

# MODIFYING WASTE POLYSTYRENE TO ION EXCHANGE MATERIAL: OPTIMIZING THE SULFONATION PROCESS AND COLUMN STUDY FOR THE REMOVAL OF Cr<sup>3+</sup>

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**Abstract.** The incredible growth of plastic waste is a major concern for the whole society in recent years. The accumulation of plastic waste has a badly effects on wildlife, habitat, and humans. Plastics that act as pollutants are categorized into different sizes, from micro to macro. This study focuses on modifying waste plastic by sulfuric acid to bind the sulfonated function group on the structure of the polystyrene chain at room temperature. The sulfonated product was used for removing heavy metal ion in water with the mechanism of the ion exchange process. The prepared ion exchange material was characterized by FTIR and SEM to ensure that the sulfonation process has happened. The chromium (III) ion removal by modified ion exchange product in continuous mode was affected by an operational parameter such as the bed height of sulfonated material. The Yoon-Nelson and Thomas model were used to analyze the experimental result and the model parameters were evaluated. From this result, it can be concluded that with the increasing amount of sulfonated waste polystyrene, exchange capacity and the time required for a 50 % adsorbate breakthrough was higher.

*Keywords:* sulfonation, chromium removal, wastewater treatment, polystyrene waste, ion exchange.

*Classification numbers:* 2.9.3, 3.3.2, 3.4.2.

## 1. INTRODUCTION

Plastic plays a very important role in the fast-paced life today. This common polymer product is very important to all aspects of society. With the development of chemical engineering techniques, many convenient and useful product has come to human life, and plastic is one of the outstanding inventions. Plastics are made from petroleum by-products, most commonly sourced from natural gas-producing countries at very affordable prices. Our present plastic waste management and recycling capabilities will be far exceeded in the next two decades with the enormous increase in plastic production which was foreseen to double at that time [1].

Because plastic is a product of the oil industry, as the industry grows, so does the plastic production. The plastics industry explains that this increase in production is driven by an increase in demand for disposable plastics, such as soft drinks and packaging, and that this market is particularly flourishing in developing countries. This means that most plastics produced are planned to be exported to developing countries, where waste management services may not be properly equipped for disposal. Nowadays, plastic waste is existing in every part of the environment, ocean, earth, soil, etc. With approximate 730,000 tons of plastic waste discharged to the ocean annually and a lot of other mismanaged plastic waste, Viet Nam, which ranked number 15 in the list of countries (and dependencies) by population took a 4<sup>th</sup> position on the list of countries which discharge the largest amount of plastic [2]. On both land and sea, plastic waste damages the environment and cause harmful consequence to the life and health of the animal and aquatic species, as well as human health.

Heavy metal pollution is usually generated from specific sources, such as mining, chemical manufacturing, tannery, etc. In order to control this type of pollution, one of the most effective recommended methods is to control and minimize the contaminant at the source.

While hexavalent chromium is a highly toxic substance, trivalent chromium has an important role in the body of living organisms. In humans, Cr (III) is an essential nutrient that plays a crucial role in sugar metabolism in the body. Chromium deficiency also affects the function of insulin (a hormone playing a vital role in sugar, proteins, and fat metabolism) which relates to diabetes. Chromium (III) is also considered as a toxic substance that having mutagenic effects on DNA if it exceeds the limited concentration. Epidemiological studies have shown that the addition of chromium improves the effectiveness of insulin action on the lipid. However, uptake too much amount of Cr (III) can lead to some allergic reactions concluding of severe redness and swelling of the skin [3].

Many methods have been studied by scientists all around the world to remove heavy metals from water. These can be chemical, physical, or biological methods such as chemical precipitation, oxidation, coagulation, membrane separation, adsorption, ion exchanges, etc. [4]. These processes have many disadvantages, including high inputs, toxic by-products, and incomplete metal removal. High initial heavy metal concentration is required for high supersaturation, which causes the large volume of discharged wastewater was generated as an unexpected result. During the last decades, low-priced and more effective methods have been developed for the removal of heavy metals at low concentrations from water.

