

# Adsorption of Selenite and Selenate Ions onto Thiourea-Formaldehyde Resin

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**ABSTRACT:** In the present work, thiourea-formaldehyde (TUF) chelating resin was synthesized and used in the adsorptions of selenite ( $\text{SeO}_3^{2-}$ ) and selenate ( $\text{SeO}_4^{2-}$ ) ions. The effects of initial acidity and initial selenium concentrations on the adsorptions were examined by batch technique. The synthesized resin was applied to the elemental analysis to determine its composition. FT-IR spectra and SEM/EDS were also recorded before and after selenite adsorption. It was found that selenite and selenate ions were adsorbed onto TUF resin at strong acidic conditions (3–5M HCl). The adsorption capacities of the resin were

calculated as  $833.3 \text{ mg g}^{-1}$  TUF resin for selenite ions and  $526.3 \text{ mg g}^{-1}$  TUF resin for selenate. All the adsorption data obtained for both selenite and selenate ions fitted well to the Langmuir isotherm. It was seen that the adsorption mechanisms in the both adsorptions were governed by the reduction of selenite or selenate to elemental selenium,  $\text{Se}^0$ . © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1134–1141, 2011

**Key words:** adsorption; selenium; selenite; selenate; thiourea-formaldehyde resin; chelating resin

## INTRODUCTION

Selenium is a trace element, which occurs naturally in the environment. It can be either an essential element or a potential toxicant for organisms depending on its concentration and chemical form. Selenium is used in the manufacture of photocells, rectifiers, xerography equipments dandruff shampoos, and electronic devices. It was also used in glasses and the coating of stainless steel and copper.<sup>1</sup>

When the health effects of selenium were examined, its toxicity occurs at selenium ingestion levels of  $0.7\text{--}7.0 \text{ mg day}^{-1}$  while  $200 \text{ }\mu\text{g day}^{-1}$  ( $0.2 \text{ mg day}^{-1}$ ) is nutritionally adequate. The US Environmental Protection Agency (EPA or USEPA) has set the Maximum Contaminant Level (MCL) in drinking water for selenium at  $0.05 \text{ mg L}^{-1}$ . EPA has found that selenium causes potentially the following health effects when people are exposed to it at levels above the MCL for relatively short periods of time: hair and fingernail changes; damage to the peripheral nervous system; fatigue and irritability. Long-term, selenium has the potential to cause the following effects from a lifetime exposure at levels above the

MCL: hair and fingernail loss; damage to kidney and liver tissue, and problems with the nervous and circulatory systems.<sup>1</sup>

In the nature, selenium can exist in different oxidation states, elemental selenium ( $\text{Se}^0$ ), selenite ( $\text{SeO}_3^{2-}$ ), selenate ( $\text{SeO}_4^{2-}$ ), inorganic and organic selenides ( $\text{Se}^{2-}$ ), (methylated compounds, selenoamino acids, selenoproteins, and their derivatives).<sup>2–4</sup> The majority of selenium is concentrated in the anode slimes during the refining of copper in the metallurgical processes. These anode slimes are the most important raw material of selenium in industry.<sup>5</sup>

Selenium separation from industrial intermediate solutions, waste water, and drinking water is important for later usages. Several techniques may be used to reduce the level of selenium from aqueous media: anion exchange, activated alumina (AA), reverse osmosis (RO), and distillation.<sup>1</sup> There are a lot of adsorbents studied by many researchers for selenite or selenate ions. These include amberlite IRA-67 with secondary and tertiary amines, duolite A7 with primary and secondary amines,<sup>2</sup> eporasu K-6 with polyamine,<sup>5</sup> activated carbon,<sup>4,6</sup> Al- or Fe- or binary oxides,<sup>7,8</sup> dowex  $1 \times 2$  resin, a strongly basic anion exchanger,<sup>2</sup> chitosan resin with 3,4-diamino benzoic acid (CCTS-DBA resin),<sup>9</sup> poly(*N,N*-dimethylacrylamide-*co*-allylthiourea),<sup>10</sup> some chelating resins with ammonium pyrrolidine dithiocarbamate (APDC),<sup>11</sup> bismuthiol-II and diamionaphthalene,<sup>12</sup> and grafted with 2,3-diamionaphthalene on amberlite-XAD-4 resin,<sup>13</sup> polymer with aromatic diamine (*o*-phylene-diamine),<sup>14</sup> bentonite,<sup>15</sup> agricultural wastes,<sup>16</sup> and silica gel modified with 3-mercaptopropyl.<sup>17</sup>

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However, thiourea-formaldehyde (TUF) resin has not been examined by focusing on the adsorption of selenite or selenate ions. It has amine ( $>NH_2$ ) and thiourea ( $>C=S$ ) functionality as chelating ligands. The resin has the capability of anion adsorption via  $>NH_3^+$  after amine group is protonated. Selenite and selenate ions can be bound to protonated amine.<sup>18–23</sup> Moreover selenite reacts with thiol compounds such as glutathione and 2-mercaptoethanol. In other words, selenium can form selenodiglutathione (GSSeSG) or selenopersulfide (GSSeH) in animal tissues.<sup>24</sup> In addition, selenite and selenate ions are reduced to elemental selenium in thiourea solution. It was thought that TUF resin may be a potential adsorbent for selenite or selenate ions. Also, TUF resin can be synthesized easily in aqueous solutions by controlling the acidity during the synthesis.<sup>18–23</sup> In the present work, thiourea-formaldehyde resin was synthesized and it was used in the adsorption of selenite and selenate ions by batch technique.

