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Evaluation of strong anion exchange hyper-crosslinked resin for lanthanum removal

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Abstract. In this study, strong anion exchange hyper-crosslinked resin was used for the removal of rare earth element, lanthanum. Poly (styrene-*co*-EDGMA-*co*-VBC) is a resin that was synthesized and used in this research. The objective of this research is to study the pH stability and to evaluate the resin for lanthanum removal by using the Solid Phase Extraction (SPE) batch method where the influent of lanthanum solution will be loaded to the designed column containing resin. The pH stability test of resin was studied at different pH (pH 2-5). The evaluation of resin for resin loading (0.5, 1.0, and 1.5 g) and concentration of lanthanum (10, 30, and 50 ppm) were investigated. From the experiment, the resin is stable in acid solution since there is no change in the functional group. The morphology surface using Scanning Electron Microscope (SEM) shows a rough surface and beads attach on the resin without porous on the surface of resin except the resin at the condition of 50 ppm of with 1.0g resin. The resin that performed at 50 ppm with 1.0 g was successful remove lanthanum for 26.7 ppm based on ICP-MS analysis. As a conclusion, this resin can be used for removal of lanthanum.

1. Introduction

Yttrium and scandium are one of the fifteen lanthanides elements of rare earth elements (REEs) which present in the periodic table. Identical chemical properties and tended to occur similar deposit as lanthanides make yttrium and scandium element are considered REEs [1,2]. The demand of lanthanum is growing because of its exceptional chemical and physical properties, Usually, lanthanum is used for metal utilization especially for creating alloys, catalyst, good quality ceramics and condenser [3,4]. Lanthanum is considered as low toxicity but, excess buildup of lanthanum into the environment may cause unwanted problem such as health-related problem and environmental issues. The removal of lanthanum is still in progress. Thus, it is vital to find relatively a save-cost method for lanthanum eradication and recovery [5].

Present methods have proposed for the recovery of REEs for example coagulation, solvent extraction, co-precipitation, chemical precipitation, ion exchange, solid phase extraction, adsorption, floatation, hyper-filtration and reverse osmosis [3]. Though, solvent ion exchange and extraction methods are the most common method that used for recovery of REEs as reported by Morais and Ciminelli [6]. It is not preferred as this method need a large amount of solvent and time consuming [7]. Therefore, many researchers have started developing method to recover REEs. Many researchers claimed that adsorption is a best method as it is very effective, inexpensive and REEs removal can easily be achieved [8]. Besides, adsorption method is widely known as a simple, highly efficient outlay and easy to handle the operations. Furthermore, adsorption method also can reduce of unwanted sludge, as it will not lead to the creation of hazardous constituent [9, 10].

Ion exchange is the useful material as it is can act as absorber [8]. The removal of REEs by using ion exchange method in the presence of active sites on the anion exchanger resin is still a poorly studied field [11]. Other than that, the low concentration in rare earth elements in most geological material makes their measurement is not trivial. Therefore, it is important to optimize sample preparation and measurement methods to reduce uncertainty and maximize recovery [12]. Other than that, the selective separation and decontamination of rare earth elements still remain challenging.

The objective of this study is to investigate the resin stability on pH and evaluate the resin for lanthanum removal. The pH stability was study at pH 2, 3, 4 and 5 meanwhile, the resin was evaluated at different resin loading (0.5, 1.0 and 1.5 g) and concentration of lanthanum (10, 30 and 50 ppm). Poly(styrene-*co*-EDGMA-*co*-VBC) was a resin that synthesis and used in this study. The resin was characterized using Fourier Transforms Infrared (FTIR) in order to determine the functional group that present in the resin. Then, the surface morphology was observed using Scanning Electron Microscope (SEM). ICP-MS is used in order to determine the concentration removal of lanthanum after the treatment.

