( \tau \) are presented in Table 2. These coefficients were determined from the slope and intercepts obtained from the linear regression performed on each set of transformed data. The rate constant \( K_{YN} \) increased and the 50 % breakthrough time \( \tau \) decreased with increasing \( \text{pNP} \) initial concentration. Besides, \( K_{YN} \) increased while \( \tau \) decreased, as the flow rate increased. It was also observed that as the bed height increased, the \( \tau \) increased and the values of \( K_{YN} \) decreased. Analysis of the regression coefficients indicated that the regressed lines provided excellent fits to the experimental data with \( R^2 \) values ranging from 0.84 to 0.964. Data showed that the Yoon-Nelson model can be used to describe the behaviour of the adsorption of pNP in a fixed bed column.

**Table 2 : Yoon-Nelson parameters at different column conditions**

<table>
<thead>
<tr>
<th>Bed height (cm)</th>
<th>( C_0 ) (mg/L)</th>
<th>Flow rate (mL/min)</th>
<th>( K_{YN} ) (1/min)</th>
<th>( \tau ) (min)</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
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<td>4</td>
<td>0.037</td>
<td>125.43</td>
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</tr>
<tr>
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<td>100</td>
<td>4</td>
<td>0.041</td>
<td>97</td>
<td>0.963</td>
</tr>
<tr>
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<td>4</td>
<td>0.062</td>
<td>72.11</td>
<td>0.964</td>
</tr>
<tr>
<td>2.5</td>
<td>100</td>
<td>4</td>
<td>0.041</td>
<td>97</td>
<td>0.963</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>4</td>
<td>0.027</td>
<td>194.44</td>
<td>0.911</td>
</tr>
<tr>
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<td>100</td>
<td>4</td>
<td>0.016</td>
<td>315.62</td>
<td>0.84</td>
</tr>
<tr>
<td>2.5</td>
<td>100</td>
<td>4</td>
<td>0.041</td>
<td>97</td>
<td>0.963</td>
</tr>
<tr>
<td>2.5</td>
<td>100</td>
<td>6</td>
<td>0.07</td>
<td>55.87</td>
<td>0.959</td>
</tr>
<tr>
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<td>100</td>
<td>8</td>
<td>0.092</td>
<td>38.2</td>
<td>0.947</td>
</tr>
</tbody>
</table>

**CONCLUSION**

The adsorbent prepared from the cross-linking of starch with HMDI was an effective adsorbent for the removal of para-nitrophenol (pNP) from waste water. The removal efficiency of pNP from waste water strongly depended on influent concentration, bed height and flow rate. The prepared adsorbent was capable of holding a maximum equilibrium capacity of 42.64 mg/g for pNP at 100 mg/L of influent concentration, bed height 7.5 cm and flow rate of 4 mL/min. The equilibrium capacity increased with increase in influent concentration, bed height and decreased with increase in flow rate. Yoon-Nelson model was used to follow the fixed bed dynamics, the calculated breakthrough curves agreed well with the measured results. Yoon-Nelson can be used to describe the behaviour of the adsorption of the pNP on cross-linked starch.

**REFERENCES**