The reason for the widespread use of disposable dishes, as well as the other type of food-storage container made of PS, become very popular in modern-day due to their comfortable and cheap. The rise of the demand leads to the increase of production from polystyrene while its life cycle is relatively short, leading to a huge amount of waste disposal each year, in which 79 % of the plastic disposal is landfilling, 12 % with incineration and just 9 % with recycling [5].

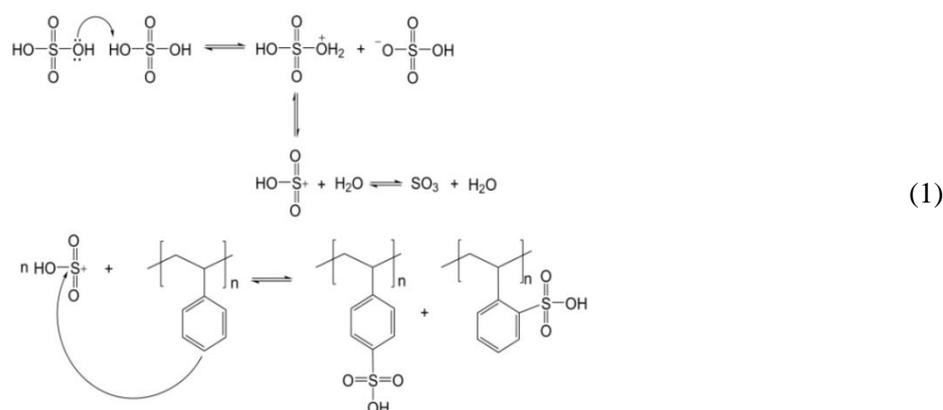
However, with landfilling and incineration, scarcity of land needed for waste dumping and hazardous emissions that now cause the obstacle to polystyrene waste treatment. That is the reason why recycling is recommended to deal with the inherent properties of them as slow degradable plastic waste. Plastic waste, especially polystyrene was considered as a feasible alternative material source to produce ion exchange resins due to their large quantities and very low price. Sulfonated polystyrene waste is a potential method to bind the activated group on the structure of polystyrene and give them the ability as the ion exchange resin [6, 7, 8]. In previous studies, the modification of plastic waste was carried out with the organic solvent [9]. In this study, the straightforward modification method with sulfuric acid was investigated, then the kinetic model for this new material was also studied.

## 2. MATERIALS AND METHODS

### 2.1. Material preparation

Polystyrene waste was collected from the disposable plates which are used in restaurants or fast food stores. The plates were cleaned and dried with tap water and NaOH 1M at room temperature. They were cut into small squares (2 - 3 mm length) then modified by acid sulfuric 98 %.

The amount of PS (5 g) was put in the Erlenmeyer flask (250 ml), then H<sub>2</sub>SO<sub>4</sub> 98 % was added for the modification process following the reaction (1) below. The optimal conditions of the modification process were obtained by adjusting the parameters of reaction as shaking time, shaking speed, and the volume of used sulfuric acid for the reaction.



After that, the plastic flakes were separated from acid, the residue acid was eliminated the material was dried at 55 °C in drying oven for 12 h. The product called sulfonated polystyrene waste (S-PSW) was used for chromium (III) removal from the wastewater. The material after modification process was treated as ion exchange material for the removal of chromium (III). In this process, ions Cr<sup>3+</sup> in solution are exchanged for the ions with the same charge (H<sup>+</sup> from -SO<sub>3</sub>H) that are available on exchange plastic.

### 2.2. Column experiments

This column was made of glass, tube in shape with 2 cm internal diameter, and 30 cm in height. The bed length depended on the purpose of each experiment was different. At room temperature, the solutions with known initial metal concentrations enter the bottom of a packed column, flow upward, and meets ion exchange resin (S-PSW). The flowrate was kept stable and a bed height of modified polystyrene waste resin was measure before opening the valve.

The samples were taken in the exit of the column at the pre-defined time intervals. The length of the modified polystyrene pack in the column was studied by varying the bed height from 5 cm to 15 cm to find out the operation parameter of the pellet reactor. At the end of the tube, glass wool was plugged just to help prevent its floating from the outlet. The column experiment was carried out within 5 hours.