## EXPERIMENTAL

### Chemical reagents

All the reagents were of analytical grade and used as received. Formaldehyde (37% aqueous solution,  $1.09 \text{ g mL}^{-1}$ ) and thiourea used in the synthesis of TUF resin were purchased from Merck (Darmstadt, Germany).  $Na_2SeO_3$  and  $Na_2SeO_4$  were obtained from Fluka (UK). The other chemicals used in the studies were from Merck (Darmstadt, Germany). Selenite or selenate solutions were prepared by dissolving  $Na_2SeO_3$  or  $Na_2SeO_4$ , and diluted to the desired concentration using distilled water.

### Apparatus

A Shimadzu AA-6701 model (Japan) flame atomic absorption spectrometer (FAAS) was used for the measurements of selenite and selenate ions. Selenium hollow-cathode lamp (Koto, Japan) was employed as radiation source at wavelength of 196.0 nm and lamp current of 23 mA. The FAAS spectrometer was operated by using acetylene–air gas mixture without hydride system and in the concentration range of  $5\text{--}50 \text{ mg L}^{-1}$  for the determination of the selenium ions. FT-IR spectra of the resin before and after the adsorption of selenite ions were recorded on a Shimadzu-IR Prestige-21 model spectrophotometer. The elemental analysis was performed by using a LECO CHNS 932 elemental analyzer (Leco, USA). SEM/EDS analyses were carried out using a JEOL JSM 6060-LV type scanning electron microscope (SEM) equipped with an energy-dispersive spectrometer (EDS).

### Synthesis of thiourea-formaldehyde resin

TUF, a well-known resin, can be synthesized by reacting formaldehyde (HCHO) with thiourea

( $H_2NCSNH_2$ ) at  $80^\circ\text{C}$ .<sup>21–23</sup> The synthesis includes hydroxymethylation and condensation steps (Scheme 1). TUF resin has very complex structure depending on the mole ratio of thiourea to formaldehyde, synthesis temperature, and dehydration or drying conditions of the resin.

A linear or less crosslinked resin for the adsorption studies was aimed in this study. Therefore, the TUF resin was prepared in the molar ratio of thiourea : formaldehyde of 1 : 1. In the synthesis, 15.2 g (0.2 mol) of thiourea was dissolved in 50 mL distilled water and then 15 mL (0.2 mol) of formaldehyde solution was added. pH was adjusted to 10 using 0.1M NaOH solution and temperature was to  $80^\circ\text{C}$ . After 2 h stirring for the hydroxymethylation reactions, pH was adjusted to 2 using 10% HCl solution while the mixture was stirred at the temperature of  $80^\circ\text{C}$ . After white TUF resin condensates began to precipitate, the reaction was carried out for 6 h. The obtained condensates were filtered, washed using 0.1M HCl solution and distilled water, and dried at  $80^\circ\text{C}$ . Washing with the acid and water was performed in a filtering system. The resin was ground into less particle size than  $150 \mu\text{m}$ . It was washed using 0.1M HCl solution and distilled water, and dried at  $80^\circ\text{C}$ , again. It was used in all the experimental studies.<sup>21–23,25,26</sup>

### Adsorption studies

#### Effect of initial acidity

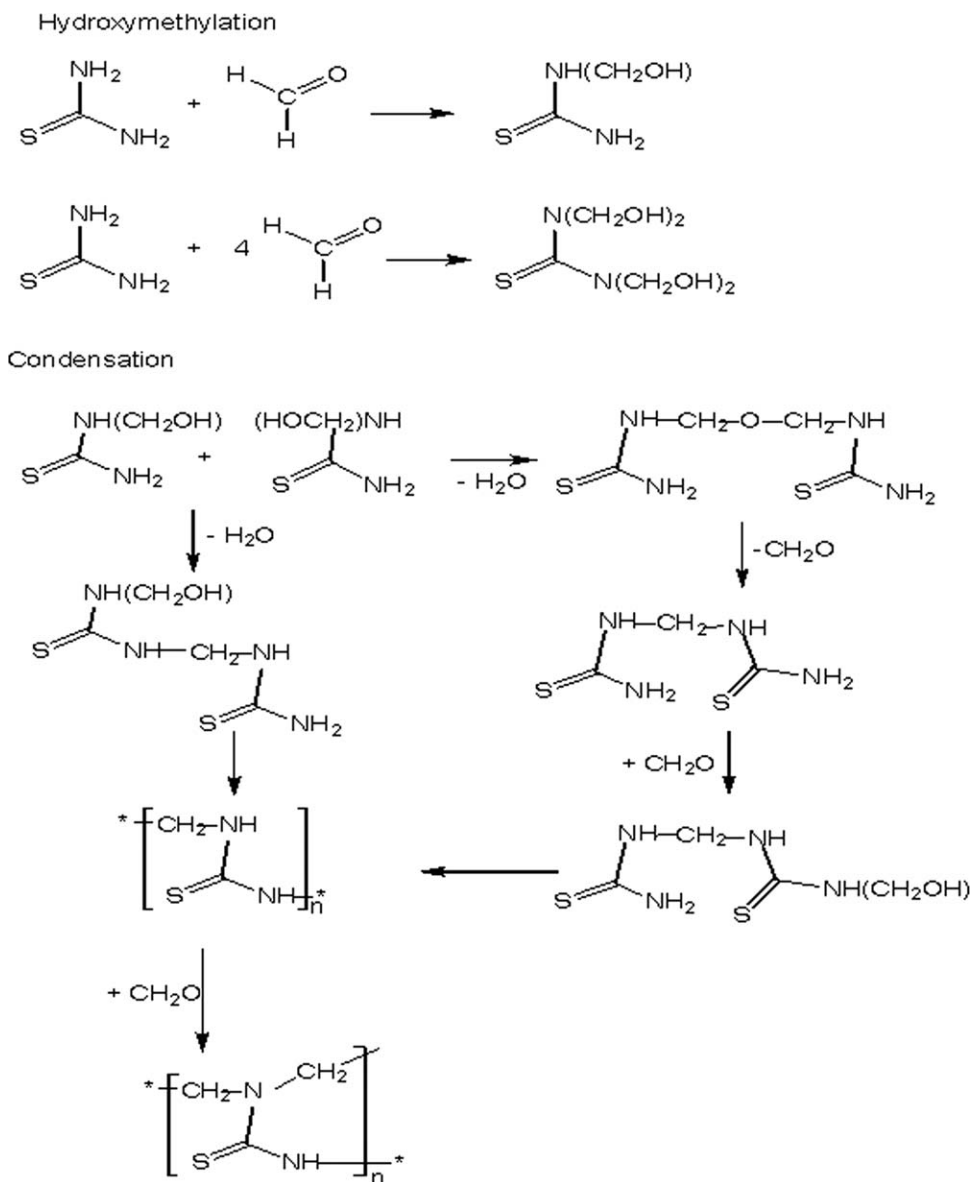
To examine the effect of the initial acidity on the adsorption of selenite ions, the sorption experiments were carried out by stirring 0.5 g of TUF resin in 250 mL  $50 \text{ mg L}^{-1}$  selenium ( $Na_2SeO_3$ ) solutions in the pH range of 0–6 and strong acidity range of 1–5M HCl. Selenium concentrations in the sample solutions taken at predetermined time intervals of 0.5, 1, 24, 48, and 120 h were determined by FAAS. On the other hand, selenate adsorption studies were carried out similarly. The adsorption density,  $q_e$  ( $\text{mg g}^{-1}$ ), of selenite or selenate ions onto the resin was calculated from Eq. (1).

