EVALUATION OF ION EXCHANGE MATERIAL FROM SULFONATED POLYSTYRENE WASTE SYNTHESIZED FOR REMOVAL CR^{3+} FROM AQUEOUS SOLUTION BY COLUMN EXPERIMENT

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Abstract

The paper aims to study the effect of operatiing conditions in the column experiment with the ion exchange material which was prepared in optimum synthesized conditions. Polystyrene waste from disposable food packaging was dissolved in cyclohexane and sulfonated by sulfuric acid to synthesize cation exchange materials which were applied to remove Cr^{3+} in water by the ion exchange principle. The optimum conditions for this method were found out and described in previously published literature of the author. Characterization by SEM and Fourier Transforms Infrared (FT-IR) spectroscopy proved that the additional Sulfonic groups were presented. The efficiency of Cr^{3+} removal was highly affected by column bed height, initial ion concentrations and flow rate of effluent. The highest efficiency of material was 84.0% with a material bed height of 10 cm in the removal of Cr^{3+} from simulated wastewater containing initial Cr^{3+} concentration of 120 mg/l. The experimental data obtained from this study was consistent with Thomas and Yoon-Nelson kinetic models, which will be applied for column design in practical study and design. The results from this method can help reduce the plastic waste and easy to apply in practice for removal of Cr^{3+} in wastewater.

Keywords: ion exchange; polystyrene waste; synthesize; chromium.

1. Introduction

In the last decades, chromium (Cr) progressively pollutes the aqueous environment through wastewater disposal emanating 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]. In addition, chromium is one of the regulated toxic heavy metals in the environment. This element exists in nature mainly in two oxidation states, +3 and +6. Trivalent chromium (Cr^{3+}) is extensively used in the leather tanning, paints and pigments, and fungicides industries and in ceramic and glass manufacture. Although trivalent chromium is considerably less toxic than hexavalent chromium, its disposal as a dissolved species in natural waters or as sludge in soils may pose serious health risks because it can be oxidized to hexavalent chromium in the environment [2, 3]. Especially, their accumulation and high dispersion through the

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food chain have a high potential to affect human health. Therefore, the study of chromium ion extraction from contaminated water sources is an important issue to protect the public and receives intensive care. The drinking water guideline recommended by USEPA is 100 g/l. The legal discharge limit of Cr^{3+} varies from 0.05 mg/l (in surface waters) to 2.0 mg/l (in sewers) depending on the processing, country, and wastewater treatment methods [4].

Another problem exists in parallel is that the economic development is causing an elevated demand for using and consumption of disposable products, outstanding as plates, bowls, and forks made of plastic [5]. Annually, a large quantity of these products is discharged into the environment and accumulated over a long period of time, caused critical problems for the environment, the ecosystem, and whole society. The main component of these disposable items is polystyrene, 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 [6, 7]. Therefore, the collecting and recycling of polycarbonate resins waste are extremely imperative.

Recently, many methods have been implemented to eliminate chromium in aqueous such as chemical precipitation, membrane separation, adsorption, and ion exchange. Ionic exchange resin has been being used as an effective material to remove ions from aqueous. Therefore, considering the importance of both removal of trivalent chromium and recycling of waste plastic. In the previous studies, the modification of polystyrene waste to ion exchange by sulfonation reaction was proved that there are successful process with different methods and apply in Cr^{3+} treatment [8, 9]. This paper aims to investigated the effect of the operation conditions on the efficiency of heavy metal (Cr^{3+}) removal by this ion exchange material.

2. Materials and methods

2.1. Material preparation

The ion exchange material preparation in this study was similar to that described in details in the previous study by Pham et al. [9]. The ion exchange resin synthesized from polystyrene (PS) waste call PSW-SMAX was prepared by dissolving in cyclohexane, after that, sulfonation with sulfuric acid in 15 mins. The modified resin was neutralized by immersing the resin into NaCl 0.1M and dried [9].