2. Experimental

2.1. Materials

The Poly(styrene-co-EDGMA-co-VBC) resin is an anion exchange was synthesis in Faculty of Chemical Engineering and Natural Resources laboratory using non-aqueous dispersion polymerization [13,14]. The pH stability test for resin was performed using 99.99 % purity of sulphuric acid (H_2SO_4) and supplied by Merck Millipore. The lanthanum was obtained from Rare Earth Research Centre, Universiti Malaysia Pahang, Malaysia.

2.2. pH stability test

The poly(styrene-co-EDGMA-co-VBC) resin was investigated at different pH values; pH 2 until pH 5 range was used in this study. The pH was adjusted by using sulphuric acid or distillation water. 0.1 g of resin was placed in a series of beaker. 40 ml of sulphuric acid at different pH value was added into the beakers. Throughout all pH stability test, the temperature was set as room temperature which is about 25 ºC. The mixture was stir using magnetic stirrer at 200 rpm. After 1 hour, the solution was filtered by using filter paper. The chemical structure before and after pH stability was determined by using Fourier Transforms Infrared (FTIR).

2.3. Evaluation of resin in concentration of lanthanum and resin loading

The evaluation of resin with different resin loading and concentration for lanthanum removal was studied in batch method. The resin loading used were 0.5, 1.0 and 1.5 g and the concentration of lanthanum are 50, 30 and 10 ppm. Throughout all the batch experiment, the temperature was set as room temperature which was about 25 ºC with 40 ml of 50 ppm lanthanum for different resin loading. The mixture of the resin and solution were stirred by using magnetic stirrer for 60 minutes at 600 rpm. Then, the resin and solution were separated using filter paper. The experiment was repeated for different concentration of lanthanum with constant 1.0 g of resin. The adsorption of lanthanum in resin were determined by using ICP-MS instrument.

2.4. Resin characterization

2.4.1. FTIR spectrometry. The chemical structure and functional group of the samples were identified using FTIR, Spherical Diamond ATR Nicolet iS50 (Thermo Scientific) before and after stability test and for evaluation resin using Potassium Bromide Disk technique. Solid particles sample is milled with potassium Bromide (KBr) to form a very fine powder. Then, compress it into a thin pellet which can analysed by using FTIR. All the spectra were recorded in 4000-500 cm^{-1} range; an average of 16 scans was taken per sample.

2.4.2. SEM analysis. The morphology of the resins surface was analyzed at accelerating voltage of 15kV under magnification range from 1000x to 2000x by using SEM (TM3030 Plus Hitachi). The resin was coated with platinum (Pt) on the support in the SEM for 150 s before observation.

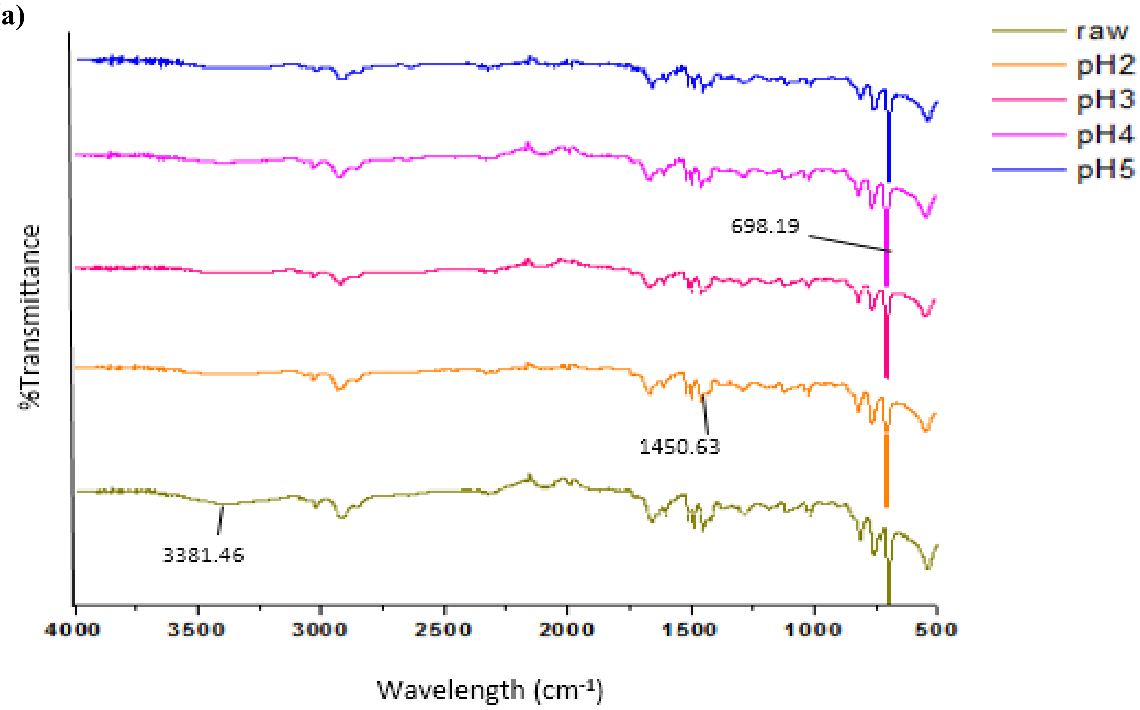
2.4.3. ICP-MS analysis. The amount of lanthanum removal was analyzed using ICP-MS (Agilent Technology with 7500 series). ICP-MS was used as the most accurate for light elements [12].