$$q_e = \frac{(C_i - C)}{m} \cdot V \quad (1)$$

where  $C_i$  and  $C$  are the concentrations ( $\text{mg L}^{-1}$ ) at initial and different adsorption periods, respectively,  $m$  is the mass of the resin (g), and  $V$  is solution volume (L).

#### Selenite and selenate adsorption isotherms

In the experimental studies designed for the Langmuir and the Freundlich isotherms, 0.1 g TUF resin was stirred in 250 mL selenite solutions at the concentrations of  $50\text{--}1000 \text{ mg mL}^{-1}$  and including 3M HCl as the optimum acidity, for 72 h. The selenite samples collected at intervals of 1, 24, 48, and 72 h



Scheme 1 Synthesis of thiourea-formaldehyde (TUF) resin.

were analyzed by FAAS. Then, similar experimental studies were carried out by using the selenate solutions at the concentrations of 100–500 mg L<sup>-1</sup>, including 5M HCl. The adsorption data obtained from the studies with selenite and selenate ions were applied to the Langmuir [Eq. (2)] and the Freundlich [Eq. (3)] adsorption models.<sup>20,27</sup>

$$\frac{C_e}{q_e} = \frac{1}{bQ_{\max}} + \frac{C_e}{Q_{\max}} \quad (2)$$

where  $C_e$  is the concentration of selenium at equilibrium in solution (mg L<sup>-1</sup>);  $q_e$  is the amount of selenium adsorbed by per gram of the resin (mg g<sup>-1</sup>); the constant  $Q_{\max}$  is the theoretical saturation adsorption capacity of the monolayer (mg g<sup>-1</sup>); and  $b$  is related to the energy of adsorption (L mg<sup>-1</sup>).

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

where  $K_F$  (mg g<sup>-1</sup>) and  $n$  are constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity. The adsorption isotherms were compared with each other and the adsorption capacities of TUF resin for selenite and selenate ions were calculated using the best isotherm.

## RESULTS AND DISCUSSION

### Characterization of TUF resin

#### Elemental analysis

The elemental composition of the synthesized TUF resin was determined experimentally. It was noted

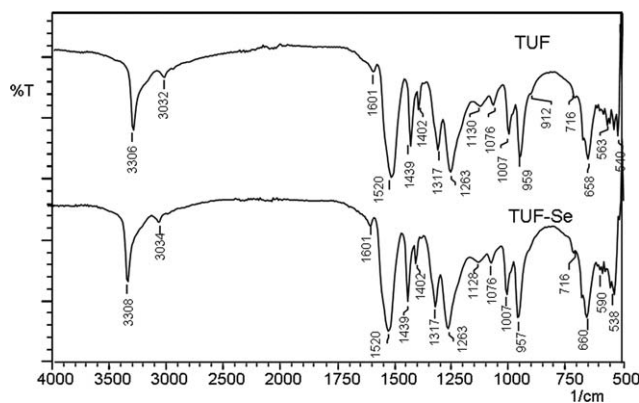


Figure 1 FT-IR spectra of TUF and Se adsorbed TUF.

that the resin contains C, H, N, and S as 25.32, 4.41, 27.92, and 32.21% (w/w), respectively. In addition, the oxygen content of the resin was calculated as 10.15% (w/w) from difference of all the other composition. It may also be noted that the synthesized resin includes 19.94 mmol g<sup>-1</sup> N and 10.06 mmol g<sup>-1</sup> S ligand atoms. It was found that the synthesized resin had nearly the expected composition of TUF resin.