Adsorption and ion exchange are grouped together as sorption for water treatment, the reason was they share many common features. These processes involve the transfer and

distribution of solutes to the liquid phase and then particles, in order to separate the solute from the liquid phase [10].

In this study, Thomas model was used to calculate the maximum concentration of heavy metal adsorbed on sulfonated polystyrene and the rate constant  $k_{TH}$  in the column test. The linearized model is described as equation (1) [11]:

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{mq_{eTH}k_{TH}}{Q} - k_{TH}C_0t \quad (1)$$

where  $k_{TH}$  is the rate constant (mL/(min.mg)),  $q_{eTH}$  is the theoretical equilibrium adsorption capacity (mg/g).

The Yoon–Nelson model was also studied to calculate the breakthrough time and rate constant. The linearized model for a single component system is described as equation (2) [12].

$$\ln\left(\frac{C_0}{C_t} - 1\right) = T_{YN}k_{YN} - k_{YN}t \quad (2)$$

where  $k_{YN}$  is the rate constant (1/min),  $T_{YN}$  is the time when getting 50 % adsorbate breakthrough (min).

### 2.3. Sample analysis

Concentrations of heavy metals ( $Cr^{3+}$ ) were determined by the ICP – OES (Perkin Elmer 7300 ICP-OES) method at the Center for Geological Experimental Analysis - General Department of Geology and Minerals of Viet Nam. The characteristics of S-PSW were described by Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM). By these methods, polystyrene waste from the disposable plastic dish (PSW) before and after sulfonation was characterized at wavenumbers ranging from 400 to 4000  $cm^{-1}$  to confirm the appearance of  $-SO_3H$  groups on polystyrene chain qualitatively using an FTIR Affinity - 1S Shimadzu spectrophotometer at Department of Inorganic Chemistry - VNU University of Science; the surface morphology of the PSW and S-PSW was investigated by scanning electron microscopy (SEM) (Nova NanoSEM 450- FEGSEM) at Faculty of Physics – VNU University of Science.

## 3. RESULTS AND DISCUSSION

### 3.1. Material characteristics

For a better understanding of the surface properties, characterization of all the adsorbents was carried out by using scanning electron microscopy, and the results are shown in Fig. 1A and Fig. 1B, respectively.

The figures show that the morphological images of polystyrene waste have a big blade shape, after sulfonation, this shape becomes small and sharp and is more porous due to reaction with sulfuric acid 98 % at room temperature for a long period. The surface of S-PSW has more space and holes than the original PSW, which is different from the polystyrene waste surface. This can be explained due to a sulfonation reaction of polystyrene plastics that means post denature polystyrene has a larger contacting surface area for the reaction between heavy metals and sulfonated polystyrene, thus, the cation exchange capacity of heavy metals could be raised.

The results of FTIR spectroscopy of S-PSW and PSW are shown in Fig. 2, showing the polystyrene structure of both resins and the presence of  $-SO_3H$  group in post-denature plastic

(sulfonated). Both resins contained the properties of polystyrene with the appearance of peaks indicated aromatic ring. C-H bonds were observed at the peaks of 750 - 3024  $\text{cm}^{-1}$ , C-C was indicated with peaks at 1493  $\text{cm}^{-1}$  [13, 14, 15].

