



## **Modification of Styrofoam Waste as a Low-Cost Adsorbent for Removal of Cadmium Ion in Aqueous Solution**

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### **Abstract**

Styrofoam waste has been modified by sulfonation using sulfuric acid to form its corresponding sulfonated adsorbent and was further used for removing cadmium ion in its aqueous solution. The effect of the styrofoam weight, sulfuric acid concentration, temperature and time on the sulfonation result was evaluated. The prepared adsorbent was characterized by XRD, FTIR, and SEM. The cadmium ion adsorption was conducted by batch technique, where the kinetic parameters were determined. The research results attribute that the sulfonated styrofoam has been successfully prepared, and the highest sulfonation is exhibited by using 18 M of the sulfuric acid, at 60 °C for 6 h with 5 g of styrofoam. The cadmium adsorption by the sulfonated styrofoam fits with the pseudo-second-order and the Langmuir isotherm model, while the native styrofoams follows the intraparticle diffusion mechanism and Freundlich isotherm model. The adsorption capacities of the sulfonated and the native styrofoams are 51.6 mg/g and 7.09 mg/g respectively, and their respective adsorption rate are  $8.20 \cdot 10^{-3} \text{ mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$  and  $26.9 \cdot 10^{-3} \text{ mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1/2}$ .



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### **Introduction**

Styrofoam is the commercial name of polystyrene produced as a petroleum-based plastic made of styrene. The chemical components of styrofoam are 5% polystyrene and 95% air.<sup>1</sup> Despite being

non-biodegradable, the styrofoam is possible to be broken into smaller pieces that are easy to be deformed by releasing styrene as a monomer that can enter the food chain.<sup>2</sup> Styrene primarily exhibits its toxicity to human as a neurotoxin by attacking the

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central and peripheral nervous systems. Moreover, the accumulation of these highly lipid-soluble materials in the lipid-rich tissues of the brain, spinal cord, and peripheral nerves is correlated with acute and chronic functional impairment of the nervous system.<sup>3</sup>

A simple and well-known way to remedy the styrofoam waste is by incineration, but it generates potentially hazardous emissions, including greenhouse gases, dioxin, and heavy metals.<sup>4</sup> Therefore, recycling is preferable for solving the problems of slow degradable plastic waste, especially for the prevention of environmental pollution. The chemical recycling of waste converts polystyrene to the corresponding monomer or hydrocarbon.<sup>5</sup> However, the process is costly since the price of the hydrocarbon and monomer is much lower than that of recovered by recycling.<sup>6</sup> Thus, considerable attention has been paid to chemical recycling of styrofoam waste to yield different useful materials.

Impregnation of dithizone as a chelating agent together with styrofoam to concentrate trace amounts of cadmium ions from aqueous solution has been reported.<sup>7</sup> The impregnation is believed to be simple, but it gives low efficiency in the cadmium uptake. Conversion of styrofoam to novel phenyl thiosemicarbazone surface has also been attempted previously.<sup>8</sup> The product was functional to treat lead-contaminated water through the chelating mechanism and gave a significant result. The other effort is a modification of the styrofoam into granular porous adsorbent immobilized with cross-linked polyethyleneimine (PEI) to obtain a functionalized adsorbent.<sup>9</sup> The obtained adsorbent had been tested for humic acid removal from drinking water and showed good activity. However, the procedures used in the above-mentioned modifications are complicated and costly, which involve a large number of chemicals.

The simple recycling technology to convert styrofoam to functional polymer is by sulfonation, popularly known as sulfonation of polystyrene. The sulfonation products include polyelectrolyte,<sup>10</sup> flocculant,<sup>11-14</sup> coagulant,<sup>15</sup> cationic exchanger resin<sup>6</sup> and adsorbent.<sup>16-23</sup> The favorable products of the conversion of the styrofoam waste by sulfonation seemed to be adsorbent, that is indicated by intensive

studies on the sulfonation of styrofoam or polystyrene waste to produce the low-cost adsorbents, that has been examined to reduce the excessive chemicals in water.<sup>16-23</sup>

The use of the different sulfonation agents for preparation of the sulfonated polystyrene adsorbent has been explored.<sup>16</sup> Then, it is depicted from the corresponding study that the sulfonated styrofoam exhibits good adsorption properties.<sup>17</sup> The sulfonated polystyrene adsorbent prepared from white coffee cups was reported to show good ability in the decreasing the hardness of water.<sup>18</sup> Further, decreasing several heavy metals by the sulfonated styrofoam adsorbent has also been addressed.<sup>19</sup> The sulfonated styrofoam adsorbent has also been assessed to remedy of Zn<sup>2+</sup> and Pb<sup>2+</sup> in the solution.<sup>20</sup> In addition to Zn<sup>2+</sup> and Pb<sup>2+</sup>, the adsorption of Cd(II) in the solution<sup>21</sup> and in the contaminated ground water<sup>22</sup> by sulfonated styrofoam prepared from the plastic waste was also reported, that show promising results. Similar work illustrated the effective removal of the toxic Cd (II), Pb(II), and Hg(II) ions in the solution by adsorption with sulfonated styrofoam produced from the plastic waste.<sup>25</sup> Many authors have studied the sulfonation of polystyrene waste, but less information of the influences of the operating parameters in the sulfonation process was presented.

Cadmium is interest of this study, since it is widely distributed in the environment and poses high toxicity. The presence of cadmium in the environment originates from the industrial wastewater disposal of rechargeable batteries manufacturing, plastics, coatings, and solar panels.<sup>2</sup> Having consumed cadmium contaminated food and drink can cause renal dysfunction, lung insufficiency, liver damage, bone degeneration, and hypertension.<sup>24</sup> Therefore, removal or decreasing concentration of cadmium in water is urgently needed. There are many studies dedicated to remove of cadmium in water by adsorption using various adsorbent materials including vermiculite, zeolite, and pumice,<sup>25</sup> biomaterial,<sup>26</sup> husk of lentil,<sup>27</sup> spirulina platensi dry biomass,<sup>28</sup> marine green algae,<sup>29</sup> algae biomass,<sup>30</sup> modified corn cob,<sup>31</sup> and microporous eggshell.<sup>32</sup> Beside the adsorbents mentioned above, some works on the removal of Cd(II) from the solution using sulfonated styrofoam adsorbents have also

been described,<sup>6,21-22</sup> but there was a limited study on the effects of the determining factors on the adsorption efficiency.