FT-IR analysis

FT-IR spectra of TUF resin before and after the adsorption of selenite ions were recorded and the results are given in Figure 1. The peaks could be analyzed as follows: strong adsorption peak at 3306 cm<sup>-1</sup> showed >N-H in secondary amino, 1603 and 1132 cm<sup>-1</sup> were the peaks of -N-(C=S)- group, 1520 cm<sup>-1</sup> was >C=NH and 959 and 540 cm<sup>-1</sup> were (>C-S-).<sup>23,25,28,29</sup> It was not seen an important change in the FT-IR spectrum of Se adsorbed resin except for the peaks at 538-563 cm<sup>-1</sup>. These peaks belong to S-S bond. It is known that thiourea dissolved in an aqueous solution (not polymerized thiourea) can be oxidized by selenite ions.<sup>30,31</sup> It may be expressed that thiourea functional group on the resin surface could be oxidized to formamidine disulfide during the adsorption [Eq. (4)].

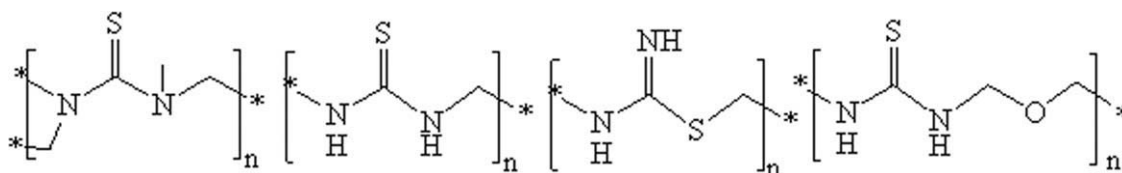
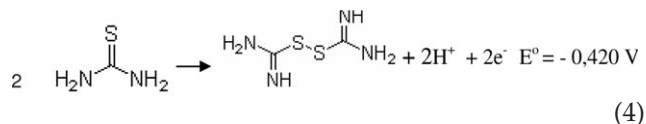


Figure 2 TUF resin.

According to the elemental analysis and the FT-IR spectra, the structure in Figure 2 may be suggested for TUF resin. The structure or chemical composition of TUF resin may show differences related to the conditions in the synthesis. When formaldehyde/thiourea mole ratio is selected as 4/1 or 2/1 before the synthesis, physical properties of the resin may be better than the mole ratio of 1/1. Different mole ratios for the resin had been tested and it had been found that TUF resin at mole ratio of 1/1 had had better adsorption properties. So, in this study, it was aimed to synthesize a linear or less crosslinked TUF resin using mole ratio of 1/1.<sup>18-23</sup> However, TUF resin synthesized at mole ratio of 1/1, also, showed crosslinked and thio-bound structures as 4/1 or 2/1. These crosslinked and thio-bound structures may be caused by polymerization after condensation.

SEM/EDS analysis

The SEM/EDS analyses of TUF resin before and after selenite adsorption were examined and the results are given in Figure 3. It was found that TUF resin included N, S, and O atoms before the adsorption and Se atoms additionally after the adsorption. EDS surface analysis was not a true chemical analysis because of carbon paper during the measurements. It should be considered as qualitative. In addition, it can be seen from the SEM micrographs that the particles of the resin were coated by a new material after the adsorption.

Adsorption studies

Effect of initial acidity

Acidity of a solution has a significant impact on the adsorption of many ions since it determines the surface charge of an adsorbent, and the degree of ionization and speciation of an adsorbate. The acidity may also play an important role in the adsorption of selenite/selenate species. To establish the effect of initial acidity on the adsorption of selenite and selenate ions, the batch equilibrium studies were carried out at different pH values and HCl concentrations. The results are given in Figure 4 for selenite and in Figure 5 for selenate ions. It was found that the adsorptions of both selenite and selenate ions were more effective in strong acidic solutions. As can be