3. Result and discussion

3.1. FTIR spectrometry

The spectrum of resins by FTIR analysis are illustrated in figure 1. Figure 1(a) shows the FTIR spectrum for pH stability test meanwhile figure 1(b) and (c) are the evaluation of resin for different resin with 50 ppm lanthanum and different concentration of lanthanum with 1.0 g of resins. Figure 1(a) shows peaks at 3381.46 cm^{-1} is assigned to the stretching vibration of O-H that is most present in the structure due to the residual hydration water [15]. The band at 1450 cm^{-1} correspond to the C=C stretching vibration in aromatic ring [16,17]. Peak that appeared at 698.19 cm^{-1} represented medium strong =CH broad bend. All trend of spectrum's shape similar in figure 1(a), can be conclude that no major functional group changes in the acid solution.

(a)



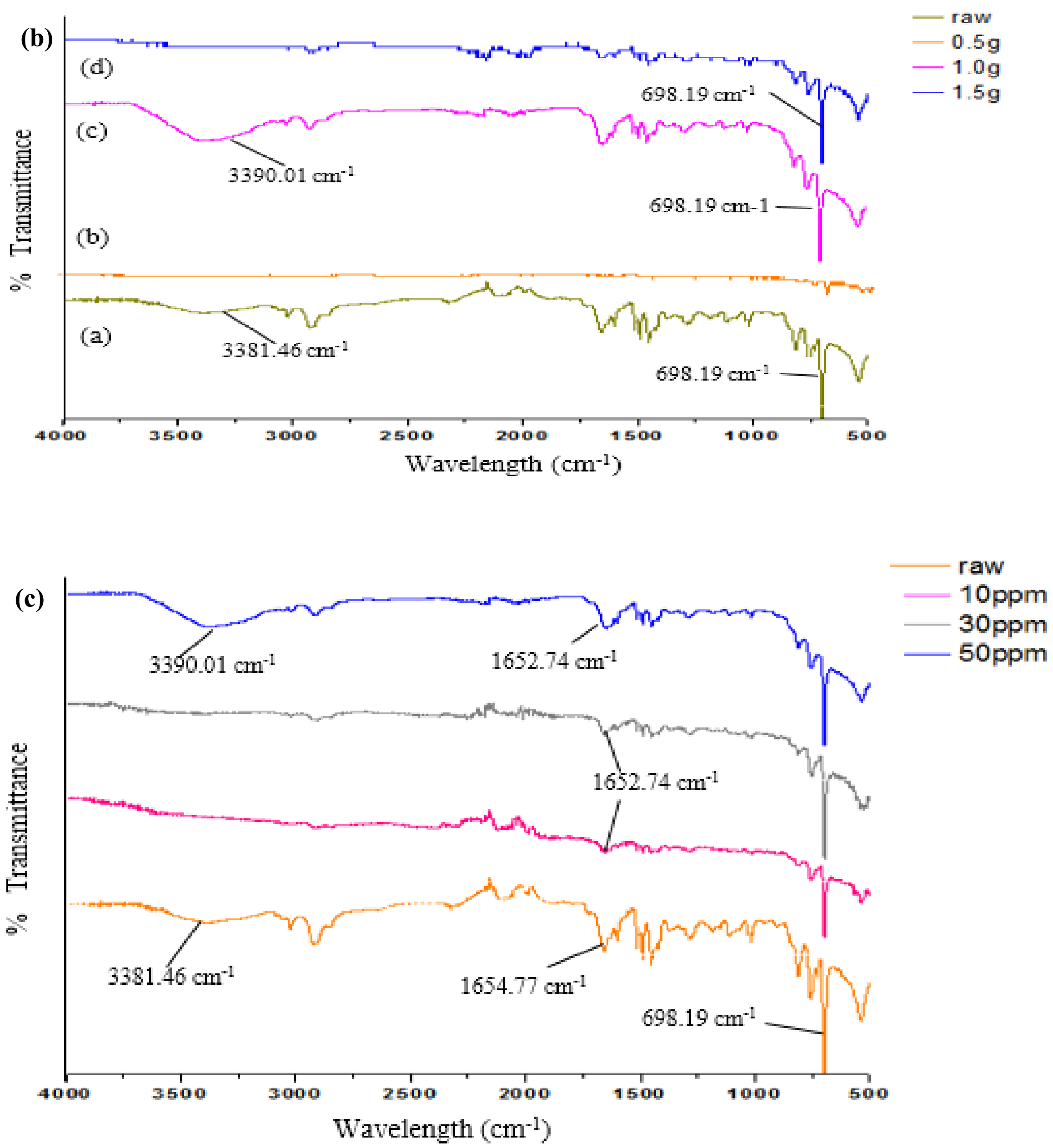


Figure 1. (a) FTIR spectra for pH stability test; (b) FTIR spectra for resin loading evaluation; and (c) FTIR spectra for concentration of lanthanum evaluation.

In figure 1(b), the resin was performed in 50 ppm of lanthanum with different resin loading. The functional group of 0.5 g resin disappeared. The peak at 3381.46 cm^{-1} in raw material is shift to 3390.01 cm^{-1} after evaluate in 50 ppm with 1.0 g of resin. This peak is assigned to abroad stretch vibration O-H where the resin is more abroad after evaluated compare to the raw material. The medium strong =CH broad bend that represented at peak 698.19 cm^{-1} is shows in all resin. The FTIR spectrum of resin after evaluated in different concentration of