This contribution paper focuses on the sulfonation of styrofoam waste, characterization of the sulfonated styrofoam formed, and its adsorption activity for cadmium ion removal. In the sulfonation process, the effect of styrofoam weight, sulfuric acid concentration, temperature and time was evaluated. Furthermore, in the process of cadmium adsorption, the optimum of the adsorbent dose, initial cadmium concentration, contact time and solution pH were determined. Additionally the adsorption isotherm and kinetic were also modeled.

## Experimental

### Materials

Styrofoam waste was collected from the disposal of food packaging. An analytical grade sulfuric acid, cadmium nitrate, hydrochloric acid, and sodium hydroxide were purchased from Merck and used as received.

### Sulfonation of the Styrofoam Waste

The styrofoam waste was crushed to a smaller flake to the size of about 100 mesh. The fine flakes were washed with liquid soap and rinsed thoroughly with water. The clean flake was dried using a conventional oven at 100 °C for 1 h. Sulfonation process was carried out by mixing 5 g of the fine flake styrofoam waste with 100 mL of concentrated sulfuric acid. The mixture was maintained under agitation at a temperature of 60 °C for 1 h. The flakes were separated from the solution by filtration and washed with distilled water to remove the excess acid. The product was dried at 100 °C for 3 h before characterization.

The procedure was repeated with variation of styrofoam weight, sulfuric acid concentration, temperature, and reaction time. The weight of styrofoam is predetermined at 2.5, 5.0 and 7.5 g, where 100 mL of concentrated sulfuric acid was used. The other sulfuric concentration of 4.5 and 9 and 4.5 M were used. The reaction temperatures were 30, 60, 75, and 100 °C. The reaction times of 1, 3, 6, and 10 h were set.

### Characterization

The success of the sulfonation of the styrofoam can be determined by titration<sup>6</sup> and by IR spectrometry.<sup>22</sup> In this work, the product characterization was done first by the IR method. The IR spectra of the samples were taken on Shimadzu with wavenumber range from 400 to 4000 cm<sup>-1</sup>. Additionally, the XRD patterns were recorded on 6000X Shimadzu with 2-theta of 3-50°. The surface morphology of the sulfonation product was investigated using a JEOL SEM. Before SEM analysis, the sulfonated styrofoam samples were mounted on a metal sample holder by double-sided adhesive tape coated with platinum, degassed and scanned.

### Adsorption Study

The cadmium adsorption by sulfonated styrofoam was studied through batch experiments as it is quick and simple. A 0.25 g sulfonated styrofoam was mixed with 100 mL of cadmium solution in polypropylene container and stirred for 30 min using a magnetic stirrer. The aqueous phase was separated from the by filtration. A GBC atomic absorption spectrometer (AAS) was used for determination of the concentration of cadmium ions remaining in the solution. The AAS was equipped with a deuterium lamp, background correction, a hollow cathode lamp, and an air-acetylene burner.

In the adsorption test, the operating parameters including the adsorbent amount, contact time, pH, and initial cadmium concentration were optimized. For the purpose, the adsorption study was carried out with variation of the adsorbent weight of 10, 20, 50, 70, and 100 mg, contact time of 10, 20, 30, 40, 50, 60, 75, 90, and 120 min, initial cadmium concentration of 10, 20, 30, 40, and 50 mg/L, and pH of 1, 2, 3, 4, 5, 6, 7, and 8. When one variable was varied, the other variables were fixed.

## Results and Discussion

### Sulfonation of the Styrofoam

The obtained sulfonated styrofoam has a brown color that is different from that of the original white styrofoam. The success of the sulfonation of the styrofoam is detected by IR spectra based on the formation of C-S bonds caused substitution of a hydrogen atom in benzene ring by sulfonate

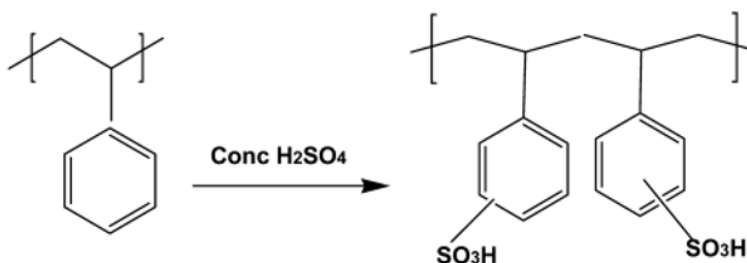


Fig. 1: The sulfonation process of styrofoam<sup>22</sup>

group.<sup>6,18,22</sup> The reaction of sulfonation on styrofoam has been proposed<sup>22</sup> as shown in Fig. 1.

#### The Effect of the Sulfuric Acid Concentration

The concentration of the sulfuric acid is an important factor in the sulfonation to yield polystyrene with the sulfonate group. The FTIR spectra of the sulfonated styrofoam with various sulfuric acid concentrations are displayed in Fig. 2. Absorption peaks are observed at wavenumbers of 3445, 3024, 2924, 1605, and 1450  $\text{cm}^{-1}$ . The peaks are attributed to O-H stretching, unsaturated aromatic  $\text{C}_{\text{sp}^2}$ -H stretching, saturated  $\text{C}_{\text{sp}^3}$ -H stretching, and aromatic C=C stretching, respectively.<sup>6</sup> The data confirmed the reported results.<sup>6,8,22</sup>

The IR spectra of sulfonated styrofoam are of resemblance that of the native one. Additional peaks in the sulfonated styrofoam spectra are observed at 1327, 1180 and 1026, and 586  $\text{cm}^{-1}$ , which can be attributed to vibration of  $\text{SO}_3$  asymmetric stretching,  $\text{SO}_3$  symmetric stretching, and S=O bending<sup>8</sup> which are observed at all concentration of  $\text{H}_2\text{SO}_4$ . A new peak at 1126  $\text{cm}^{-1}$  is found in the sulfonated styrofoam prepared with concentrated sulfuric acid (18 M) and is attributed to the bonding of the sulfonate ( $-\text{SO}_3\text{H}$ ) group to the aromatic ring. This is in a good agreement with the result reported by Bekri-Abbes *et al.*,<sup>6</sup> who observe at 1129  $\text{cm}^{-1}$  and Mahmoud *et al.* observe at 1128  $\text{cm}^{-1}$ .<sup>22</sup> It is believed that sulfonation has been successfully carried out,