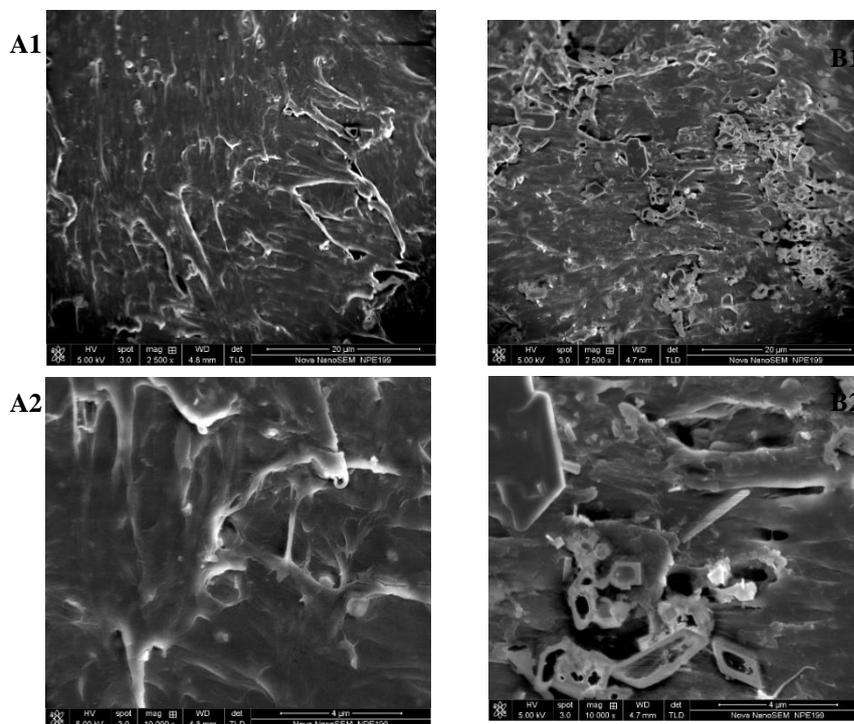


Figure 1. SEM images of polystyrene waste before (A1, A2) and after sulfonation (B1, B2).

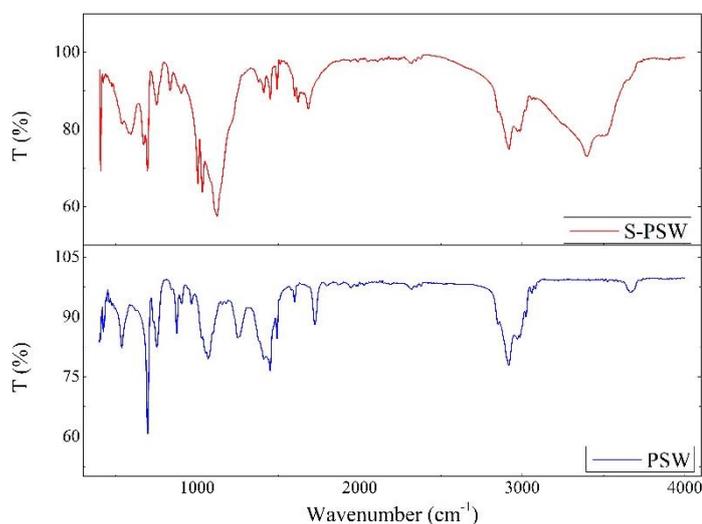


Figure 2. FTIR characterization of original PSW and sulfonated polystyrene S-PSW.

Compared to the FTIR spectrum of polystyrene waste before sulfonation, S-PSW after denaturation has the appearance of a new absorption peak at 1036  $\text{cm}^{-1}$ , which could be assigned

to the vibration of O=S=O from the sulfonic acid groups [16]. The stretch vibration of S=O and C-S was shown at  $3394\text{ cm}^{-1}$  and  $1120\text{ cm}^{-1}$ , respectively, which means attaching the  $-\text{SO}_3\text{H}$  group to the aromatic ring by changing PSW with  $\text{H}_2\text{SO}_4$  has been successfully implemented.

Moreover, the peak at  $1005\text{ cm}^{-1}$  correlates with the bending out of the plane of the ring of phenyl, which proves that the successful sulfonation of polystyrene waste (from PSW to S-PSW). This was also observed by Muller *et al.* [13].

### 3.2. Effects of sulfonation conditions to the ion exchange capacity of S-PSW

#### 3.2.1. Effect of shaking speed

Figure 3 shows the Cr (III) removal efficiency at the sampling time from 10 to 240 min which reaches equilibrium at 120 minutes. As can be seen from Fig. 3, the efficiency decreases with time, and after 120 minutes, the heavy metal removal efficiencies of 4 materials (sulfonated at 100, 125, 200 rpm) reach approximately 0 %, which means sulfonated materials denatured at these shaking speed were unable to remove heavy metal from the solution after 120 minutes.