2.2. Column experiments

A diagram for the fixed-bed column experiment was shown in Fig. 1. This column was made of glass, tube in shape with 2 cm internal diameter and 30 cm in

Figure 1. Schematic of experimental setup for column studies of trivalent chromium removal

height. The bed length depended on purpose of each experiment was different. At the room temperature, the solutions with known initial metal concentrations ran through the column with fixed flow rate and known bed height of modified polystyrene waste resin. The size of resin used for these experiments was adjusted in 2 – 3 mm. The samples were taken in the exit of the column at the pre-defined time intervals.

The simulated wastewater, which had a concentration of 120 mg/l Cr^{3+}, was prepared by diluting the stock solution with distilled water. The results of these experiment was analysing with two
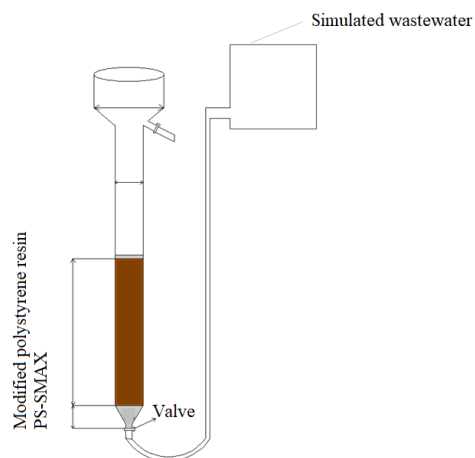
kinetic models, Thomas and Yoon-Nelson, These kinetic models not only were less complicated than other models, but also requires no detailed data concerning the characteristics of adsorbate, the type of adsorbent, and the physical properties of adsorption bed, as well as ion exchange material layer. Therefore, Thomas and Yoon Nelson kinetic model were used to determine total exchange capacity and 50% adsorbate breakthrough (min) of modified material.

The Thomas model

The maximum adsorption capacity of an adsorbent or maximum exchange capacity of ion exchange material is also needed in design [10, 11]. The Linear equation Thomas' kinetic was calculated using equation:

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{K_T q_0 m}{Q} - K_T C_0 t \tag{1}$$

where C_0 is the concentration of Cr^{3+} in the initial solution (mg/l), C_t is the concentration of Cr^{3+} in the output solution at time t (mg/l), m is the mass of ion exchange resin (g), q_0 is the equilibrium Cr^{3+} uptake per gram of the adsorbent (mg/g), Q is the flow rate (ml/min), K_T is the Thomas rate constant (ml/min/mg).

The Yoon and Nelson model

The Linear equation Thomas' kinetic was calculated using equation [10, 11]:

$$\ln\left(\frac{C_t}{C_0 - C_t}\right) = K_{YN} t - \tau K_{YN} \tag{2}$$

where C_0 is the concentration of Cr^{3+} in the initial solution (mg/l), C_t is the concentration of Cr^{3+} in the output solution at time t (mg/l), K_{YN} is the rate velocity constant (l/min), τ is the time in required for 50% adsorbate breakthrough (min).

2.3. Methods of analysis

In this study, the functional groups of polystyrene waste and modified polystyrene waste were determined by the FT-IR spectrophotometry on SHIMADZU (Japan) machine at Faculty of Chemistry, Hanoi University of Science, Vietnam National University. The concentration of Cr^{3+} 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 including H_2SO_4 98%, NaCl 99.9%, $CrCl_3 \cdot 6\,H_2O$ 99% and the organic solvent was cyclohexane (C_6H_6) 99.9%. All solutions were prepared using distilled water prepared by . . .