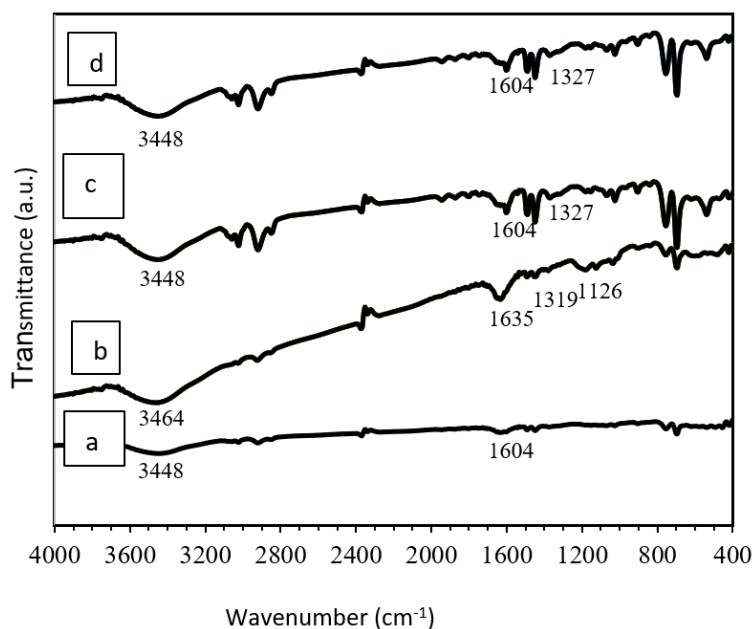


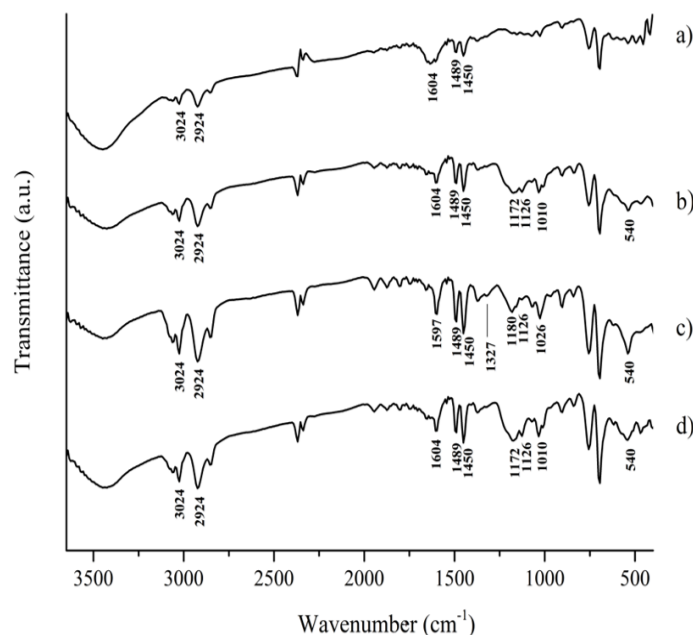
Fig. 2: FT-IR spectra of a) styrofoam, b) sulfonated styrofoam with  $\text{H}_2\text{SO}_4$  of 18 M, c) 9 M, and d) 4.5 M

which can only be realized by using concentrated sulfuric acid.

### Effect of the Reaction Temperature

In the sulfonation process, the temperature plays an important role to promote sulfonation reaction. The FTIR spectra of sulfonation at various temperature are presented in Fig 3. The peaks of asymmetric stretching of  $\text{SO}_3$  group appear at

various wavenumbers. The absorbance observed at  $1126 \text{ cm}^{-1}$  is attributed to C-S stretching of the sulfonated styrofoam prepared at 60 and 80 °C. It indicates that the sulfonation reaction of styrofoam can occur at a higher temperature only. Styrofoam is a thermally stable polymer, which needs a higher temperature to allow the substitution of a hydrogen atom in the benzene ring with sulfonate group. However, at a higher temperature such as 80 °C, the



**Fig. 3: FT-IR spectra of a) styrofoam b) sulfonated styrofoam obtained at 40 °C, c) at 60 °C, d) at 80 °C**

color of the styrofoam turns black to suggest that the polymer has turned into char. It is evident that the best temperature for sulfonation is 60 °C. The same results were also reported before.<sup>6</sup>

The effect of the sulfonation temperature on the polymer crystal structure is studied by XRD. The results are shown in Fig. 4. The XRD patterns of the sulfonated styrofoam prepared at 30 °C is depicted in Fig. 4a. The XRD patterns depend on the reaction temperature as shown in the figure. It indicates that at low temperature, the thermal energy is not enough to initiate the sulfonation reaction. The reaction at

60 °C gives semi-crystalline materials, as shown by much sharp peak observed near  $19^\circ$ . The shift from amorphous to the semi-crystalline structure is obvious. As indicated by the IR data, the optimum sulfonation temperature is found to be 60 °C.

However, the reaction at a much higher temperature of 80 °C leads to the disappearance of the peak at a low angle. The semi-crystalline structure seems to shift gradually back to amorphous. The high reaction temperature gives a better sulfonation product as suggested by IR data, but it causes the structural change in the polymer.

### The Effect of the Sulfonation Process Time

The reaction time determines the effectiveness of the contact between the sulfuric acid and the polymer chain, which also needs to be understood. The FTIR spectra of the sulfonated styrofoam prepared at various times are displayed in Fig. 5. The peaks of the sulfonated styrofoam prepared with various reaction times look similar. As presented previously,

the IR spectra of all sulfonated styrofoams also display the addition bands, which are characteristic for  $\text{SO}_3$  group. A band appears at  $1126 \text{ cm}^{-1}$ , which is attributed to C-S stretching and is only found in the product sulfonated for 6 h and 15 h. The short reaction time of less than 6 h results in the low effective reaction between sulfuric acid and styrofoam. The reaction was conducted for more than

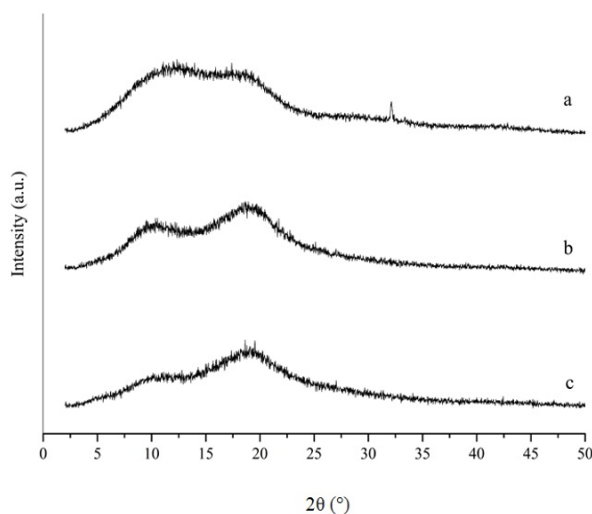


Fig. 4: XRD patterns of a) sulfonated styrofoam produced at  $30^\circ\text{C}$ , b) at  $60^\circ\text{C}$ , and c) at  $80^\circ\text{C}$