There was observed that the removal efficiency of S-PSW denatured at a shaking speed of 150 rpm was highest at all sampling period. The figure showed that the efficiency was still 87.9 % at 60th min of the experiment, much higher than the Cr (III) removal efficiency of the modified plastic sulfonated at 100, 125 and 200 rpm which was approximate 8, 24, and 16 %, respectively. Therefore, it can be concluded that 150 rpm is the optimal condition for the sulfonation process.

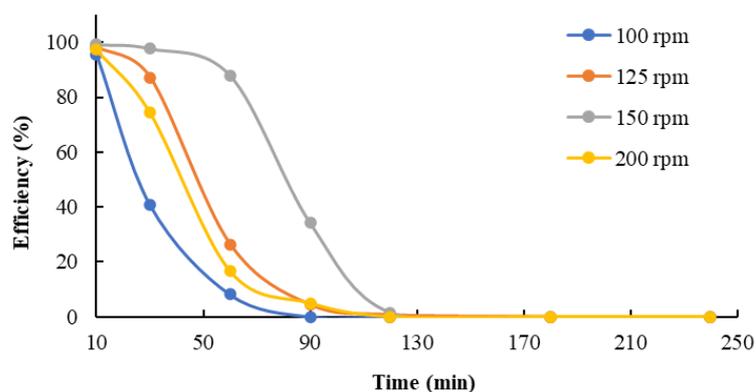


Figure 3. Removal efficiency of Cr (III) by S-PSW modified at different shaking speeds.

#### 3.2.2. Effect of shaking time

The experiment was performed with a shaking speed of 150 rpm. Different shaking times were studied at 2, 4, 8, 12, 24, and 48 hours. At the shaking time 24 hours and 48 hours, the material structure was broken completely, and its form was suspensions, this could be caused by the sulfonation reaction. With this process for long hours, waste polystyrene structure can be broken.

Therefore, in Fig. 4, the removal capacity of materials at different shaking times from 2 to 12 h was shown. It can be seen that obviously the efficiency of material shaken in 2 hours had the lowest (less than 20 %) from the first minutes and its ion exchange ability lasted for about

100 mins. In the first 60 minutes, the efficiency of materials shaken in 4, 6, and 8 h was relatively equivalent while the efficiency of material modified for 2 hours nearly reached 0 %. From the minute 90, the efficiency of material shaken in 12 h was clearly higher than the others. Its treating capacity prolonged until the 180<sup>th</sup> minute while the 2 others went down at the 120<sup>th</sup> minute of experiment.

The results can be explained as the longer reaction time was, the more  $\text{-SO}_3\text{H}$  groups were attached to the resin. This leads to a higher amount of  $\text{Cr}^{3+}$  was exchanged or removed from the aqueous solution which increased the efficiency of material. From the result, the optimum shaking time for material is 12 h.

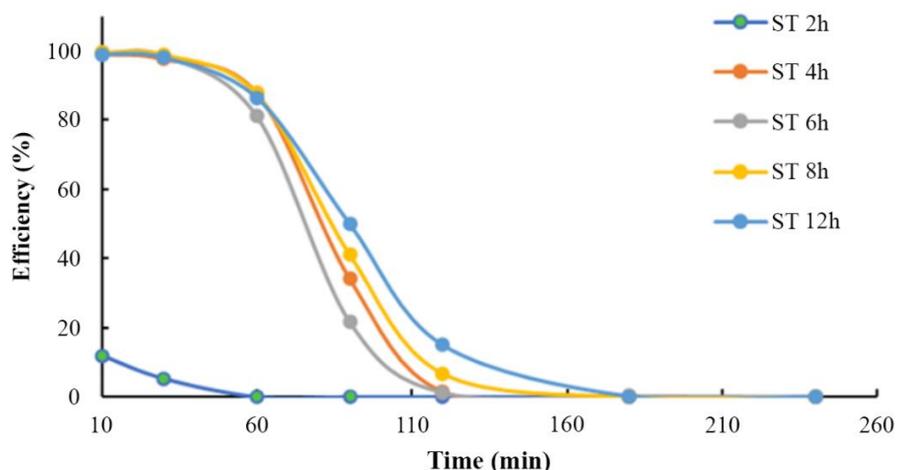


Figure 4. Removal efficiency of Cr (III) by S-PSW modified at different shaking time.

