Sulfonated polystyrene waste in liquid phase as on-exchange material to remove Cr (III) in aqueous solution

C Nguyen\textsuperscript{1}, P Nguyen, G Pham, K Nguyen and T Pham

\textsuperscript{1} Faculty of Environment, VNU University of Science, Hanoi, Vietnam

E-mail: nguyenlinhchi_t60@hus.edu.vn

Abstract. Polystyrene waste from disposal products has been sulfonated in a homogeneous phase by using sulfur acid and cyclohexane to synthesize cation exchange material, which could be used to uptake Cr(III) from aqueous solution. In this study, by analysis techniques such as SEM (Scanning Electron Microscope) and FTIR (Fourier transform infrared), the surface area of material groups is revealed that they are larger than raw materials to increase point of contact with Cr(III). Moreover, it is proven that the additional sulfonic groups were presented. The results pointed out that the dependence of ion exchange column operation on many factors (size, reaction time, flow rate,...) exert an influence on the efficiency of Cr(III) ion treatment. In addition, experimental conditions which affect the sulfonation conversion, have been investigated such as temperature, modification time, H\textsubscript{2}SO\textsubscript{4} concentration,... It was found that reducing the Cr(III) concentration by 87.51\% and 98.72\% for 10 cm and 15 cm ion-exchange height layer after 3 hours operation in the reaction conversion using the column 8 mm diameter, flow rate 2.00 ml per minute with shaking speed 220 rpm. The experimental data were consistent with Thomas and Yoon-Nelson kinetic models. The ability of sulfonated waste polystyrene to uptake chromium ion from aqueous water has been evaluated significantly.

1. Introduction
In recent decades, Chromium (Cr) is used vastly from the industrial activities such as electroplating, metal finishing, inorganic paint pigments, leather tanning industry, inhibition of water corrosion, fungicides, wood preservatives, as catalysts, ceramic glazes, and petroleum refining \[1,2\]. It is also considered as a poison group which has potentially carcinogenic to humans and animals. The human could suffer from Chromium in three ways: respiration, digestion, and direct contact (through the skin). As a result, long-term exposure to Cr(III) is responsible for chronic diseases related to anemia, weight loss, hepatic dysfunction, and kidney failure \[3\]. Therefore, it plays an integral role in the study of chromium ion extraction from contaminated water sources, which extremely attract the interest of many scientists to lessen this toxicity and protect public health \[4,5\].

In addition, due to the rapid economic development, there is increasingly becoming consumption of daily disposable products such as plates, bowls, and forks made of plastic. Annually, a large quantity of these products is released into the surrounding environments, then accumulated to the organisms, leading to ecological disturbance and risks for human health \[8\]. The main component of these disposable items is polystyrene which can release styrene into the environment. At high temperatures, polystyrene bonds are broken and release original styrene that has the toxic effect on the liver, lung functions, DNA structures and causing neurological impairment \[9\], hence, needs the emphasize on the collecting and recycling of polycarbonate resins waste.

Nowadays, many methods have been applied to resolve chromium in the aqueous solution, including...
chemical precipitation, membrane separation, adsorption, and ion exchange. One of them is ionic exchange measure mentioned as an effective way to remove ions from aqueous. In this research, polystyrene waste was modified to cation exchange resin to remove chromium (III) from sewage by cation exchange method.

2. Material and methods

2.1. Cation exchange preparation
The polystyrene waste (PSW) was collected from the restaurants as disposal plates, then classified them. After that, it was washed with tap water first, then continuously with distilled water until the leftover and oil were removed before drying.

In the next step, they are cut into small particles of approximately 4x4 mm of size, which is ready for modification. 5g of PSW was weighed and put into the Erlenmeyer Flask (250 mL), then added cyclohexane solvent based on the ratio PSW: Cyclohexane given in 1g: 10ml. The flasks were shaken by shaker, next shaken continuously at room temperature to investigate the optimal shaking time with cyclohexane. Next, added H2SO4 and shook it similar to cyclohexane. After shaking, soak those flasks in ice water for about 12 hours, and filter through a sieve having a hole size of 0.3mm, washing in water and NaCl (1N) 10 times. The material was dried for 12 hours at 100°C and crushed until reached the size evenly from 1-1.5 mm size.