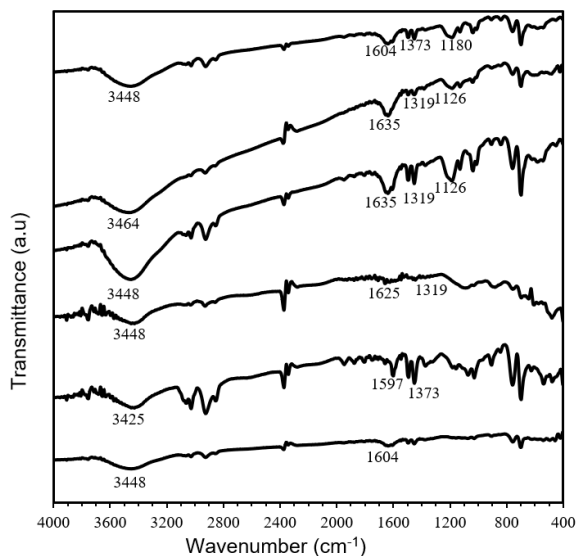
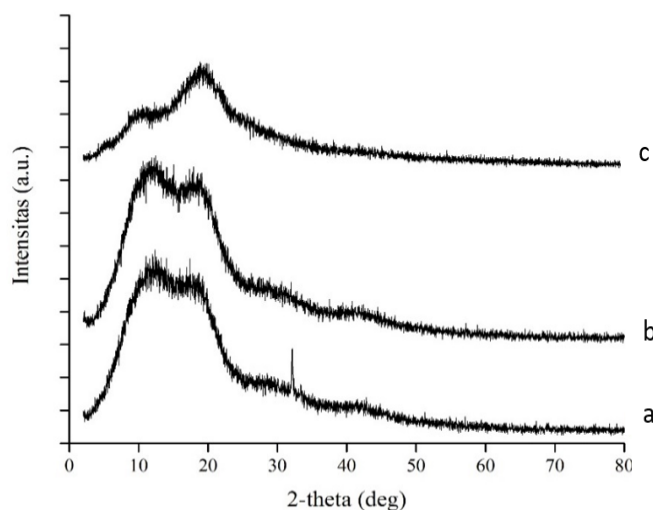


Fig. 5: The FT-IR spectra of a) original styrofoam, b) sulfonated styrofoam prepared for 1 h, c) 3 h, d) 6 h, e) 15 h, and f) 30 h

15 h results in the IR spectra without C-S stretching band, suggesting that sulfonation is not successful. It indicates that sulfonation can be achieved for 6 - 15 h. However, it is longer than the reported work by Bekri-Abbes *et al.*,<sup>6</sup> which was 1.5 h.

Fig. 6 illustrates the XRD patterns of the sulfonated styrofoam prepared with various times. This data shows that the sulfonation process for 1 h gives no different pattern. It indicates that the short reaction time does not cause structural distortion. The



**Fig. 6: The XRD patterns of a) sulfonated styrofoam with 1h, b) sulfonated styrofoam with 6 h, and c) sulfonated styrofoam with 30 h**

process is done for 6-15 h results in the sharper XRD pattern, that can be attributed to the more crystalline polymer. However, very long reaction (30 h) produces slightly amorphous material as indicated by the XRD patterns.

#### Effect of the Styrofoam Weight

With the same volume (100 mL) of the concentrated sulfuric acid (18M), the various weight of the styrofoam give different turbidity of the mixture, that result in the different sulfonation effectiveness. Therefore, it is essential to optimize the weight of the styrofoam. The IR spectra of the sulfonation product are displayed in Fig. 7.

The IR bands of the sulfonated styrofoam samples are close to that of the styrofoam. A band of  $1126\text{ cm}^{-1}$  is also observed in the spectra of the sulfonated styrofoams that were prepared with 2.5 and 5.0 g of the starting material. The smaller amount of the styrofoam with the same volume of the concentrated sulfuric acid (100 mL) allows the sulfonate to interact with the styrofoam structure

effectively. The effectiveness decreased when the amount of the styrofoam was further increased (7.5 g) due to unappropriate stoichiometric ratio of sulfuric acid to polystyrene.

#### SEM Images of the Adsorbent

The study on the effect of the sulfuric acid concentration suggests that the best condition for the sulfonation uses 18 M (100 mL) sulfuric acid, at  $60\text{ }^{\circ}\text{C}$  for 6 h of reaction, using 5 g starting styrofoam. To better understand, the product was investigated by SEM, and the results are shown in Fig. 8. The figure indicates that the native styrofoam has big ribbon-like shape, which is common for polymer morphology. After sulfonation, the ribbon-like shape becomes small and is more porous due to reaction with concentrated acid at a moderate temperature for a long period.

#### Adsorption Model

The ability of the sulfonated styrofoam to adsorb cadmium ion is evaluated via adsorption process. The interaction between  $\text{Cd}^{2+}$  ion and surface of

adsorbent is depicted in Fig. 9. Each cation forms an electrostatic bond with 2 adjacent sulfonate groups.

### Effect of the Adsorbent Weight

The results of the cadmium adsorption carried out with various adsorbent weights are illustrated in Fig. 10. The increase in the adsorbent mass

causes the adsorption to increase, implying that the adsorbent load correlates with cadmium adsorption amount. More adsorbent weight provides a more active surface resulting in more cadmium to be adsorbed. However, when a large amount adsorbent was added to the cadmium solution, the adsorption diminishes slightly. The large amount of