### 3.2.3. Effect of $\text{H}_2\text{SO}_4$ volume in sulfonation reaction

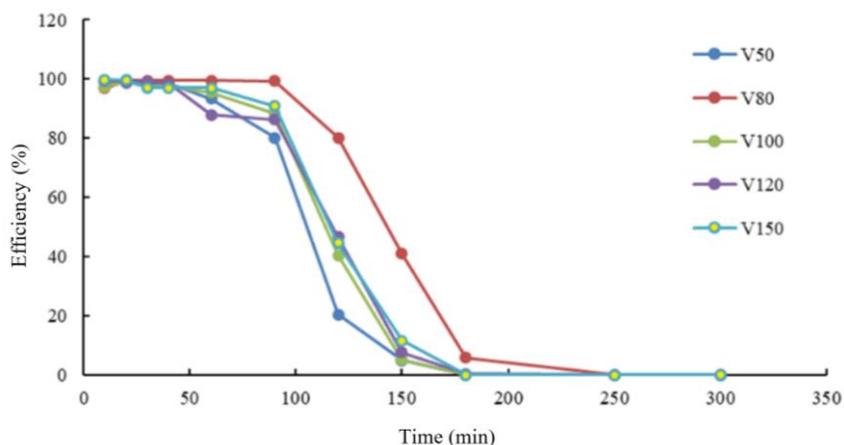


Figure 5. Removal efficiency of Cr (III) by S-PSW modified with different volume of sulfuric acid.

Figure 5 shows that the ion exchange resin which had the highest removal efficiency was the material modified with 80 ml  $\text{H}_2\text{SO}_4$ . This means under the same conditions of plastic mass, temperature, and time, the volume of sulfuric acid has effects on the sulfonation process. When

the volume of acid used for sulfonation reaction was 50 ml, this amount is not enough to sulfonate the entire amount of PS resin.

With the increase in the amount of acid from 50 ml to 80 ml, the chromium removal efficiency of the denatured resin increased markedly, the difference is visible from the 100-minute point. However, when the volume of sulfuric acid is excess than 50 ml, treatment efficiency tends to decrease because after reaching the maximum sulfonate efficiency ( $V = 80$  ml), the amount of  $H_2SO_4$  added is surplus. This can be explained that the reaction continues to break the plastic structure with excess acid, which caused the unstable status of sulfonated plastic in the water. As a result, a small amount will flow out of the experimental column, then the efficiency decreased as well. Therefore,  $V_{H_2SO_4} = 80$  ml was chosen as an optimal acid volume for the sulfonation process in this study.

### 3.3. Effect of the bed height on heavy metal removal efficiency in continuous mode experiment

Figure 6 shows the removal efficiency of chromium in the column as a function of time with a constant flow rate  $Q = 10$  mL/min and inlet metals concentration of 100 mg/L. These parameters were kept at the constant values during the ion exchange experiment.

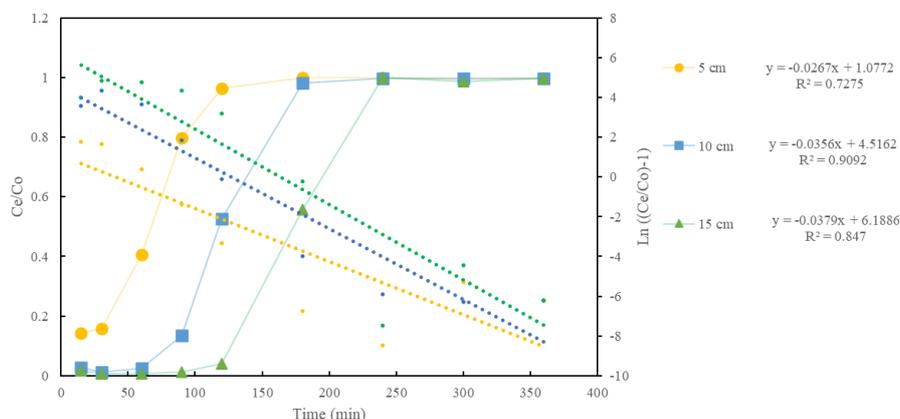


Figure 6. Experimental breakthrough curves and linearized kinetic model at different height of material packed in column.