lanthanum with 1.0 g of resin is illustrate in figure 1(c). The functional group of abroad stretch vibration O-H that performed in 10 and 30 ppm disappeared meanwhile in 50 ppm, the peak is shift to higher frequency. Appearance of peaks 1654.77 cm^{-1} from raw material resin is due to the very weak C=C medium stretch vibration and the rest resin at different concentration of lanthanum shows that, the spectrum was shift to a slightly lower frequency which are 1652.74 cm^{-1}. The only functional group that maintain in the resin after evaluated is the medium strong =CH broad bend that represented at peak 698.19 cm^{-1}. From the comparison analysis of spectrum, there is no specific modification of functional group has occurred, but some of functional group are disappeared. The peak between range 2800 to 3000 cm^{-1} are characterize for polystyrene where almost of the resin shows the peaks. Other than that, the peak at 698.19 cm^{-1} are appeared at all resin.

3.2. SEM analysis

Surface morphology of strong anion exchange hyper-crosslinked resins are illustrated in figure 2. Figure 2 (a) is the control resin, which is the resin before evaluation. Figure 2 (b) and (c) are the evaluation of resin for different resin loading with 50 ppm lanthanum and different concentration of lanthanum with 1.0 g of resins. Figure 2 (a) shows rough surface of resin meanwhile figure 2 (b) and (c) shows rough with small beads attach on the surface of resin. There are no pores except the resin that performed with 1.0 g and in 50 ppm and as shows in figure 2 (b) and (c), respectively.