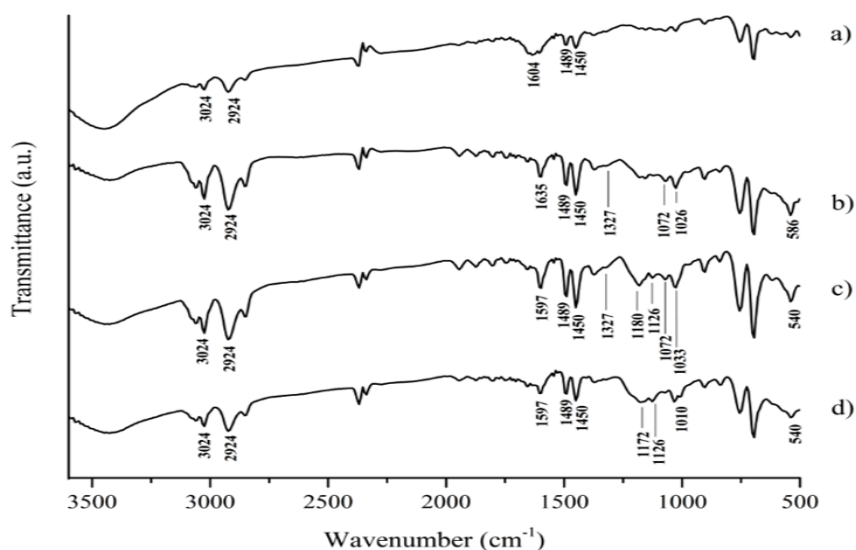
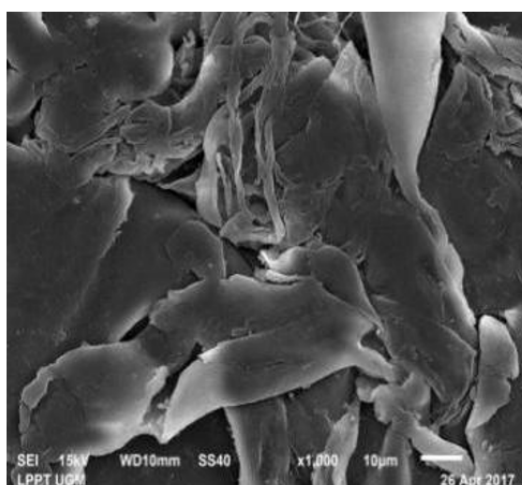
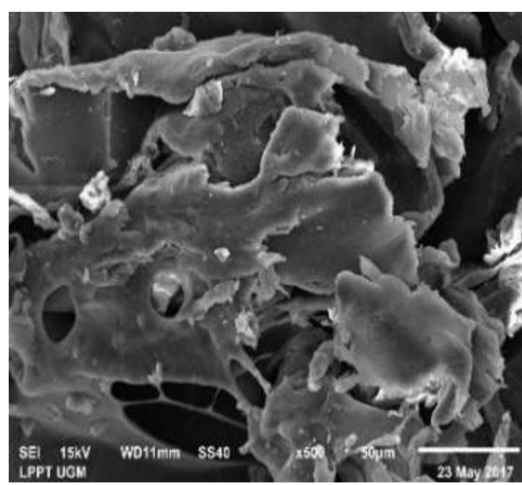


Fig. 7: The FT-IR spectra of a) Styrofoam b) Sulfonated Styrofoam 1.5 g c) Sulfonated Styrofoam 3.0 g, and d) Sulfonated Styrofoam 4.5 g



(a)



(b)

Fig. 8: The SEM images of a) styrofoam and b) sulfonated styrofoam



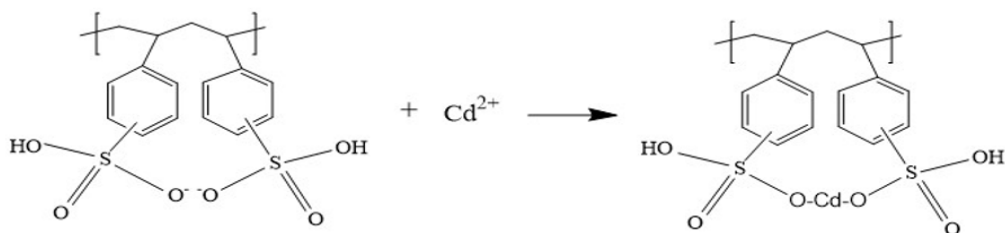


Fig. 9: Predicted interaction of the of  $\text{Cd}^{2+}$  with sulfonated styrofoam

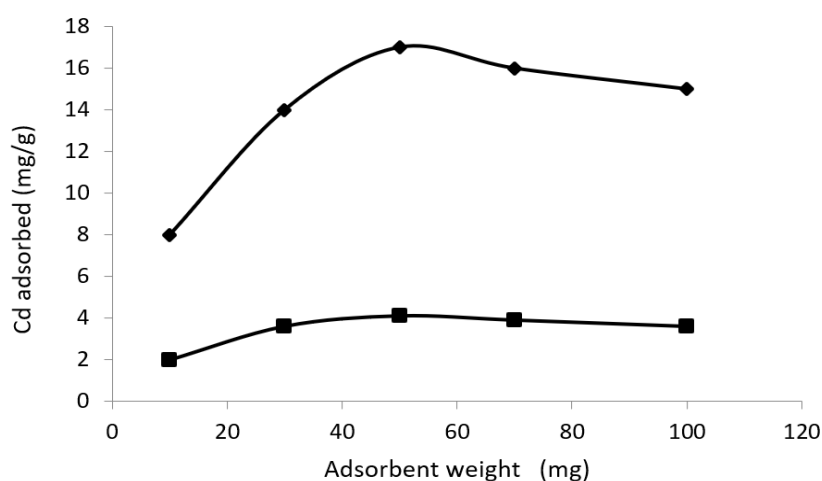


Fig. 10: Effect of the adsorbent weight on the cadmium adsorption by a) styrofoam and b) sulfonated styrofoam. A 100 mL cadmium solution of 20 mg/L was used

the adsorbent leads to the solution turbid, that inhibit the interaction between cadmium and the adsorbent.

#### The Influence of the Initial Cadmium Ion Concentration

Fig. 11 displays the effect of the initial cadmium ion concentration on the adsorption. The cadmium adsorption improves as the initial its concentration increases, but further increase in the concentration gives no effect on the adsorption. Increasing concentration raises the effective contact between the cadmium and the adsorbent surface. The further increase of the cadmium concentration makes the active surface of the adsorbent saturated. It explains the fact that no adsorption increase is observed.

When the amount of the cadmium adsorbed is compared to the correspond initial concentration, it is shown that 20 mg/L of the initial concentration can be completely adsorbed (100%). Further, the

percentage of the adsorption declines when the initial concentration is increased (the calculation is not presented in this paper).