The effect of the height of the ion exchange material layer on  $Cr^{3+}$  ion exchange with S-PSW resin was investigated by 3 different heights as 5, 10, 15 cm in the glass tube with the 20 mm inner diameter. The experimental results showed that the exhaustion time ( $T_{YN}$ ) also increased from 40 to 163 min when the height of the bed increased from 5 cm to 15 cm (Table 1) which resulted in more absorption uptake.

However, related to the kinetic parameters from Thomas model,  $K_{TH}$  increased very slightly when the bed height increased from 5 cm to 15 cm. The higher pack of material resulted in more  $-SO_3H$  functional group available, which is the reason for the rise of exchange capacity ( $q_{TH}$ ) which also increased from 8.5 mg  $Cr^{3+}/g$  to 12.4 mg  $Cr^{3+}/g$  (Table 1). A higher mass resulted in a larger number of  $-SO_3H$  functional group available, and a more contact time in a larger bed of modified ion exchange material with more adsorption sites. Therefore, the height of packed material was the factor that affected the ion exchange efficiency of the column exchange process.

The material studied by author [9] was modified using organic solvent and acid sulfuric. In comparison to the material in this study, the process with organic solvent could help to shorten the time of modification process (15 min).

Table 1. Experimental adsorption capacity and kinetic parameters for heavy metals at different bed height of sulfonated polystyrene.

<i>H</i> (cm)	$Cr^{3+}$			
	<i>Thomas</i>			<i>Yoon-Nelson</i>
	$K_{TH} \times 10^{-4}$ mL/ (min.mg)	$q_{TH}$ , (mg/g)	$R^2$	$T_{YN}$ (min)
5	2.67	8.45	0.7275	40.34
10	3.56	11.7	0.9092	126.9
15	3.79	12.4	0.9244	163.3

The reason is that after polystyrene was dissolved by organic solvent, the sulfonation process with sulfuric acid was the homogeneous reaction. This process could be applied for dissolving the polystyrene waste which was hard to break into the small flakes. However, the disadvantage of this process was that the amount of organic solvent has to be treated carefully after process. Therefore, in this study, the polystyrene waste plastic was only modified by sulfuric acid for the longer time and this method can be apply for the polystyrene waste which crushed easily to small particle. In addition, by observation, the form of sulfonated polystyrene in this study was more mechanical durable than the material studied by the author in 2019. In comparison with other ion exchange material studied by author [9] when using for 10 cm of bed height, S-PSW have much lower ion exchange capacity (11.7 and 18.98 mg/g).

#### 4. CONCLUSION

This study shows the feasibility of converting waste plastic into ion exchange material with a simple procedure at room temperature. The result of SEM and FTIR showed that after modification process,  $-SO_3H$  group was binded on the structure of polystyrene and their surface was rougher. Optimal condition for sulfonation process at room temperature with sulfuric acid was figured out. There were shaking speed at 150 rpm with 80 ml  $H_2SO_4$  98 % for 12 hours. When operating in continuous mode, the exchange capacity increased with an increasing bed height of sulfonated polystyrene. The removal of Cr (III) in the column experiment was fitted with two Thomas kinetic model and the Yoon-Nelson model with  $R^2$  higher than 80 %. With synthetic water containing  $Cr^{3+}$  with initial concentration of 100 mg/L<sup>+</sup>, the highest exchange capacity was 12.4 mg  $Cr^{3+}$ /g, with the following operational parameters: flow rate of 10 ml/min, the bed hight of sulfonated polystyrene of 15 cm.

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