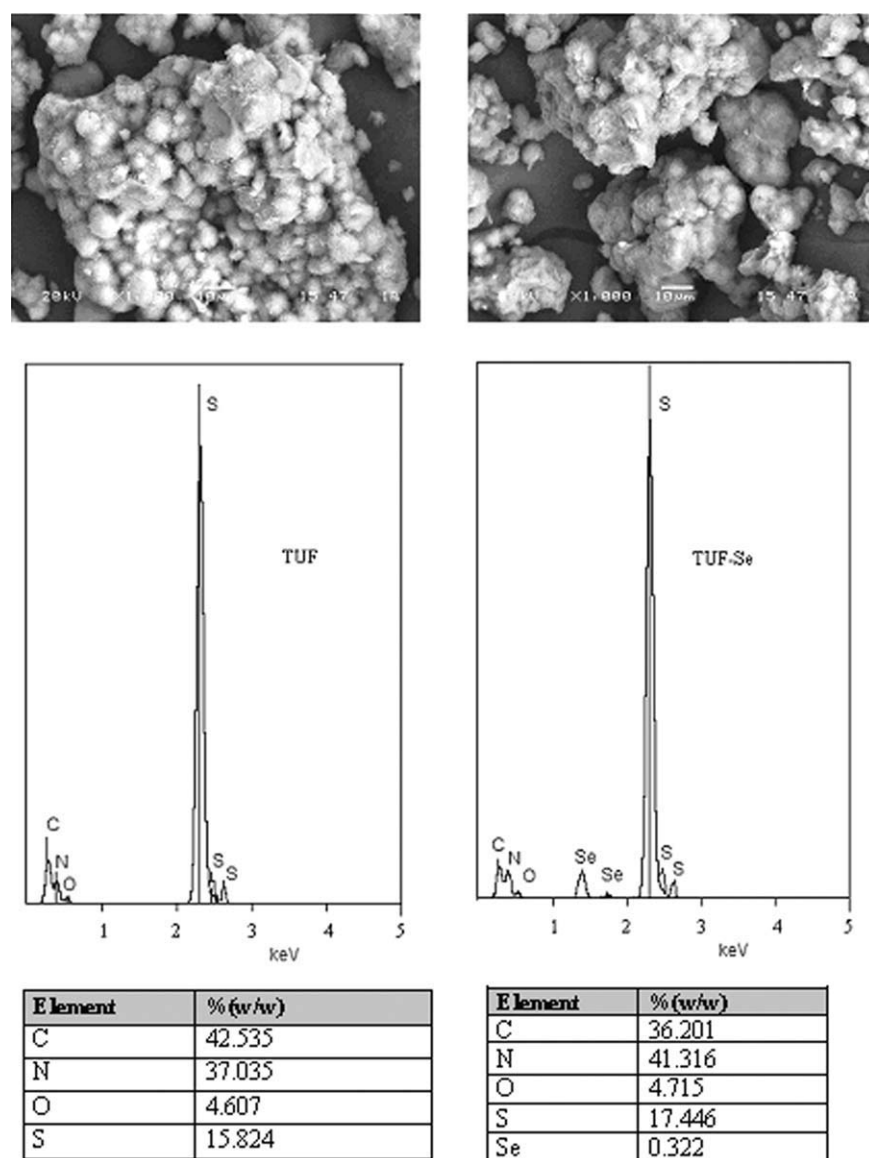


Figure 3 SEM/EDS analyses before (TUF) and after (TUF-Se) adsorption.

seen from Figures 4 and 5, selenate ions require more acidity than selenite for the adsorption. The optimum acidities for selenite and selenate ions

were selected as 3M HCl and 5M HCl, respectively. Selenate ions may require more acidity over 5M HCl. However, a stronger acidity over 5M HCl was

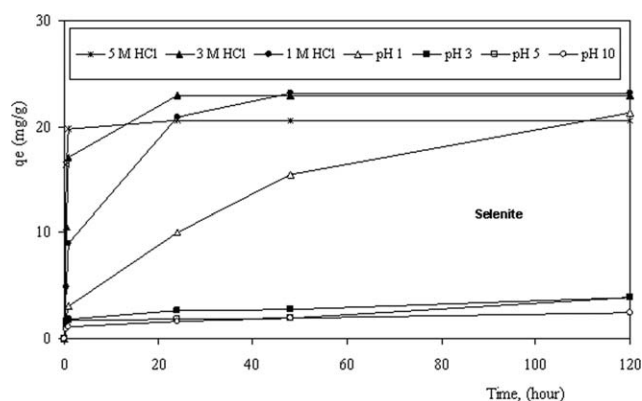


Figure 4 Effect of initial acidity on selenite adsorption.

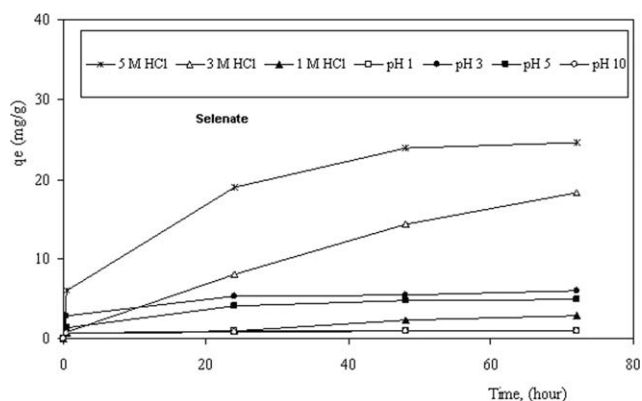
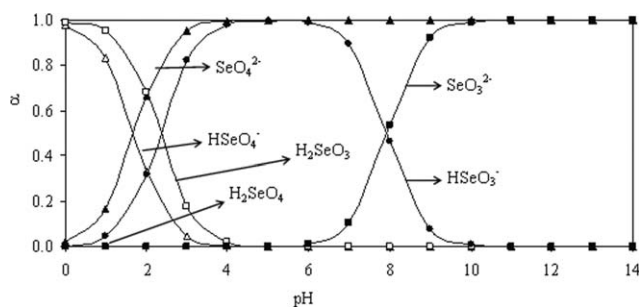


Figure 5 Effect of initial acidity on selenate adsorption.



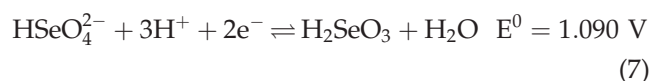
**Figure 6** Fractional species of selenous and selenic acids at different pH values.

not studied because of economic respect and resin stability.