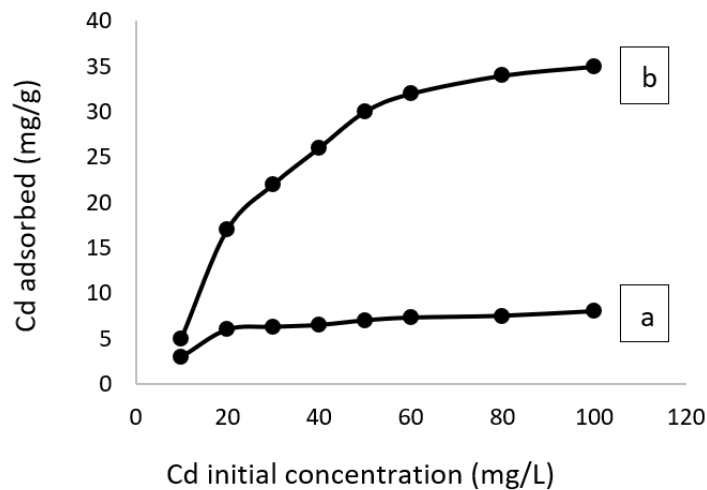
#### The Influence of the Contact Time

The results of the adsorption of cadmium ion with various of the contact time are demonstrated in Fig. 12. It appears that the adsorption increases with time. The maximum adsorption on the sulfonate styrofoam reaches after 60 min of interaction, and the adsorption is the independence of the contact time after 60 min. In the beginning, the active sites of the adsorbent surface are free that facilitates rapid cadmium adsorption. After 60 min, the active sites of the adsorbent becomes saturated with cadmium ions, accordingly the adsorption does not change appreciably. The similar trend is observed for the unsulfonated adsorbent, with the shorter optimum time, that is 20 mins.

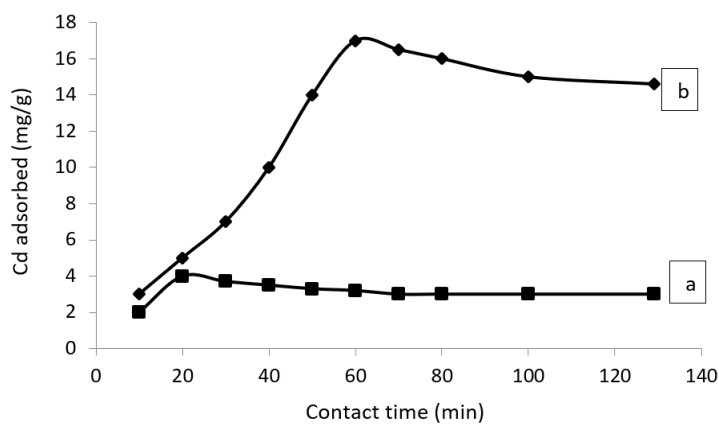
**The Effect of the System pH**

Another important variable in the adsorption is pH. The pH determines the surface properties of the sulfonated styrofoam adsorbent and the speciation of cadmium ion. The effect of pH on the adsorption both by unsulfonated and sulfonated adsorbent is presented in Fig. 13. The adsorption changes with the pH and it reaches maximum at pH 4. In the low pH, the H<sup>+</sup> concentration is high enough to protonate sulfonate group (-SO<sub>3</sub>H). Since the cadmium exists as Cd<sup>2+</sup>, less effective adsorption is expected due to the competition of Cd<sup>2+</sup> with H<sup>+</sup>. Increasing pH

up to 4, the number of H<sup>+</sup> are reduced and so the less competition, that promotes more adsorption. An interesting adsorption data is observed for the native styrofoam, that is constant adsorption in the pH solution from 1 to 4. Such trend can be understood since at pH 1-4, the cadmium exist as Cd<sup>2+</sup> while the hydrophobic surface of the styrofoam is independence on the pH. The adsorption declines at the pH higher than 4, it is because in such range pH, the concentration of OH<sup>-</sup> is high, which could react with the cadmium ion to form Cd(OH)<sub>2</sub> precipitate, leading to the low adsorption.



**Fig. 11: Effect of the initial cadmium concentration on the Cd adsorption by a) styrofoam and b) sulfonated styrofoam**



**Fig. 12: Effect of the contact time on the cadmium adsorption by a) styrofoam and b) sulfonated styrofoam**

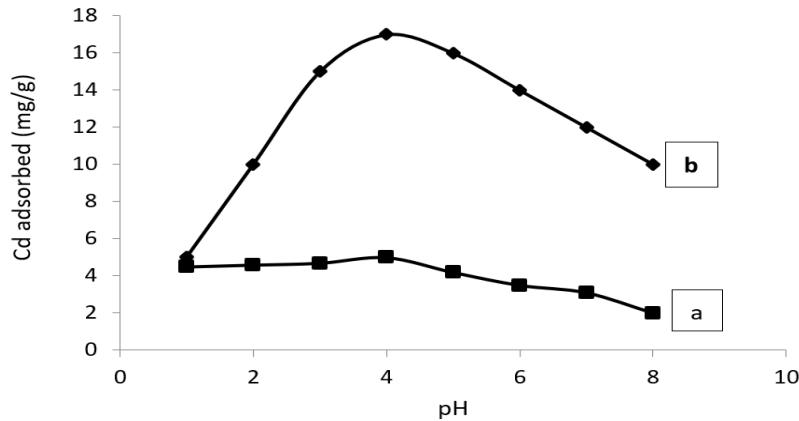


Fig. 13: Effect of the pH on the cadmium adsorption by a) styrofoam, and b) sulfonated styrofoam

**Adsorption Isotherm and Kinetics**

The isotherm adsorption is modeled as Langmuir and Freundlich for both native and sulfonated styrofoam as displayed in Fig. 14 and Fig. 15, respectively. Fig. 14 produces the correlation coefficient ( $r^2$ ) of around 1, meaning that the adsorption on the native styrofoam is fitted well with the Freundlich model. The model represents the fact that the adsorbent surface is heterogeneous so that the adsorbate can be adsorbed through various interactions. For styrofoam, there are no active sites but provides porous with diverse size. The adsorption is believed to take place through diffusion into the porous material and to form multilayers. The adsorption

constant and adsorption capacity are found to be 1.99 L/g and 7.09 mg/g, respectively.

Fig. 15 depicts the cadmium adsorption by the sulfonated styrofoam following the Langmuir and Freundlich models. The adsorption agrees well to the Langmuir isotherm model as indicated by the  $r^2$  value of 0.99. The sulfonated styrofoam has  $SO_3^-$  group attached to the structure, enabling it to interact with  $Cd^{2+}$  ions forms a monolayer as suggested by the Langmuir model. The adsorption constant and capacity are found to be 5.85 L/g and 51.6 mg/g, respectively.