The total exchange capacity of the material of modified resin was tested by the fixed bed column experiments with 8 mm diameter column to explore suitable agitation time. The synthesis wastewater which had a concentration of 100 mg/l Cr (III) was driving through the column with a flow rate of 2 ml/min. The modified cation exchange material which was made with the set of optimal conditions from experiments above. Fix bed column study was carried out with 8mm inner diameter column. The synthesis wastewater which had a concentration of 30 mg/l Cr(III) was run through the column with a flow rate of 2 ml/min. Modified cation exchange was packed in the column with different height, 10 cm, and 15 cm. The effluent samples were collected at the range of time from 30 mins to 720 mins.

2.2. Methods of analysis
In this study, the functional groups of original and modified PS waste were determined by the FT-IR spectrophotometry on SHIMADZU (Japan) machine at Faculty of Chemistry, Hanoi University of Science, Vietnam National University. In addition, the concentration of Cr(III) was analyzed by the Plasma emission spectroscopy (ICP - OES) machine at the Center for Geological Experimental Analysis - General Department of Geology and Minerals of Vietnam. The inorganic chemicals were used in this research including NaCl 99.9%, CrCl3.6H2O 99%, and the organic solvent was cyclohexane (C6H6) 99.9%. All processes were prepared using distilled water.

3. Results and discussion

3.1. Characterization
The surface morphological results of original polystyrene waste (PSW) and modified polystyrene waste (PSW-S) were done using a Scanning electron microscope at magnifications 8.2mm x 10 kV and 8.3m x 25K in turn, were shown in Figure 3.1.a and Figure 3.1.b respectively. The surface of the original material was very smooth and shiny, almost without any holes, with high density, which hindered the contact between the material and the ionic base. The PSW-S surface was porous with many voids and openings, which may be due to the sulfonation of polystyrene. This surface morphology means that the addition of the -SO3H base to the waste plastics had occurred. As a result, the material had a large surface area to increase the contact between the ion and the Cr(III) material, which improved the efficiency of Cr(III) treatment.
Figure 3.1. Scanning electron micrograph of (a) Original Polystyrene waste (PSW); (b) Modified Polystyrene waste (PSW-S)

FT-IR spectrophotometry is used to study the association and structural characteristics of the material. In this study, the FT-IR technique proves the exits of functional group that was bound to polystyrene by the reaction of sulfonation. The appearance of the peaks in the wave number range from 4000 to 400 cm\(^{-1}\) (indicated exactly the component bonds in PS resin, original PSW resin and modified PSW resin (bonding of the \(-\text{SO}_3\text{H}\) group) in Figure 3.2 and Figure 3.3 that were done using the FTIR Affinity - 1S.

![FTIR spectrum of Original Polystyrene Waste (PSW)](image)

Figure 3.2. FTIR spectrum of Original Polystyrene Waste (PSW)

The FTIR spectra of the modified material PSW-S showed that there were some peaks lost, however, some new peaks also appeared such as O-H bond of \(-\text{SO}_3\text{H}\) group (absorption band at 1375.25 cm\(^{-1}\)); S=O bond of \(-\text{SO}_3\text{H}\) group (absorption band at 1128.36 cm\(^{-1}\)); C-S bond of R-\text{SO}_3\text{H}\) group (absorption band at 1029.99 cm\(^{-1}\) and 572.86 cm\(^{-1}\)), all of them demonstrate the presence of \text{SO}_3\text{H}\ group in PSW-S. In particular, the presence of the (830 cm\(^{-1}\)) peak and the 1125 cm\(^{-1}\) peak indicated that: At peak 830 cm\(^{-1}\): A group substitute at the para position on the aromatic ring [54]. This result demonstrates that process by \text{H}_2\text{SO}_4\ is effective for PSW.
Figure 3.3. FTIR spectrum of Modified Polystyrene Waste (PSW-S)