Selenite or selenate species in a solution may be  $H_2SeO_3$ ,  $HSeO_3^-$ , and  $SeO_3^{2-}$ , or  $H_2SeO_4$ ,  $HSeO_4^-$ , and  $SeO_4^{2-}$ , depending on the pH values of the selenium solutions. The fractional species of selenite and selenate ions were calculated using  $pK_{a1} : 2.63$ ,  $pK_{a1} : 8.40$  for  $H_2SeO_3$  and  $pK_{a1} : 3.0$ ,  $pK_{a2} : 1.70$  for  $H_2SeO_4$ . Their graphs are given in Figure 6. Thiourea-formaldehyde resin has protonable amine group ( $>NH_2^+$ ) and this group may bind Se(IV) or Se(VI) species in solution. In other words, selenium species may interact with protonated amines via ionic interaction (For example;  $>NH_2^+ HSeO_3^-$ ). However, the observed low selenium adsorption values in the pH range of 1–10 showed that the ionic interaction was not effective in the adsorption process due to the absence of  $HSeO_3^-$  and  $SeO_3^{2-}$  or  $HSeO_4^-$  and  $SeO_4^{2-}$  species.

Selenite or selenate ions can be reduced to elemental selenium ( $Se^0$ ) by the thiourea dissolved in solution.<sup>31,32</sup> The standard reduction potentials of thiourea, selenite, and selenate are given in eqs. (5)–(8). In this study, the color of TUF resin changed from white into orange red, which is a characteristic color of reduced elemental selenium. It may be expressed that the adsorption mechanism is governed by chemical reduction from selenite or selenate to elemental selenium. When examined the effect of initial

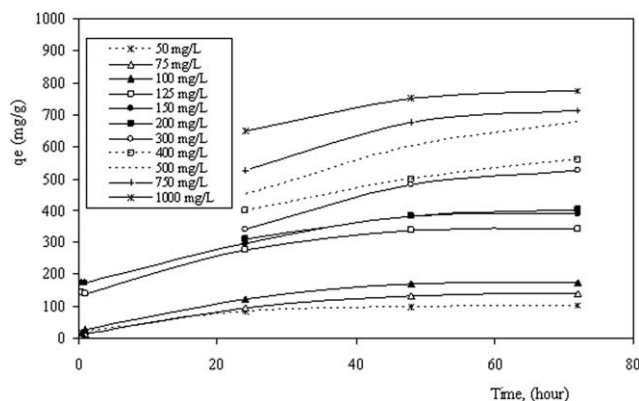
acidity on selenite or selenate adsorption, it can be seen that the both adsorptions require strong acidity. This may be expressed that the required strong acidity for the adsorptions is due to the acidity required in the reduction reactions [eqs. (7) and (8)]. Some researchers examined selenite or selenate adsorption by thio-functionalized adsorbents. Tanaka et al.<sup>33</sup> suggested selenotrisulfide formation ( $-S-Se-S-$ ) with bismuthiol-II functionality (yellow color) and Inam et al.<sup>10</sup> did elemental selenium formation with allylthiourea (red color).



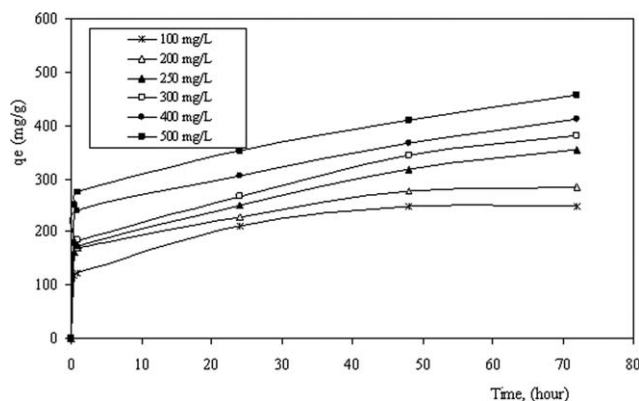
After the adsorption of selenium, the functional groups on the surface would be changed. It may be expressed that thiourea/thiol functional group on the resin surface could be oxidized to formamidine disulfide during the adsorption. Because selenite/selenate ions reduced to elemental selenium, a redox solution to oxidize elemental selenium and reduce the resin can be selected considering acidity and concentration. The selenium adsorption conditions found in this study can be used in the analytical pre-concentration studies including complete digestion process and in the separation of selenium from industrial intermediate solutions such as anode slimes and electronic wastes etc.

### Adsorption isotherms

To examine the adsorption isotherms, the adsorption studies were carried out at different initial concentrations of selenite (50–1000 mg L<sup>-1</sup>) and selenate ions (50–1000 mg L<sup>-1</sup>). Selenite and selenate



**Figure 7** Adsorption of selenite ions at different initial concentrations.



**Figure 8** Adsorption of selenate ions at different initial concentrations.

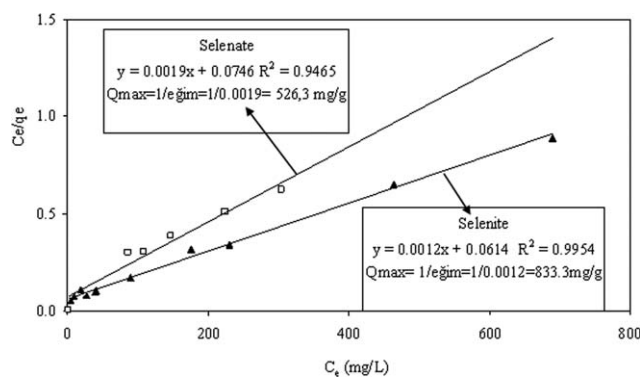


Figure 9 The Langmuir isotherms.