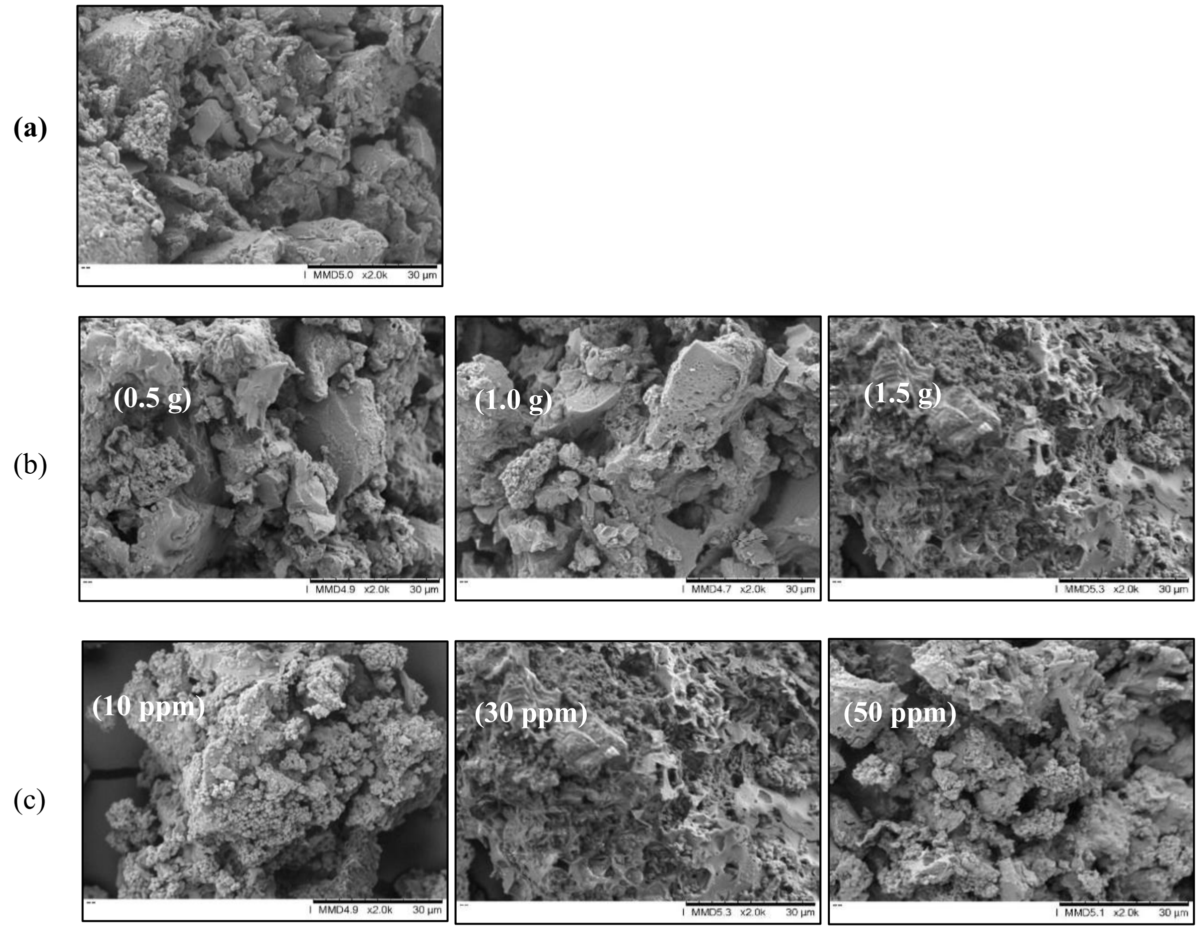