3.2. The effect of modification conditions of PSW material to the Chromium (III) removal treatment ability

3.2.1. The solubility of PSW in C₆H₁₂ solvent. The image showed the solubility of PSW in cyclohexane solvent after settling for 1 hour. By naked eyes, at flask P1 (1 ml cyclohexane), the material was only sticky at the surface but not completely dissolved to become homogeneous solution. At flash P2 and the rest flask, the PSW was more soluble, and the solubility was proportional to the volume of the cyclohexane solvent added. After 1 hour, all 5 flasks formed stable and non-separable suspensions. However, there was still sticky residues on the bottom of flask P2 and excess residues after filtering through the sieve having a hole size of 0.3 mm.

Figure 3.4. The solubility of PSW in cyclohexane solvent after settling for 1 hour

3.2.2. The effect of C₆H₁₂ shaking time. According to the chart, the Cr(III) output concentration of C₆H₁₂ shaking period for the lowest was 70 minutes with the value ranged from 0 mg/L to 78.25 mg/L after 5 hours of ion exchange period. After 4 hours of the ion exchange period, all samples had gradually equal Cr(III) output values, and the values were approximately equal. This can be predicted that from 5 hours onwards the Cr(III) removal treatment efficiency of all samples was the same. After 50-60 minutes on dissolution, the solubility in homogeneous form was nearly equal. Therefore, the optimal C₆H₁₂ shaking time to dissolve PSW from solid to liquid phase (suspension) was 70 minutes and the PSW-S7 sample was chosen to represent for optimal C₆H₁₂ shaking time condition.
3.2.3. The effect of H$_2$SO$_4$ shaking time. After PSW-S7 was chosen as the optimal time to dissolve PSW perfectly at homogeneous form or the optimal shaking time between PSW and C$_6$H$_{12}$, the effect of H$_2$SO$_4$ shaking time on Cr(III) treated efficiency was beginning studied. Figure 3.6 showed the change in Cr(III) concentration over time in the column experiment, which was performed to check the removal efficiency of the Cr(III) after the PSW modification. The Cr(III) removal efficiency of PSW-S715 is higher than the PSW-S730 in all time of trials, with the highest efficiency of 44.09% and 39.68%, respectively. Therefore, 15 minutes was chosen as the optimal time to sulfonate polystyrene waste resin.

Therefore, the optimal H$_2$SO$_4$ shaking time to modified PSW in liquid phase (suspension) to sulfonate polystyrene was 15 minutes. PSW-S715 sample was chosen to represent for optimal H$_2$SO$_4$ shaking time condition.

![Figure 3.5](image1.png)

**Figure 3.5.** The Effect of C$_6$H$_{12}$ shaking time after dissolving polystyrene in cyclohexane on Cr(III)output concentration of the modified PSW-S material

3.2.4. The effect of H$_2$SO$_4$ shaking speed. The shaking speed also affects the bonding of -SO$_3$H to the polystyrene resin. At low speed, the reaction was slow, the PSW granules were focused in the central solution. From 2 hours onwards, both the treatment systems were stable performance. Moreover, from 2 hours onwards, the efficiency PSW-S71520 and PSW-S71530 were almost similar, for example at 2 hours point, the processing efficiency PSW-S71520 and PSW-S71530 were 27.29% and 28.05% respectively.

Therefore, the optimal H$_2$SO$_4$ shaking speed to modified PSW in liquid phase (suspension) to sulfonate polystyrene was 200 rpm. PSW-S71520 sample was chosen to represent for optimal H$_2$SO$_4$ shaking speed time condition.