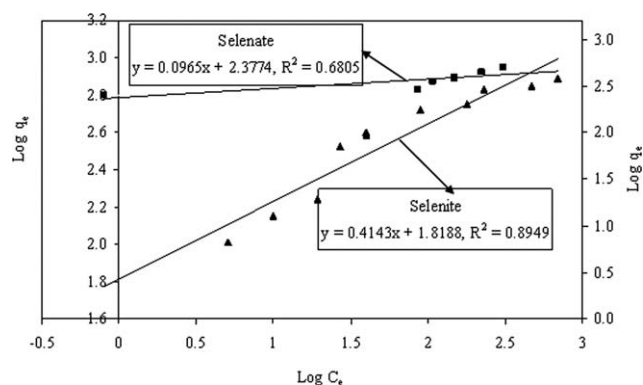


Figure 10 The Freundlich isotherms.

adsorption profiles obtained for 72 h contact time are given in Figures 7 and 8.

The adsorption data from the studies at different initial concentrations were analyzed using the Langmuir [Eq. (2)] and Freundlich isotherm equations [Eq. (3)].<sup>31,33</sup> Figures 9 and 10 show the Langmuir and Freundlich adsorption isotherms plotted  $C_e/q_e$  versus  $C_e$  and  $\ln q_e$  versus  $\ln C_e$  for the adsorption of selenite and selenate ions, respectively. The Langmuir and Freundlich coefficients were also calculated from the graphs and they are given in Table I. When examined the isotherms, it can be seen that the Langmuir isotherm has bigger regression coefficients ( $R^2$ ) with both selenite and selenate ions. Hence, it was found that both the adsorption data were better fitted to the Langmuir isotherm than the Freundlich. Selenite and selenate adsorption capacities of TUF resin were found as 833.3 and 526.3  $\text{mg g}^{-1}$  TUF resin, respectively. Moreover selenium adsorption capacities found by some researchers were listed in Table II. It was seen that TUF resin showed highest selenium adsorption capacity and a different adsorption mechanism from the other adsorbents in Table II. While many adsorbents in literature adsorb selenite/selenate ions via ion exchange mechanism at pH 1–8, TUF resin is via reduction mechanism in 3–5M HCl media. Initial acidity of selenium solutions is very effective in the adsorption. Selenium in strong acidic solutions, in which other constituents do not precipitate, can be separated and concentrated. However, selenium adsorption capacity of TUF resin will change with different acidities.

In addition the essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter or a separation factor,  $R_L$  [Eq. (9)].

$$R_L = \frac{1}{1 + bC_0} \quad (9)$$

where  $b$  is the Langmuir constant ( $\text{L mg}^{-1}$ ) and  $C_0$  is the initial concentration ( $\text{mg L}^{-1}$ ).  $R_L$  value indicates the type of isotherm, and the value between 0 and 1 indicates favorable adsorption. The  $R_L$  values in this study were found to be between 0 and 1 for all the concentrations of selenite and selenate.<sup>42</sup>

## CONCLUSIONS

TUF resin was synthesized and used in the adsorption of selenite and selenate ions. Some important results are summarized in following: Initial acidity of selenium solutions is very effective in the adsorption. The optimum acidities of 3M and 5M HCl were found in the adsorption of selenite and selenate ions, respectively. It was seen that strong acidity required for the adsorption of the both ions. The data obtained from the adsorption of both selenite and selenate ions were better fitted to the Langmuir isotherm than Freundlich. The adsorption capacities of 823.3  $\text{mg g}^{-1}$  TUF resin for selenite and 526.3  $\text{mg g}^{-1}$  TUF resin for selenate were achieved. The adsorption mechanisms for these ions were governed by the reduction to elemental selenium ( $\text{Se}^0$ ).

TABLE I  
Coefficients of the Langmuir and Freundlich Isotherms

|          | The Langmuir isotherm             |                            |        | The Freundlich isotherm      |         |        |
|----------|-----------------------------------|----------------------------|--------|------------------------------|---------|--------|
|          | $Q_{\max}$ ( $\text{mg g}^{-1}$ ) | $b$ ( $\text{L mg}^{-1}$ ) | $R^2$  | $k_F$ ( $\text{mg g}^{-1}$ ) | $n$     | $R^2$  |
| Selenite | 833.3                             | 0.0195                     | 0.9954 | 65.88                        | 2.41371 | 0.8949 |
| Selenate | 526.3                             | 0.0254                     | 0.9465 | 238.45                       | 10.36   | 0.6805 |

**TABLE II**  
**Selenium Adsorption Capacities of Some Adsorbents**

| Adsorbent  | Sorption capacity (mg g <sup>-1</sup> ) | pH                | Reference                      |
|--|---|-------------------|--------------------------------|
| Chelating resin (diethylenetriamine-polyacetic acid) | 30.02                                   | 4.0               | [34]                           |
| Green algae ( <i>Cladophora hutchinsiae</i> )        | 74.9                                    | 5.0               | [35]                           |
| Double hydroxides (Zn/Al, Mg/Al, Zn/Fe)              | 106.38–131.58                           | 5.0               | [36,37]                        |
| Iron and aluminium oxides                            | 2.4–32.7                                | 5.0               | [7]                            |
| Double hydroxides (Zn/Mg–Al)                         | 125.0–152.0                             | 5–10              | [38]                           |
| Rice husk (wet–dry sorbent)                          | 40.9–32.1                               | 1.5               | [39]                           |
| Aluminum oxide coated sand                           | 1.08                                    | 4.8               | [40]                           |
| Iron oxide coated sand                               | 1.34                                    | 4.5–6             | [41]                           |
| Ion-exchange resin (polyamine-type weakly basic)     | 134.2                                   | 3–12              | [5]                            |
| Thiourea–formaldehyde resin                          | Selenite: 833.3<br>Selenate: 526.3      | 3M HCl<br>5 M HCl | In this study<br>In this study |

It may be concluded that selenite and selenate ions can be separated effectively by TUF resin.

