STUDY OF COPPER REMOVAL IN WATER BY ION EXCHANGE MATERIAL

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Received: 09 May 2018; Accepted for publication: 24 August 2018

ABSTRACT

In this study, sulfonation of polystyrene waste was investigated for the possibility of removing Cu (II) ions in solution. Fourier transform infrared (FTIR) of sulfonation polystyrene waste was performed to study the material characteristics and the results showed the presence of sulfonic group bands. The efficiency of Cu (II) ion removal in ion exchange column experiments indicated that the quality of sulfonation of polystyrene waste depended on some factors as the reaction time, height of the column and the velocity of the flow rate. Ion exchange experiments were carried out with the columns of 8 and 6 mm internal diameter, of which 10 cm of column bed height in the 8 mm-diameter column obtained the highest efficiency of 74.13 % at 1 hr reaction time, and flow rate of 1.48 mL per min. The experimental data were consistent with Thomas and Yoon-Nelson kinetic models.

Keywords: ion exchange, polystyrene plastic, sulfonation, copper, contaminated water.

1. INTRODUCTION

Economic development is caused of high demand on using instant products such as bowls, plates, spoons and forks. Annually, large quantities of these products, especially plastic waste, are discharged into the environment and accumulated over a long period of time, which caused serious problems to environment and human health. The main component of these disposal items is polystyrene [1], at high temperature there are migration of styrene from them into environment, this potentially toxic may have a toxic effect on the liver, lung functions and causing neurological impairment, etc. [1, 2]. Therefore, collecting and recycling polycarbonate resins are imperative.

Copper (Cu) is very common heavy metal that occurs naturally in the environment. They are widely used in industrial for many purposes and spreads through the environment through waste disposal systems, especially wastewater discharges. The exposure of copper even with tiny amount will have negative effects on aquatic animals and plants [3]. Especially, their accumulation and high dispersion through the food chain has high potential affect to human
health. Therefore, the study of copper ion extraction from contaminated water sources is an important issue to protect the public and receives intensive care.

Recently, many methods have been implemented to eliminate copper in industrial wastewater such as chemical precipitation, ion exchange, membrane separation and adsorption [4]. Ionic exchange resin has been being used as an effective material to remove ions from water [5]. This study focused on modification of original polystyrene (PS-S) and polystyrene waste (PSW-S) as a cation-exchange material to remove Cu (II) ions from aqueous solution; and then comparison their treatment efficiency.

2. MATERIALS AND METHODS

2.1. Materials

Polystyrene waste plastics (PSW) were obtained from the plastic disposal spoons, plates, which were used to be converted into ion exchange material. Solution concentration of 100 mg/L Cu (II) was prepared in the laboratory as wastewater.

2.2. Methods

Materials preparation: Plastic wastes were crushed into small particles of 1 mm to 1.5 mm of size. 5 g of material were weighed and shaken in 100 mL H$_2$SO$_4$ 98 % at a constant stirring speed of 150 rpm for 4 hrs. The materials were eliminated by washing the resins with distilled water until the pH value reaches 6 – 7, and then dried for 30 minutes at 40 °C. After that, the dried resin was shaken with NaCl 1 M (1 g of plastic/100 mL of NaCl) for 2 hrs, at the speed of 150 rpm [6, 7].

Methods of analysis: In this study, the functional groups of original and modified waste PS were determined by the FT-IR spectrophotometry. The concentration of Cu (II) ions in solutions were analyzed by the Plasma emission spectroscopy (ICP - OES).

3. RESULTS AND DISCUSSION

3.1. Material characteristics

The FTIR spectrum identified functional group characteristics that adsorb Cu (II) ion. Figure 1 and Fig. 2 showed FTIR spectra of the original polystyrene (PS) and polystyrene waste (PSW) before and after modification with H$_2$SO$_4$ (linkage of the -SO$_3$H group).

The FTIR spectra of PS and PSW were not much different in material structure as the number of peaks as well as the wavelength of the oscillations were equivalent. Both materials present a number of functional groups in the structure of polystyrene, such as C-C, C-H (aromatic rings), C-H (CH$_2$X) [8, 9, 10].

The FTIR spectrum of PSW-S appears with new peak of O-H bond (absorption bands at 1492.90 cm$^{-1}$); S = O bond (absorption bands at 1128.36 cm$^{-1}$); C-S bond (absorption bands at 1029.99 cm$^{-1}$) demonstrates the presence of functional groups -SO$_3$H in PSW-S. Whereas PS-S has two peaks of 1369,45 cm$^{-1}$ (O-H bond) and 1,028 cm$^{-1}$ (C-S band) of the functional group -SO$_3$H [10, 11]. Therefore, both materials after modification with 98 % sulfuric acid has new
peaks, and presents the -SO₃H, but the FTIR spectrum of the PSW-S expresses the appearance of the -SO₃H group more clearly than that of PS-S.

Figure 1. FTIR spectrum of polystyrene waste before and after modification.

Figure 2. FTIR spectrum of original polystyrene before and after modification.

3.2. The effect of column size

The input Cu (II) concentration was 100 mg/L and the height of cation-exchange layer was 10 cm, the removal efficiency of Cu (II) in reaction time with 8 and 6 mm-diameter column was shown in Fig. 3a and Fig. 3b, respectively. The treatment efficiency of 8 mm-diameter with PSW-S reached 74.13 % after 1 hr of reaction. In the first 4 hrs, the efficiency of material was shown to be relatively high, after 14 hrs the material was completely saturated. The Cu (II) removal efficiency of PS-S was 49.42 times lower than PSW-S with highest efficiency attended after 2 hrs, the material was saturated after 12 hrs.