3. Results and discussion

3.1. Characteristics of experimental materials

a. Surface characteristics of the material

The surface morphological results of polystyrene waste (PSW) and modified polystyrene waste (PSW-SMAX) were done using a scanning electron microscope at magnifications 8.2 mm × 5K and 8.3 mm × 25K, were shown in Fig. 2(a) and Fig. 2(b), respectively.
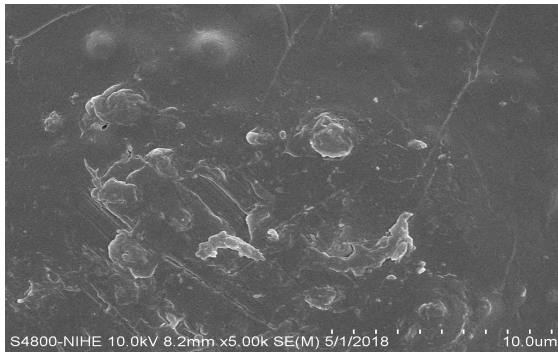
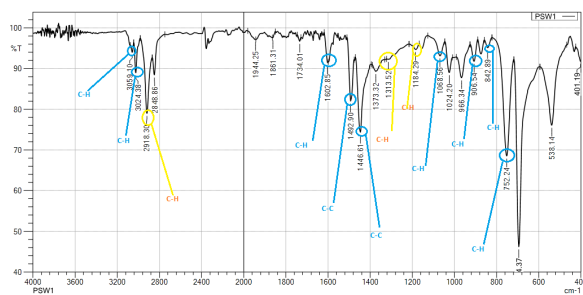(a) of Polystyrene Waste (PSW) before modification
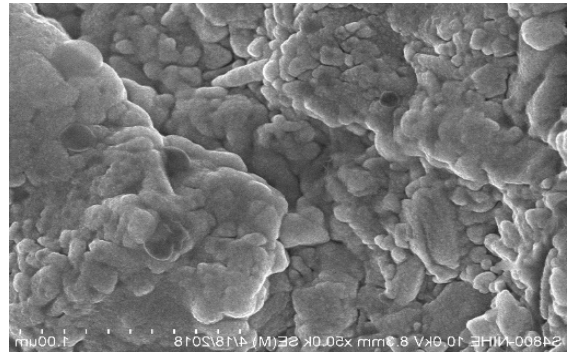
(b) of Modified Polystyrene Waste (PSW-S)

Figure 2. Scanning electron micrograph

The surface of pre-modified had few big blocks, but they are quite smooth. With PSW-SMAX material, the surface structure of the material consisted of a large number of plastic units of 2-6 μm in length as small pile blocks. These small pile blocks were attached, interwoven and stacked together to form larger blocks for the surface of PSW-S that were extremely different from the material before modification. These proved that the sulfonation process had the effect on the change of the surface of polystyrene waste. As a result, the material had a large surface area to increase the contact between the ion and the Cr^{3+} material, which improved the efficiency of Cr^{3+} treatment.

b. FTIR study results

The appearance of the peaks in the wavenumber range from 4000 to 400 cm^{-1} (indicated exactly the component bonds in PSW resin and modified resin PSW-SMAX (bonding of the $-SO_3H$ group) in Figs. 3(a) and 3(b) that were done using the FTIR Affinity - 1S. Moreover. Table 1 showed the wavenumbers of the oscillations in PSW, and PSW-SMAX structures. The data in Table 1 only showed the peaks in the chemical composition of the polystyrene sulfonate, while the other peaks were H_2O fluctuations and impurities.

(a) of Polystyrene Waste (PSW)
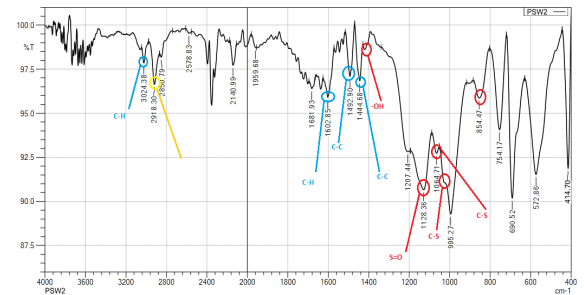
(b) of Modified Polystyrene Waste (PSW-S)

Figure 3. FTIR spectrum

The results from Table 1 show that the PSW-SMAX still had all characteristic of polystyrene resin. In the FTIR image, the $C-H$ and $C-C$ bonding of aromatic ring in structures of PSW and PSW-SMAX were unchanged. Moreover, the $C-H$ bonding of $-CH_2X$ (PS) and $-C-H$ (CH_2/PS)

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Table 1. Functional groups were expressed by FTIR spectra of PSW before and after modification with H_2SO_4 [12, 13]