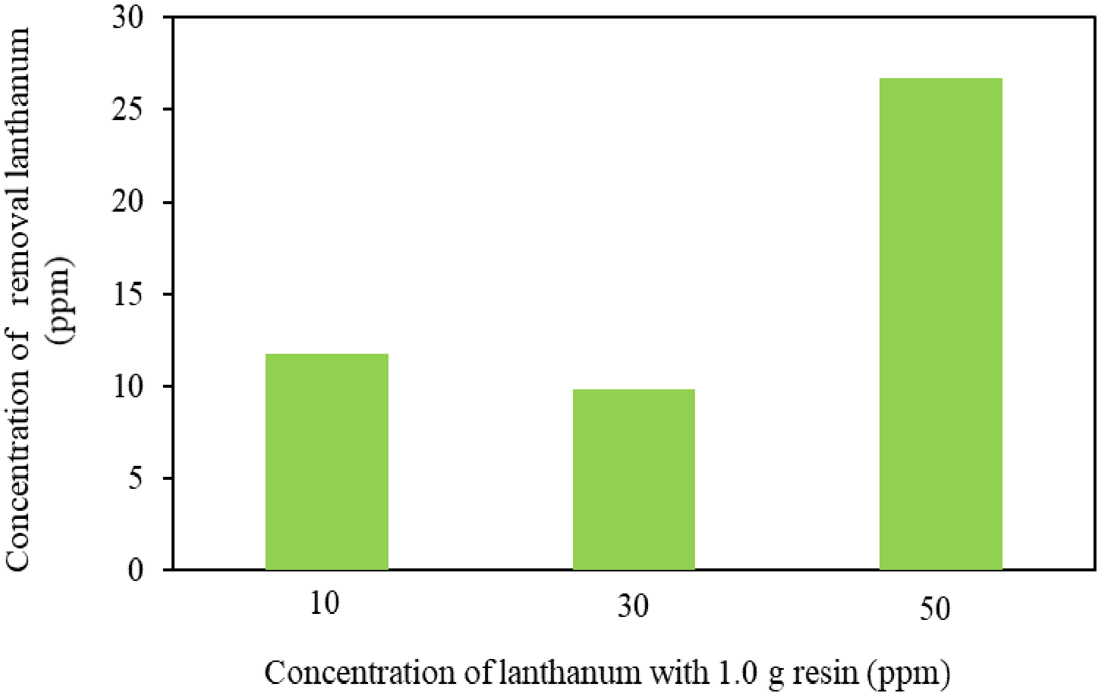