For 6 mm-diameter column, the highest efficiency of PSW-S achieved 37.73 % after 30 mins and the material was saturated after 8 hrs. In the first 2 hrs, the Cu (II) removal capacity of the exchange resin decreased rapidly, so this is the optimal reaction time and after 8 hrs, the material is completely saturated, similar to 8 mm-diameter column. The Cu (II) removal efficiency of PSW-S was 11.39 times higher than that of PS-S. The optimal response time of PS-S was 2 hrs and the material saturation time was 16 hrs.

The efficiency of PSW-S was much higher than PS-S, therefore subsequent experiments were conducted with PSW-S.

Figure 3. The efficiency of treatment of Cu (II) by PS-S, PSW-S versus reaction time using 8 mm-diameter (a) and 6 mm-diameter (b) column.
3.3. The effect of flow rate

The effect of flow rate on Cu (II) ion exchange of PSW-S was investigated by changing the flow rate. Reaction time of ion exchange reaction with 8 mm and 6 mm internal diameter column was fixed in the experiments for each type of column, 1 hour and 30 minutes, respectively. The Cu (II) removal efficiency of 8 mm-diameter column corresponding to different flow rates is shown in Fig. 4a. When the flow rate of 8 mm-diameter column increased from 1.48 mL/min to 9.55 mL/min, the efficiency has decreased significantly, from 74.13 % to 5.43 % (reduced 13.7 times).

For 6 mm-diameter column, the highest efficiency which was shown in Fig. 4b was 37.73 % at 1.02 mL/min and the efficiency decreased significantly to 6.4 % at 2.68 mL/min (reduced 5.9 times). The results of the experiments can be explained that for slow of flow rate, aqueous solution have enough contact time between metal ions and ion exchange resins, so the amount of ion retained on the surface of the ion exchanger increased.

![Figure 4](image)

**Figure 4.** The efficiency of treatment of Cu (II) by PSW-S versus flow rate using 8 mm-diameter (a) and 6 mm-diameter (b) column.

3.4. The effect of the height of packed material

The effect of the height of ion exchange material layer on Cu (II) removal was investigated by experiments with 5 different heights, at optimal conditions. The ion treatment efficiency of Cu (II) for each column was shown in Fig. 5a and Fig. 5b. The highest cation exchange efficiency was 74.13 % with the 8 mm-diameter column, 10 cm height material layer; and 44.34 % with the 6 mm-diameter column and 15 cm height of packed material.

![Figure 5](image)

**Figure 5.** The efficiency of treatment of Cu (II) by PSW-S versus height of packed material with 8 mm-diameter (a) and 6 mm-diameter (b) column.
3.5. Thomas and Yoon-Nelson kinetic model

At the optimal conditions, the maximum adsorption capacity of material and the time in required for 50% adsorbate breakthrough were predicted by Thomas and Yoon-Nelson’s kinetic modeling [2]. The parameter of the models were shown in Table 1 and Fig. 6.

The maximum ion exchange capacity of the 8 mm column is 4.06 mg/g, and the 6 mm column is not suitable for calculating. The high correlation coefficient of Thomas kinetic model \( R^2 \) (\( R^2 > 0.8 \)) indicates that experimental data with the 8 mm column is consistent with the Thomas kinetic model. According to the Yoon–Nelson model, the high correlation coefficient \( R^2 \) (\( R^2 > 0.8 \)) showed that the experimental data of the 8 mm column was in accordance with the Yoon - Nelson kinetic model while the 6 mm column (\( R^2 < 0.8 \)) is not described by the Yoon-Nelson model. Basing on the results, the reaction time required for 50% adsorbate breakthrough of 8 mm column was 43.89 mins.

Table 1. Parameters of Thomas kinetic model and Yoon - Nelson kinetic model of PSW-S.

<table>
<thead>
<tr>
<th></th>
<th>6 mm-diameter column</th>
<th>8 mm-diameter column</th>
</tr>
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<tbody>
<tr>
<td>Thomas Kinetic model</td>
<td>( R^2 ) 0.6973</td>
<td>0.8072</td>
</tr>
<tr>
<td></td>
<td>( K_T ) (mL/min/mg)</td>
<td>-0.0940 0.0750</td>
</tr>
<tr>
<td></td>
<td>( q_0 ) (mg/g)</td>
<td>18.700 4.0600</td>
</tr>
<tr>
<td>Yoon – Nelson model</td>
<td>( R^2 ) 0.6973</td>
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</tr>
<tr>
<td></td>
<td>( K_{YN} ) (l/min)</td>
<td>0.0094 0.0075</td>
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<tr>
<td></td>
<td>( \tau ) (min)</td>
<td>43.890</td>
</tr>
</tbody>
</table>

Figure 6. Linear dynamics of Thomas kinetic model (a) and Yoon-Nelson kinetic model (b) of PSW-S.

4. CONCLUSION

FTIR spectrum showed that PS and PSW after being modified by \( \text{H}_2\text{SO}_4 \) contained –SO\(_3\)H functional group, and the appearance of –SO\(_3\)H in PSW is more remarkable comparing to PS. PSW-S, shows a much higher adsorption efficiency of Cu(II) comparing to PS-S (74.13 and 9.61% respectively). The set of optimal conditions for the 8 mm-diameter ion exchange column
Ion exchange material from waste plastic for copper contaminated water treatment

to reach the highest efficiency removal Cu (II) (74.13 %) was 10 cm of column bed height, flow rate of 1.48 mL/min and reaction time of 1 hr. The data of 8 mm column was also well described by Thomas and Yoon-Nelson kinetic equations, with maximum exchange capacity of 4.11 mg/g.

Acknowledgements. This research is funded by the VNU University of Science under project code: TN.18.19.

REFERENCES