



# Speciation and removal of selenium (IV, VI) from water and wastewaters based on dried activated sludge before determination by flame atomic absorption spectrometry

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## ABSTRACT

In recent decades, large amount of pollutants enters to the environment due to development of technology. Therefore, it is necessary to use ecofriendly sorbent to eliminate pollutants. In this research, 0.5 g of a dried activated sludge (DAS) was used for speciation selenium and removal of selenite [Se(IV)] from water and wastewater samples. The effect of operating parameters such as solution pH, the amount of bio-sorbent, contact time, temperature and initial concentration of selenium were studied by flame atomic absorption spectrometry (F-AAS). Kinetic data was adjusted to the Langmuir and Freundlich kinetic equations. The resulted showed that the Langmuir equation with a correlation coefficient of 0.9825 has the best match to tetravalent selenium biosorption on DAS. The FT-IR results showed that the biosorption mechanism of Se(IV) on DAS is due to functional groups on the DAS surface (Se(IV)... DAS). For reduction of soluble selenate [Se(VI), SeO<sub>4</sub><sup>2-</sup>] to selenite [Se(IV), SeO<sub>3</sub><sup>2-</sup>], the concentrated HCl was used at 70°C (30 min). So, the Se(VI) reduced to Se(IV) and total selenium (TSe) was determined and the Se (VI) was simply calculated by difference of TSe from Se(IV) content. The method was validated based on spiking samples in water and wastewater samples by F-AAS and using HG-AAS.

## 1. Introduction

Recently, the selenium studies are considered strongly because of the direct correlation between biological functions and the amount of selenium in the body [1, 2]. Selenium is an essential bioelement and has an important role in the proper biological functioning of many organisms [3, 4], although it becomes toxic when the concentration is more than 1.7 µg L<sup>-1</sup> [5]. Modern industrial processes such as the oil refining, the electrolytic copper refining, the

glass manufacturing, the agriculture and mining activities increase the selenium concentration in the environment matrixes [6-8]. Selenium is also used in thermal power stations, the solar panels, insecticides, semiconductors and rectifiers [9]. Two species of this element exist in aqueous systems contain Se(IV) and Se(VI) in the form of selenite (SeO<sub>3</sub><sup>2-</sup>) and selenate (SeO<sub>4</sub><sup>2-</sup>), respectively. Se(IV) is more toxic than Se(VI) [2, 10]. World Health Organization (WHO) proposed the permissible limit of selenium concentration in drinking water should be below 10 µg L<sup>-1</sup> [11-14]. Therefore, removal of selenium from wastewaters by an

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economic and effective methods is necessary. The most appropriate methods for removing selenium from contaminated water include catalytic reduction, chemical precipitation, electrochemical process, evaporation, floatation, ion exchange, membrane processes, biosorption and adsorption [2, 15]. Most of these techniques are expensive and improper for removal of selenium from aqueous samples. However, biosorption can be an effective and ecofriendly method for this purpose. Low cost and availability are two major factors for using biomass to remove the environmental pollutant [15, 16]. Biosorption of selenium by several sorbents such as seaweed, crustacean shell, peanut shell, rice barn, maize, wheat and dry yeast biomass is reported [17-20]. Recently the usage of DAS for removing selenium is extended [21, 22]. In addition, the different instrumental analysis was used for determination of selenium and other metals in different matrixes [23-27]. In this study, the removal of selenium by DAS from aqueous solutions were studied by F-AAS and validated by HG-AAS. The effect of pH, concentration, temperature and contact time was investigated. Kinetic models and thermodynamic parameters were determined.

## 2. Experimental

### 2.1. Chemicals

Sodium selenite ( $\text{Na}_2\text{SeO}_3$ ) with a purity of 98%, was purchased from Merck (India) and used as a source of Se(IV) ions in the aqueous samples for analytical purpose, sodium hydroxide (NaOH) with a purity of 98% was purchased from Merck (Darmstadt, Germany, <http://www.merck.com>), hydrochloric acid (HCl) with a purity of 37% was purchased from Merck (Darmstadt, Germany, <http://www.merck.com>), dried activated sludge was obtained from Kerman Zamzam refinery, Iran. The different concentration of Selenium was prepared by dilution of deionized water (DW) and ultrapure water was purchased from Millipore Company. The acetate and phosphate buffer was used to adjust the pH between 2.6–6.4 and 6.4–8.0, respectively.

### 2.2. Apparatus

Flame atomic absorption spectrometer (F-AAS, Varian spectra 220 model, Australia) with wavelength 196.0 nm; slit 1.0 nm; current 10 mA was used ( $10\text{-}200\text{ mg L}^{-1}$ ). The hydride generation atomic absorption spectrometer (HG-AAS,  $1\text{-}100\text{ }\mu\text{g L}^{-1}$ ) and electro thermal atomic absorption spectrometer (ET-AAS,  $15\text{-}400\text{ }\mu\text{g L}^{-1}$ ) were applied as ultra-trace analysis for Se (IV). The analytical pH meter (Benchtop meter inoLab pH 7110 model, WTW company, Germany), analytical balance (ALC model, Acculab company, America), magnetic hitted stirrer (IKA RH basic 2 model, IKA company, Germany), and centrifuge (EBA 20 model, Hettich company, Germany) were used for this study.