![Figure 3.6](image2.png)

**Figure 3.6.** The Effect of H$_2$SO$_4$ shaking time on efficiency treatment of the modified PSW-S material
3.3. The effect of the height of the PSW-S material layer

The effect of the height of ion exchange material layer on Cr(III) ion exchange with PSW-S resin was investigated by 3 different heights as 5cm, 10cm, 15 cm in the 20 mm column. The velocity of the output flow and the sampling time was 10 mL/min. The initial metal ion concentration of 120 mg/L and the flow rate 10 mL/min were kept at the constant values during the adsorption. The Cr(III) removal efficiency was shown in Figure 3.8. The experimental results showed that the highest cationic exchanger performance for PSW-S-5cm, PSW-S-10cm, and PSW-S-15cm were 52.25%, 84.01%, and 81.23%, respectively. After 6 hours, the percentage of efficiency decreases by 0.85% per hour for the PSW-S-5cm; 2.9% per hour for column PSW-S-10cm and 4.64% per hour for column PSW-S-15cm. The highest Cr(III) treatment efficiency which did not always for the highest layer of material. As the results, the height of packed material was the factor that affected the ion exchange efficiency of the column exchange process.

3.4. Thomas and Yoon Nelson’s kinetic model

In order to more accurately evaluate the maximum exchange capacity of the material and the time required for 50% adsorbate breakthrough were predicted by Thomas and Yoon - Nelson’s kinetic model, erected for the exchange column in 12 hours with 20 mm column. PSW-S was exchanged ion in a glass column 20 mm, thought 24 hours, the Cr(III) input concentration was 50 mg/L, the flow rate was 10 mL/min. The height of packed material was 10 cm. PSW was modified in optimal condition. PSW was dissolved at 60°C during 20 mins by Magnetic stirrer, after that was continuously dissolved at room temperature by Shaker in 70 mins until PSW existed at homogenous form. PSW was modified by
sulfuric acid during 15 mins with 200rpm of speed.

- Thomas kinetic modeling:
  
  Linear model kinetic model Thomas demonstrated the dependence of ln \([ (C_t / C_0) -1 ]\) on time (t) for the exchange of Cr(III) as shown in Figure 3.9. The constants of the KT and q₀ models were calculated and presented in Table 3.2. Accordingly, the maximum exchange capacity of the 20 mm column was 18.43 mg/g, which is equivalent to q measured in the experimental period (q = 18.76 mg/g). The high correlation coefficient R² (R² > 0.94) indicates that the experimental data in the 20 mm column matched the Thomas kinetic model.

![Figure 3.9. Linear dynamics of Thomas kinetic model](image)

- Yoon-Nelson kinetic modeling:

  The linear model of the Yoon-Nelson adsorption model for the exchange of Cr(III) to PSW - S in diameter columns was shown in Figure 3.10. The Yoon-Nelson constant values and corresponding parameters were presented in Table 3.1. Moreover, the high value of the system correlation coefficient R² (R² > 0.94) showed that the empirical data in the 20 mm column matched kinetic model Yoon-Nelson.

![Figure 3.10. Linear dynamics of Yoon-Nelson kinetic model](image)

| Table 3.1. Parameters of Thomas kinetic model and Yoon-Nelson kinetic model of PSW-S |
|---------------------------------------------|
| Column 20mm | Thomas kinetic model | Yoon-Nelson kinetic model |
| | R² | 0.9578 | 0.9578 |
| | K_T (mL/min/mg) | 0.000067 | 0.0034 |
| | q₀ (mg/g) | 18.979018601 | 498.5 |

![Algebraic representation](image)
4. Conclusion
After being modified by sulfuric acid, the FT-IR spectrum of modified material showed that it contained -SO\textsubscript{3}H functional group. The total exchange capacity depends on some factors, including agitation time and the speed when dissolving polystyrene waste in cyclohexane, and the sulfonation time. The lab-scale optimal conditions for sulfonation PS waste in the liquid phase were dissolving in cyclohexane in 50 mins at room temperature, followed by sulfonation with sulfuric acid in 15 mins with 200rpm. In addition, the removal chromium (III) efficiency also depends on the height of the material layer. The results calculated with Thomas kinetic model and Yoon-Nelson model were approximated in comparison with experimental results. The study only provides the feasibility of using the polystyrene waste as raw material for synthesizing ion exchange material. The study is only the first steps in synthesizing the modification of PSW materials. In order to increase the possibility of discovering other effects of sulfonate PSW resin in particular and processing of Cr(III) metals in water, more research is needed. This is necessary to conduct deeper research on factors affecting material modification such as temperature, catalyst.

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