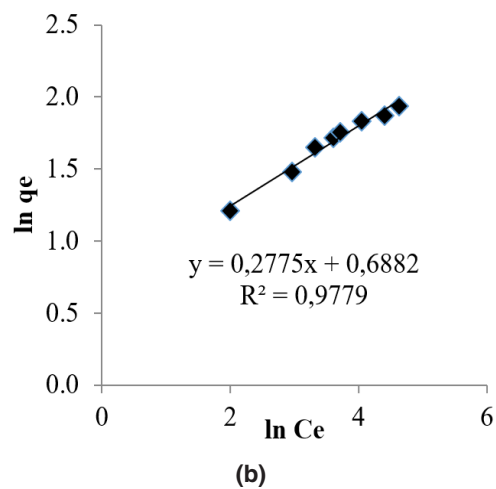
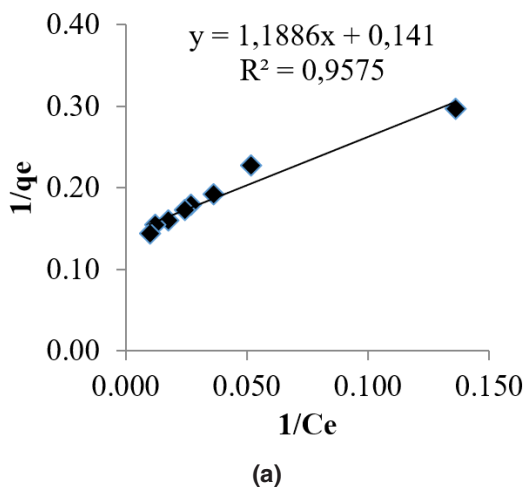
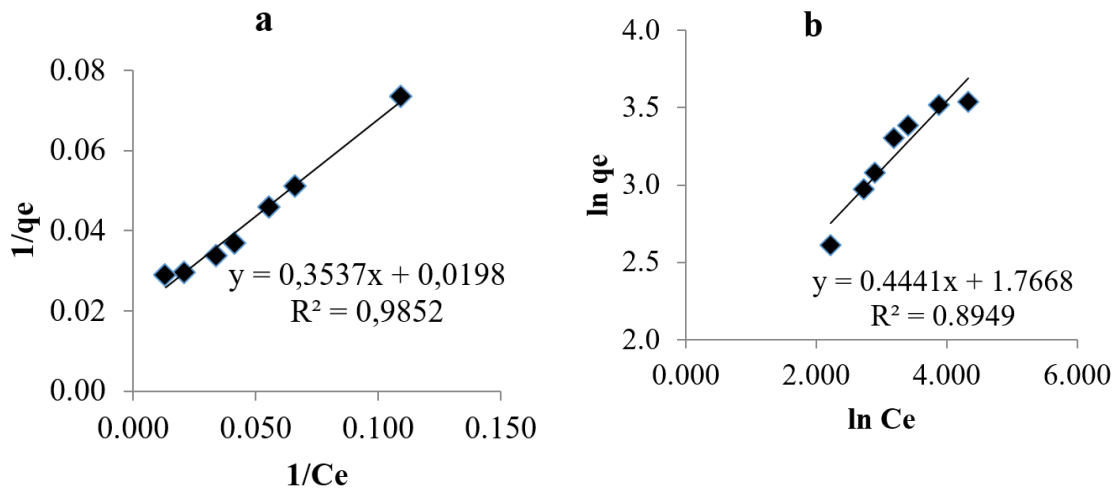
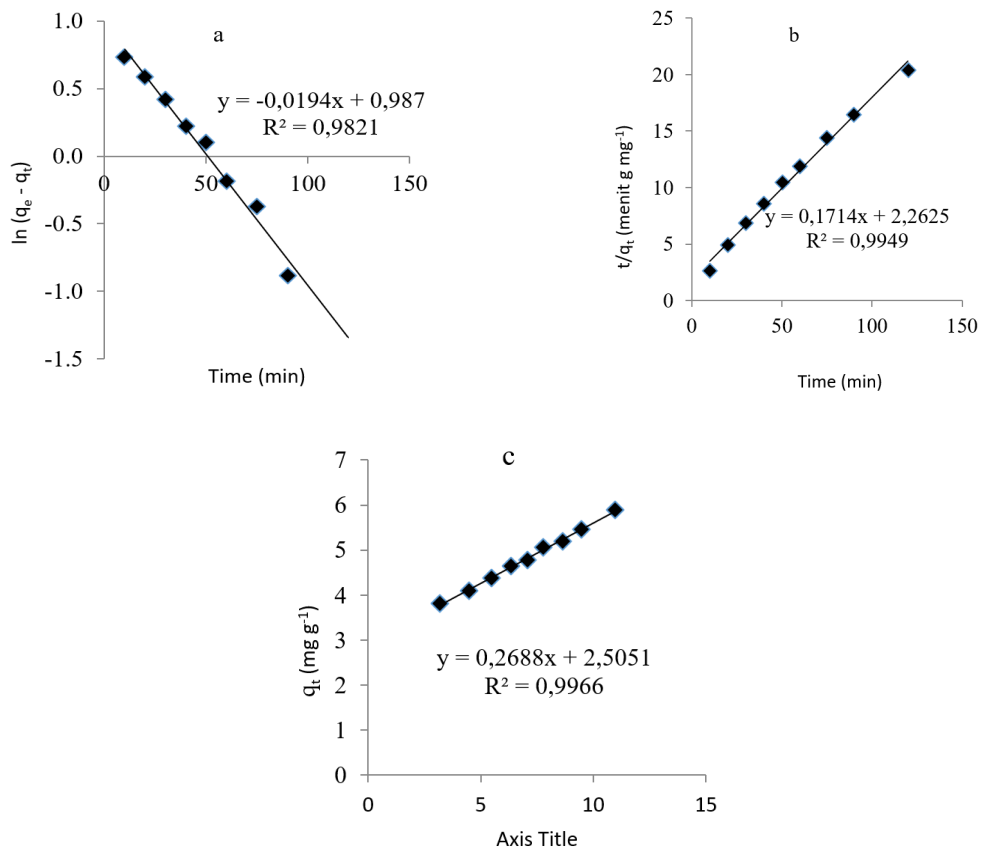


Fig. 14: The isotherm adsorption of the unsulfonated styrofoam that is modeled by a) Langmuir and b) Freundlich