### 2.3. Preparation of dried activated sludge as a biosorbent

The activated sludge obtained from Zamzam company was suspended in a beaker containing 500 ml of deionized water on a magnetic stirrer for a day at  $25^\circ\text{C}$ . Let the suspension to precipitate. Then the upper liquid was decanted and the remaining suspension was centrifuged. The resulted sludge was washed with deionized water several times to be neutralized. The collected sample was dried in oven at  $80^\circ\text{C}$  for 36 h. The dried biomass was powdered and sieved with mesh No. 25.

### 2.4. Preparation of sample and selenium solutions

All glass or PCV tubes were cleaned with a 2M of  $\text{HNO}_3$  solution for at least one day and then washed for ten times with ultrapure water. As low concentrations of Se(IV) and Se(VI) in water samples, the ion contamination effected on results of analysis, so, we used ultra-trace reagents for sampling processes. Sodium selenite was used to prepare a selenium stock solution with concentration of 1000 ppm ( $\text{mg L}^{-1}$ ). The desired solutions obtained of diluting stock solution. The diluted solutions with concentrations in the range 2-9.5 ppm were used for calibration.

### 2.5. SPE procedure and Batch experiments

Biosorption of Se(IV) by DAS was achieved in optimized experimental conditions such as pH, contact time, amount of biosorbent and temperature. The experiments were carried out in 100 ml Erlenmeyer flasks. Experiments were achieved with pH 2 to 9, contact time 2 to 35 minute, amount of biosorbent 0.5 to 3 g, temperature 10 to 40°C and selenium concentration 10 to 140 mg L<sup>-1</sup>. To adjust required pH of aqueous solution, HCl 0.2 M and NaOH 0.1 M were added. Finally, the kinetic models and isotherms were studied. The absorption capacity of DAS for Se(IV) was obtained 124.2 mg g<sup>-1</sup> by 140 mg L<sup>-1</sup> selenium concentration and 1 g of DAS.

By solid phase extraction procedure (SPE), 0.5 g of biosorbent of DAS added to 100 mL of water and wastewater solution and shaken for 15 min at pH=5. After adsorption, based on chemical bonding between DAS with Se(IV) [ $-\text{NH}^+:-\text{NH}_2^+ \text{---} \text{SeO}_3^{2-}$ ] the solid phase separated/collected in bottom of tube and removed upper liquid phase of water/wastewater. Finally, the Se(IV) determined with F-AAS after desorption Se(IV) from DAS by adding of HNO<sub>3</sub> (0.5 M, 5 mL). The concentration Se(IV) validated by HG-AAS after dilution with DW. For reduction of Se(VI) to Se(IV) the concentrated HCl (50%) was used at 70°C for 30 min. After reduction, the total selenium (TSe) was determined and the Se (VI) was simply calculated by difference of TSe

from Se(IV) content. The linear range(LR), LOD, perconcentration factor (PF) and recovery were obtained 0.5-10.2 mg L<sup>-1</sup>, 0.12 mg L<sup>-1</sup> and 19.8, and 96.5%, respectively

## 3. Results and discussion

### 3.1. FT-IR analysis

Fourier Transform Infrared (FT-IR) spectrum of DAS was recorded (Fig. 1) to gain the information about surface functional group. As seen in this spectrum, the stretching vibrations of hydroxyl group (-OH) on DAS surface gives the broad and strong band at 3443 cm<sup>-1</sup>. The weak peaks at about 2300 cm<sup>-1</sup> show the stretching vibrations of -NH, -NH<sup>+</sup>, -NH<sub>2</sub><sup>+</sup> functional groups of DAS. The band peak at 1646 cm<sup>-1</sup> refers to stretching vibrations of -C=O group. The stretching vibrations of -C-O group appears at 1088 cm<sup>-1</sup>. The band peak at 876 cm<sup>-1</sup> is concerned to carbonate group.