Figure 2. Morphology of resin (a) before evaluation; (b) after evaluation at different resin loading and (c) after evaluation at different lanthanum concentration, respectively.

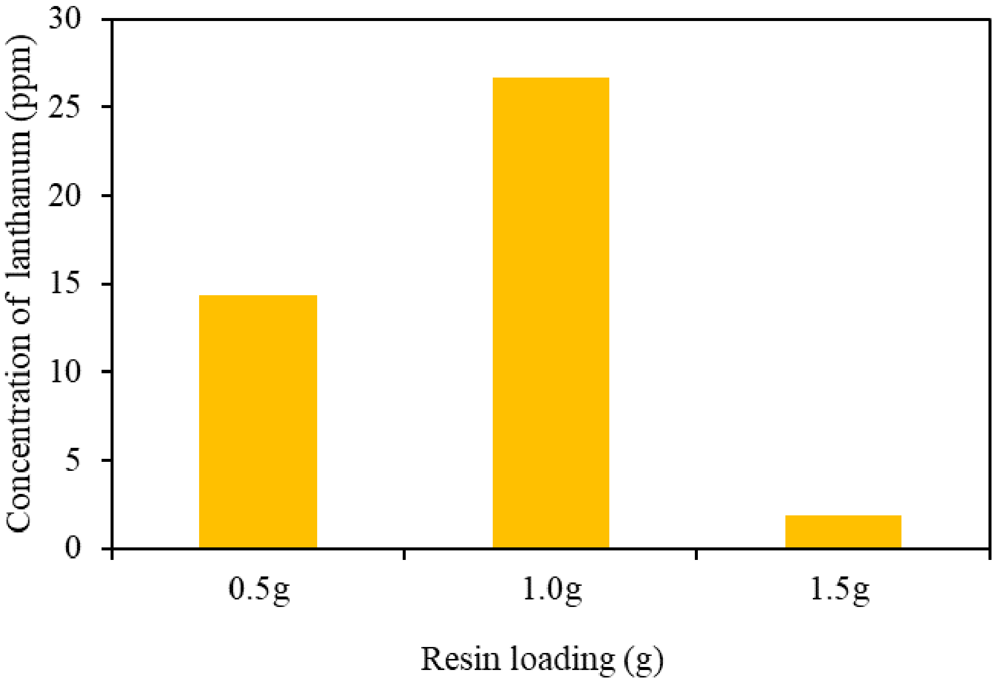
3.3. ICP-MS analysis

The amount of lanthanum removal was determined using ICP-MS and illustrated in figure 3. Figure 3(a) is showing the amount of lanthanum removal at different concentration with 1.0 g resin. The resin at 50 ppm was removed 26.7 ppm of lanthanum. The resin at 30 and 10 ppm were removed 9.8 ppm and 11.8 ppm respectively. Based on figure 3(b), the resin in 50 ppm of lanthanum with different resin loading shows that 1.0 g of resin have adsorb 26.7 ppm of lanthanum. The rest of resin, which are 0.5 and 1.5 g were removed 14.4 and 1.9 ppm respectively.

The resin was evaluated at different resin loading and concentration of lanthanum. Based on the FTIR result for resin evaluation, some of functional group was disappeared without any modifications of functional group. Only the resin that performed in 50 ppm of lanthanum with 1.0 g resin loading have the same trends of spectrum as raw material and the only that forms pores with small beads attach to the surface of resin based on SEM analysis. According to ICP-MS analysis shows that 26.7 ppm of lanthanum have been successful removed by same resin. The amount of lanthanum removal in 50 ppm with 1.0 g resin is the highest due to the pores that form after evaluate. Thus, this resin has larger surface area and able to absorb more lanthanum compared to the others. The porous structure will increase surface area and consequently efficiency of adsorption but also the kinetics of the adsorption. A better adsorbent is the one with large surface area and which requires less time for adsorption equilibrium [9].



(a)



(b)

Figure 3. Amount of lanthanum removal at (a) different concentration lanthanum and (b) resin loading.

3.4. pH effect

pH is one of the important parameters affecting the stability of a product. Stability can be well-defined as the degree to which a product holds means how the product maintains its physical and chemical properties within specified limits, and throughout its period of storage [18]. The pH affects not only the surface charge of the resin but also the degree of ionization the heavy metal in solution. Furthermore, pH also influencing the adsorption capacity of resin [3]. Based on the result of FTIR spectrum, there is no change of functional group or modification occurred. Therefore, the resin was stable and suitable for using in removal rare earth.

4. Conclusion

As the conclusion, the resin of poly(styrene-*co*-EDGMA-*co*-VBC) is suitable for lanthanum removal. This is because, the resin is stable in acid solution based on FTIR analysis. These resin act as adsorbent material for up taking of lanthanum in aqueous solution. The adsorption characteristic was examined at different resin loading and lanthanum concentration. It found that the resin is able to adsorb the lanthanum. The amount lanthanum removal in 50 ppm with 0.5, 1.0 and 1.5 g are 14.4, 26.7 and 1.9 ppm of lanthanum, respectively. Meanwhile, the amount of lanthanum removal with 1.0g in 10, 30 and 50 ppm are 9.8, 11.8 and 26.7 ppm, respectively. The highest lanthanum removal occurs in 50 ppm with 1.0 g resin loading and it is the effective condition for removal lanthanum. In this study, the resin that performed in 50 ppm with 1.0 g is the best condition compare the others. It is recommended for future work to evaluate the performance of lanthanum removal by using different method or resin with varying more parameters to get more optimum and efficient removal.

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