**References**

- Brigano, F. A.; Ruhstorfer, R. B.; Gottlieb, M.; Trickle, G.; Harrison, J. F.; Ver Strat, S. J.; Petty, B. L. Technical Application Bull; Selenium, Water Quality Association: USA, 2005.
- Erosa, M. S. D.; Holl, W. H.; Horst, J. React Funct Polym 2009, 69, 576.
- Lin, T. S. J Hazard Mater 2007, 149, 80.
- Zhang, N.; Lin, L. S.; Gang, D. C. Water Res 2008, 42, 3809.
- Nishimura, T.; Hashimoto, H.; Nakayama, M. Sep Sci Technol 2007, 42, 3155.
- Wasewar, K. L.; Prasad, B.; Gulipalli, S. Clean-Soil Air Water 2009, 37, 872.
- Chan, Y. T.; Kuan, W. H.; Chen, T. Y.; Wang, M. K. Water Res 2009, 43, 4412.
- Rovira, M.; Gimenez, J.; Martinez, M.; Martinez-Liado, X.; de Pablo, J.; Marti, V.; Duro, L. J Hazard Mater 2008, 150, 279.
- Sabarudin, A.; Oshita, K.; Oshima, M.; Motomizu, S. Anal Chim Acta 2005, 542, 207.
- İnam, R.; Caykara, T.; Ozcan S.; Yagmur, M. J Anal Chem 2005, 60, 1139.
- Kucukbay, F. Z.; Demir, M. Turk J Chem 2001, 25, 341.
- Itoh, K.; Nakayama, M.; Chikuma, M.; Tanaka, H. Fresen Z Anal Chem 1985, 321, 56.
- Depecker, G.; Branger, C.; Margaillan, A.; Pigot, T.; Blanc, S.; Robert-Peillard, F.; Coulomb, B.; Boudenne, J. L. React Funct Polym 2009, 69, 877.
- Khajeh, M.; Yamini, Y.; Ghasemi, E.; Fasihi, J.; Shamsipur, M. Anal Chim Acta 2007, 581, 208.
- Boult, K. A.; Cowper, M. M.; Heath, T. G.; Sato, H.; Shibutani, T.; Yui, M. J Contam Hydrol 1998, 35, 141.
- El-Shafey, E. I. J Environ Manag 2007, 84, 620.
- Sahin, F.; Volkan, M.; Howard A. G.; Ataman, O. Y. Talanta 2003, 60, 1003.
- Aydın, A.; Imamoglu, M.; Gulfen, M. J Appl Polym Sci 2008, 107, 1201.
- Yirikoglu, H.; Gülfen, M. Sep Sci Technol 2008, 43, 376.
- Birinci, E.; Gülfen M.; Aydın, A. O. Hydrometallurgy 2009, 95, 15.
- Ertan, E.; Gülfen, M. J Appl Polym Sci 2009, 111, 2798.
- Kırcı, S.; Gülfen, M.; Aydın, A. O. Sep Sci Technol 2009, 44, 1869.
- Çelik, Z.; Gülfen M.; Aydın, A. O. J Hazard Mater 2010, 174, 556.
- Hsieh, H. S.; Ganther, H. E. Biochemistry 1975, 14, 1632.
- Nalwa, H. S.; Vasudevan, P. Mater Res Bull 1983, 18, 897.
- Zuo, G. J.; Muhammed, M. React Polym 1995, 24, 165.
- Panahi, H. A.; Sharif, A. A. M.; Bigonah, M.; Moniri, E. Korean J Chem Eng 2009, 26, 1723.
- Ni, C.; Yi, C.; Feng, Z. J Appl Polym Sci 2001, 82, 3127.
- Sengil, I. A.; Özacar, M. J Hazard Mater 2009, 166, 1488.
- Hao, Z. X.; Wu, P. F.; Li, Z.; Luo, H.; Zhu, Z. R.; Lin, R. Acta Chim Sinica 2010, 68, 309.
- Qiu, J.; Wang, Q.; Ma, Y.; Yang, L.; Huang, B. Spectrochim Acta Part B 2006, 61, 803.
- Ullrey, D. E. Selenium in Nutrition, 2nd ed.; National Academy Press: Washington, 1983.
- Tanaka, H.; Nakagawa, T.; Okabayashi, Y.; Aoyama, H. Pure Appl Chem 1987, 59, 573.
- Suzuki, T. M.; Tanaka, D. A. P.; Tanco, M. A. L.; Kanesato, M.; Yokoyama, T. J Environ Monit 2000, 2, 550.
- Tuzen, M.; Sarı, A. Chem Eng J 2010, 158, 200.
- Namasivayam, C.; Prathap, K. Toxicol Environ Chem 2006, 88, 85.
- Mandal, S.; Mayadevi, S.; Kulkarni, B. D. Ind Eng Chem Res 2009, 48, 7893.
- You, Y.; Vance, G. F.; Zhao, H. Appl Clay Sci 2001, 20, 13.
- El-Shafey, E. I. J Hazard Mater 2007, 147, 546.
- Kuan, W.; Lo, S.; Wang, M. K.; Lin, C. Water Res 1998, 32, 915.
- Lo, S.; Chen, T. Chemosphere 1997, 45, 919.
- Akar, S. T.; Yetimoglu, Y.; Gedikbey, T. Desalination 2009, 244, 97.