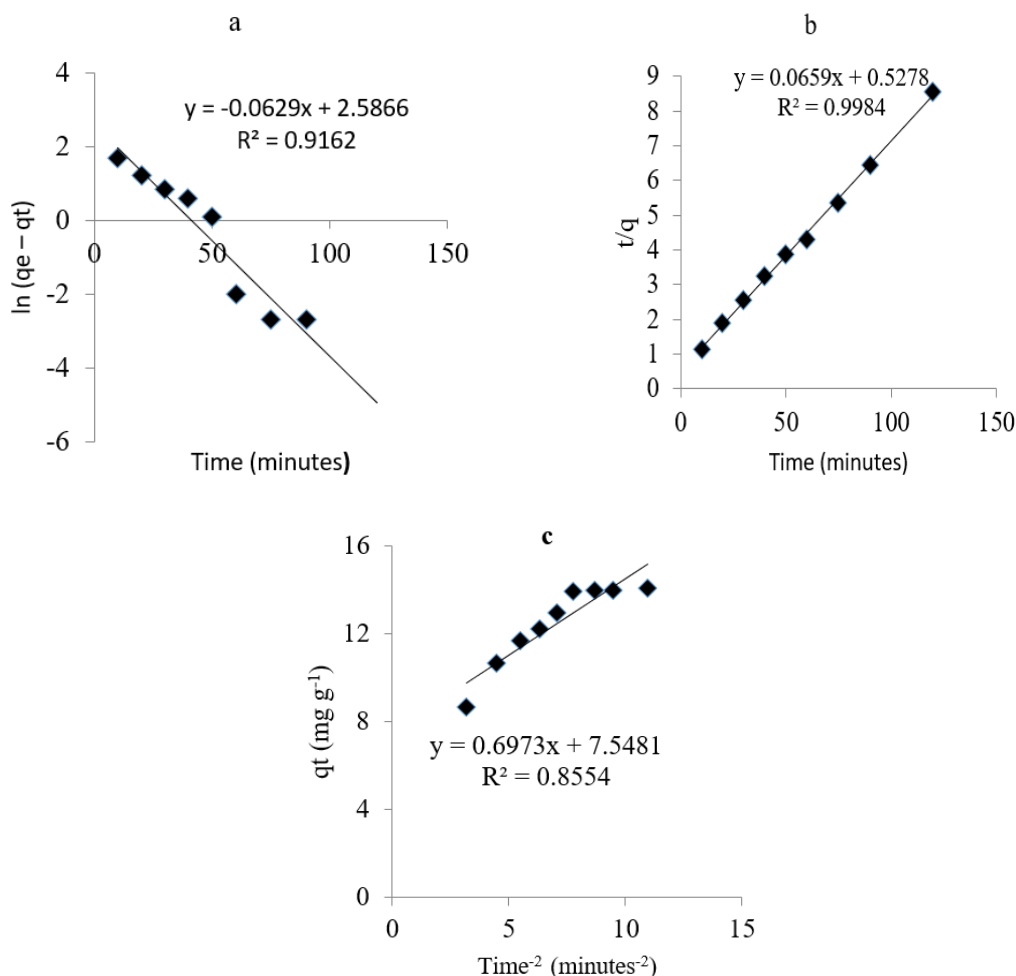
**Fig. 15: The isotherm adsorption of the sulfonated styrofoam that is modeled as a) Langmuir, and b) Freundlich**



**Fig. 16: The kinetic adsorption by styrofoam modeled with a) Lagergren pseudo-first order, b) Ho pseudo-second order, and c) intraparticle diffusion**

The rate of cadmium adsorption is presented in Fig. 16 and Fig. 17 for sulfonated and untreated styrofoam, respectively. Three commonly accepted kinetic models, i.e. Lagergren pseudo-first order, Ho pseudo-second order, and intraparticle diffusion are simulated.<sup>23</sup> Fig. 16 shows that the cadmium adsorption kinetics by styrofoam is believed to

follow the intraparticle diffusion as indicated by the correlation coefficient ( $r$ ) value that is close to 1. This finding is consistent with that of the Freundlich model. The rate constant is obtained to be  $26.9 \cdot 10^{-3} \text{ mg/g} \cdot \text{min}^{1/2}$ . The same result was also reported elsewhere.<sup>32</sup>



**Fig. 17: The adsorption by sulfonated styrofoam as modeled with a) Lagergren pseudo-first order, b) Ho pseudo-second order, and c) intraparticle diffusion**

The kinetic adsorption model for sulfonated styrofoam as depicted in Fig. 17 shows  $r^2 = 0.998$ , which is matched well with the Ho, pseudo-second-order model. The pseudo-second-order model suggests that the adsorption rate is determined by the two reactants. In this case,  $\text{Cd}^{2+}$  ions are adsorbed on the active sites of  $-\text{SO}_3^-$  attached to

the sulfonated styrofoam surface. The ion exchange reaction between  $\text{H}^+$  (attached to  $\text{SO}_3\text{H}$ ) and  $\text{Cd}^{2+}$  may also happen. Such adsorption commonly takes place on the homogeneous adsorbent surface, as it agrees with the isotherm Langmuir model. The calculated adsorption rate constant is about  $8.2 \cdot 10^{-3} \text{ mg/g} \cdot \text{min}$ .

The adsorption capacity of the sulfonated styrofoam is higher than that of the unmodified one. The modified styrofoam has sulfonate group that gives the negative charge on the surface and acts as an active site for cation adsorption. These negative surfaces facilitate effective electrostatic interaction. Meanwhile, styrofoam that is hydrophobic has low interaction with the cations. Based on this fact, styrofoam is expected to be unable to adsorb cadmium ion. The limited cadmium adsorption may be due to the limited porous nature of the network of the polymer long chain.

The opposite trend was observed on the adsorption rate data. The adsorption rate of cadmium by sulfonated styrofoam is 3.5 times slower than that of on the unmodified styrofoam. It indicates that the electrostatic interaction between  $\text{Cd}^{2+}$  in the solution and  $-\text{SO}_3^-$  on the surface of the adsorbent takes more time than the diffusion pathway.

### Conclusions

The sulfonation of styrofoam has been successfully realized by mixing 5 g of styrofoam waste with 100

mL of the concentrated sulfuric acid (18 M) and heating at 60 °C for 6 h. The negative charges are given by  $\text{SO}_3^-$  groups attached to the styrofoam structure are created, which are useful for adsorption of  $\text{Cd}^{2+}$  ion effectively. The cadmium adsorption by using 50 mg adsorbents in 100 mL solution of 20 mg Cd/L takes place effectively at pH 4 with a contact time of 60 for sulfonated and 20 min for original styrofoam, respectively. The cadmium adsorption by styrofoam fits the Freundlich model and intraparticle diffusion mechanism whereas adsorption by sulfonated styrofoam fits the pseudo-second-order model and the Langmuir isotherm. The adsorption capacity of the sulfonated styrofoam (51.6 mg/g) is higher than that of native styrofoam (7.09 mg/g), but its rate is lower ( $8.20 \cdot 10^{-3} \text{ mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$ ) than that of the native styrofoam ( $26.9 \cdot 10^{-3} \text{ mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1/2}$ ).

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