Oscillate	Functional groups	Wavenumber (cm^{-1})	
		PSW (Polystyrenewaste)	PSW – SMAX (Modified polystyrene waste)
C–H	Aromatic ring (PS)	3059.10 3024.38 1602.85 1068.56 906.54 842.89 752.24	3024.38 1602.85 1064.71 906.54 854.47 754.17
C–C	Aromatic ring (PS)	1492.90 1446.61	1492.90
C–H	$-CH_2X$ (PS)	1313.52 1184.29	1313.52
C–H	$-C-H$ (CH_2/PS)	2918.30 2848.60	2918.30 2848.86
O–H	$-SO_3H$	-	1375.25
S=O	$-SO_3H$	-	1128.36
C–S	$R-SO_3H$	-	572.86 1029.90

functional group were the same. The data in Table 1 indicates that the sulfonation process does not disrupt carbon polymer bondings

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 $-SO_3H$ group (absorption band at 1375.25 cm^{-1}); S=O bond of $-SO_3H$ group (absorption band at 1128.36 cm^{-1}); C–S bond of $R-SO_3H$ group (absorption band at 1029.99 cm^{-1} and 572.86 cm^{-1}), all of them demonstrate the presence of $-SO_3H$ group in PSW-S. In comparison with the FTIR results of ion exchange material from plastic waste which was studied by I. Bekri-Abbes [8], this material also showed the same peaks which demonstrated the exist of sulfonic group afte the process modification.

In particular, the 1125 cm^{-1} peak indicated the oscillations associated with the sulfonate group ($-R-SO_3^-$) [12–14]. This result demonstrates that modification process by H_2SO_4 is effective for PSW.

3.2. The effect of operation conditions of PSW material on the Cr^{3+} removal by ion exchange material from sulfonated polystyrene waste

a. The effect of the flow rate

The effect of flow velocity on Cr^{3+} ion exchange with PSW-S resin was investigated by changing the flow rate from the 20 mm column. The velocity of the output flow was stable at 5, 10 and 15

ml/min for each column. The initial metal ion concentration of 120 mg/l and the column bed height of 10 cm were kept at the constant values during the ion exchange process. The Cr^{3+} removal efficiency was shown in Fig. 4.
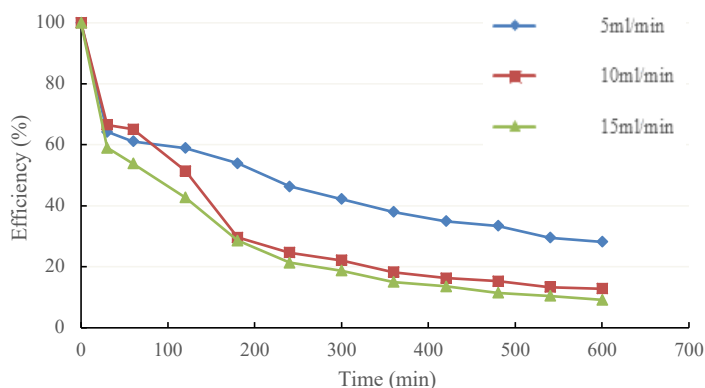

Figure 4. The effect flow rate on efficiency treatment of the modified PSW-S material

It can be seen from the diagram that the greater the flow rate, the lower the efficiency. In the first 30 minutes time from the start of ion exchange process, the ion exchange efficiency of three speeds was quite the same. It was found that as the feed flow rate increased, the breakthrough of Cr^{3+} occured earlier. This was expected as the amount of Cr^{3+} loaded onto the bed packing increased. From 3 hours onwards, the performance of the three systems was gradually reduced. The Cr^{3+} treatment efficiency of the column with the flow rate of 10 ml/min and 15 ml/min was nearly the same at any time during the experiment (the difference is only about 1-3%). Meanwhile, the removal efficiency with feed flow of 5 ml/min was almost double that of 10 ml/min and 15 ml/min.

The results of the experiments could be explained that for slow of flow rate, aqueous solution had enough constant time between metal ions and ion exchange resins, so the amount of ion retainded on the surface of the ion exchanger increased.

b. The effect of the heigh of the PSW-S material layer

The effect of the height of ion exchange material layer on Cr^{3+} ion exchange with PSW-S resin was investigated by 3 different heights as 5 cm, 10 cm, 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 ion exchange experiment. The Cr^{3+} removal efficiency was shown in Fig. 5. The experimental results showed that the highest cationic exchanger performance for 5 cm, 10 cm, and 15 cm were 52.25%, 84.01%, and 81.23%, respectively, for the first sample which was taken at 30 mins. After 6 hours, the percentage of efficiency decreases by 0.85% per hour for the 5 cm; 2.9% per hour for column with material height of 10 cm and 4.64% per hour for column with fixed bed height of 15 cm.

As the results, the height of packed material was the factor that affected the ion exchange efficiency of the column exchange process.

c. The effect of input Cr^{3+} concentration

The effect of the Cr^{3+} input flow concentration on Cr^{3+} ion exchange with PSW-SMAX resin was investigated by 3 different heights as 10 mg/l, 50 mg/l and 120 mg/l in the 20 mm column. These concentrations represent the degree of trivalent chromium in wastewater at low, medium and high
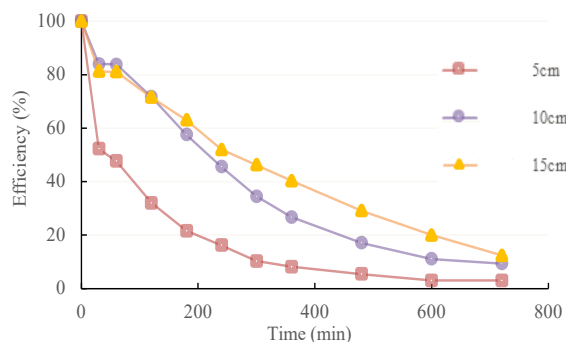
Figure 5. The effect of the height of packed material on efficiency treatment of the modified PSW-SMAX material
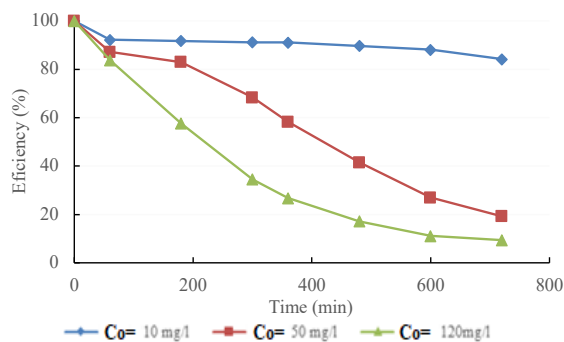

Figure 6. The effect of the input Cr^{3+} concentration on efficiency treatment of the modified PSW-S material

level. The velocity of the output flow was 10 ml/min. The height of packed material 10 cm and the flow rate 10 ml/min were kept at the constant values during the ion exchange experiment. The Cr^{3+} removal efficiency was shown in Fig. 6.

From the chart, the processing efficiency of PSW-SMAX was extremely high with a value of 92.22% for the input concentration of 10 mg/l, this remained above 84% after 12 hours. With higher concentrations, processing efficiency decreased considerably over time. After 8 hours, Cr^{3+} treatment efficiency at 50 mg/l was reduced to less than 50%, whereas this occurred after 3 hours at 120 mg/l. This was extremely reasonable because the higher the concentration, the greater the amount of ion exchanged, but to improve efficiency, encourage with a concentration of input smaller than or equal to 50 mg/l. This is also what should be expected based on ion exchange theory. At the same time, with lower input concentration, the amount of metal ions in the solution exchanged with Na+ ions in the material is also lower, thus prolonging the use of the material and this also give high efficiency at heavy metal removal for longer time

3.3. Thomas and Yoon Nelson kinetic model

Under optimum conditions, the results of the study show that the PSW resin was a cation exchange material, as well as a remarkable chromium-removal efficiency. In order to more accurately evaluate the maximum exchange capacity of the material and the time required for 50% adsorbate predicted by Thomas and Yoon-Nelson's kinetic model which were obtained from the data generated by the ion exchange column experiment. The 20 mm inner diameter columns with bed height of 10 cm PSW-SMAX were operated in approximate 24 hours, the Cr^{3+} input concentration was kept at 10 mg/l and flow rate of 10 ml/min.

• Thomas kinetic modeling [13, 14]:

Linear model kinetic model Thomas demonstrated the dependence of $\ln[(C_t/C_0) - 1]$ on time (t) for the exchange of Cr^{3+} as shown in Fig. 7. The constants of the M and q_0 models were calculated and presented in Table 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 R^2 ($R^2 > 0.95$) indicates that the experimental data in the 20 mm column matched the Thomas kinetic model.

• Yoon-Nelson kinetic modeling [10, 11]:

The linear model of the Yoon-Nelson adsorption model for the exchange of Cr^{3+} to PSW-S in diameter columns was shown in Fig. 8. The Yoon-Nelson constant values and corresponding parameters were presented in Table 2. Moreover, the high value of the system correlation coefficient $R^2 (R^2 > 0.95)$ showed that the empirical data in the 20 mm column matched kinetic model Yoon-Nelson.
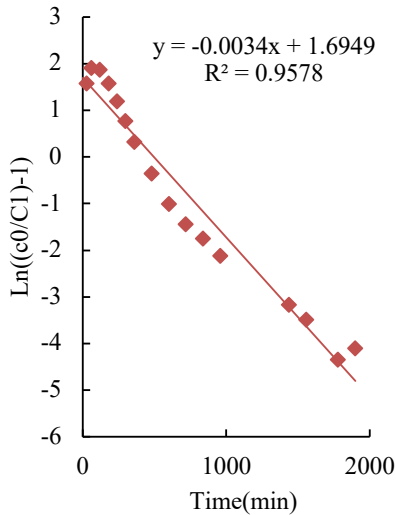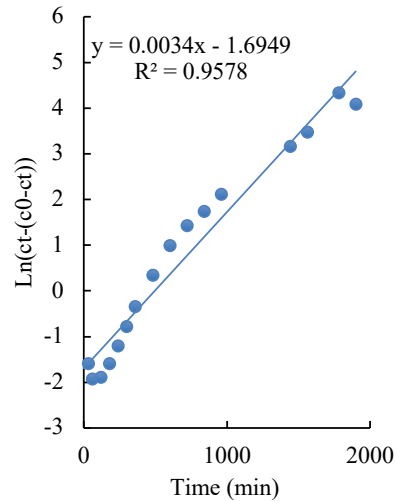

Figure 7. Linear dyamics of Thomas kinetic model

Figure 8. Linear dyamics of Yoon-Nelson kinetic model

Table 2. Parameters of Thomas kinetic model and Yoon-Nelson kinetic model of PSW-S

		Colum 20 mm
Thomas kinetic model	R^2	0.9578
	K_T (ml/min/mg)	0.000067
	q_0 (mg/g)	18.979
Yoon-Nelson kinetic model	R^2	0.9578
	K_{YN} (l/min)	0.0034
	τ (min)	2492.5

4. Conclusions

This research has shown the sulfonated polystyrene from polystyrene waste by the homogeneous reaction was called PSW-SMAX. SEM results demonstrated the feasibility of using polystyrene resin as a raw material for ion-exchanging materials. Moreover, the PSW-SMAX had a large surface area to increase the ability of contact between Cr^{3+} ions and materials, which ultimately improved the performance of Cr^{3+} treatment. The results of the FTIR spectra described that the PSW after modification contained the group $-SO_3H$. It was observed that the efficiency of removal Cr^{3+} was strongly dependent on the bed heights, flow rate and initial concentration of Cr^{3+}. The efficiency increased with

the increase in bed height, but they declined with the increase of flow rate and input concentration of chromium ion.

The exchange process on the column was shown that the Cr^{3+} treatment efficiency was inversely proportional to the flow rate, the lower the flow rate, the higher the processing efficiency and vice versa. The efficiency of trivalent chromium removal was also depended on the height of the material in the column and the concentration of Cr^{3+} in wastewater.

Thomas kinetic model of ion exchange resin modified from PSW had the correlation coefficient $R^2 = 0.9578$. Therefore, the ion exchange column data followed the Thomas kinetic model with K_T constant of 0.000067 and maximum exchange capacity of 18.98 mg/g. Besides, the ion exchange column data also followed Yoon-Nelson model with $R^2 = 0.9578$ and the time in required for 50% adsorbate breakthrough was 2492.5 mins.

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