### 3.2. Effect of pH

The effect of pH on the biosorption of Se (IV) by DAS were studied at pH in the range of 2 to 11 for SPE. First, 100 mL selenium solution with concentration 2-9.5 ppm (mg L<sup>-1</sup>) and 0.5 g DAS at temperature of 25°C (15 min) was used. The results were shown in Figure 2. Three species of selenium in these aqueous solutions include selenite (SeO<sub>3</sub><sup>2-</sup>), biselenite (HSeO<sub>3</sub><sup>-</sup>) and selenious

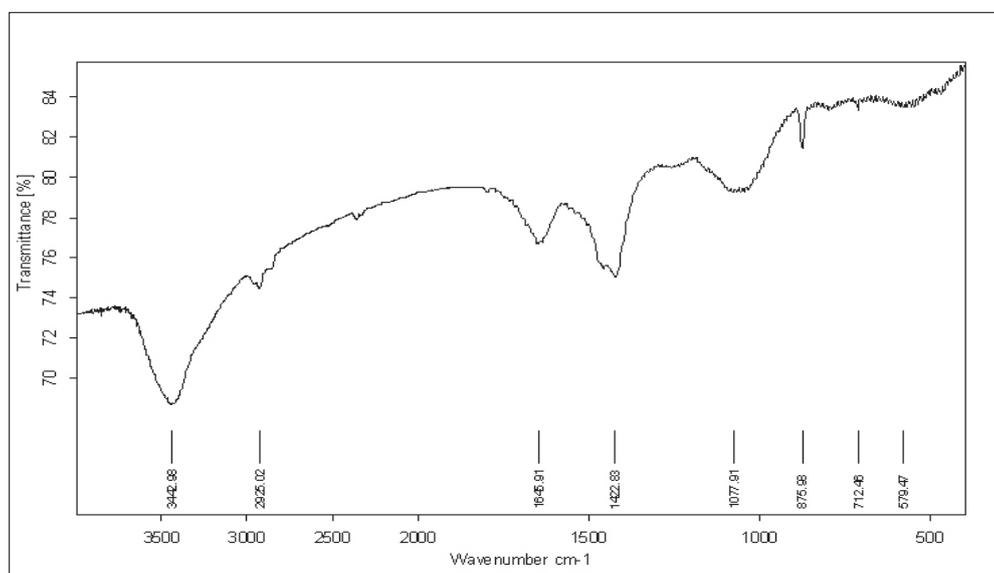


Fig.1. Fourier Transform Infrared (FT-IR) spectrum of DAS

acid ( $H_2SeO_3$ ) [28, 29]. The selenious acid prevails when pH decreases below 3.5, biselenite prevails when pH is in the range of 3.5 to 9 [2]. The lowest selenium biosorption at pH less than 3.5 is because of inability of neutral selenious acid to interact electrostatically with the DAS. In this work, the highest chemical biosorption of Se(IV) based on DAS was achieved with high recovery more than 95% for batch system and SPE procedure at pH=5.

### 3.3. Effect of contact time

The effect of contact time, as the next parameter was investigated in the range of 2 to 35 minute at pH=5. As observed in Figure 3, the most proper contact time for selenium biosorption was obtained 15 minutes for SPE. After this contact time, equilibrium occurred. The best time for batch system was obtained 30 min (2 g) for selenium concentration 10 to 140 mg L<sup>-1</sup>.

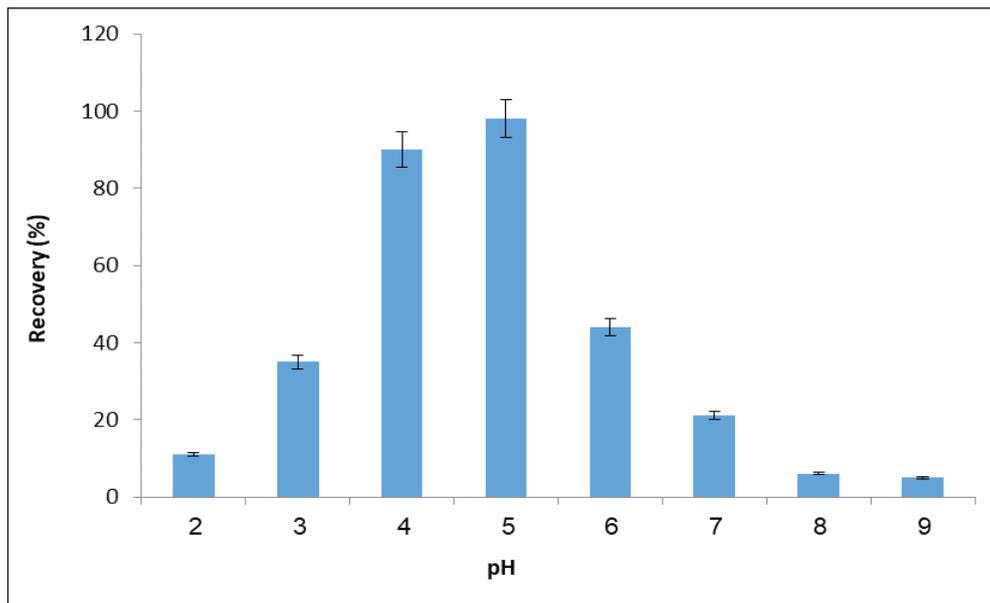


Fig.2. The effect of pH on Se(IV) removal from water and wastewater by DAS

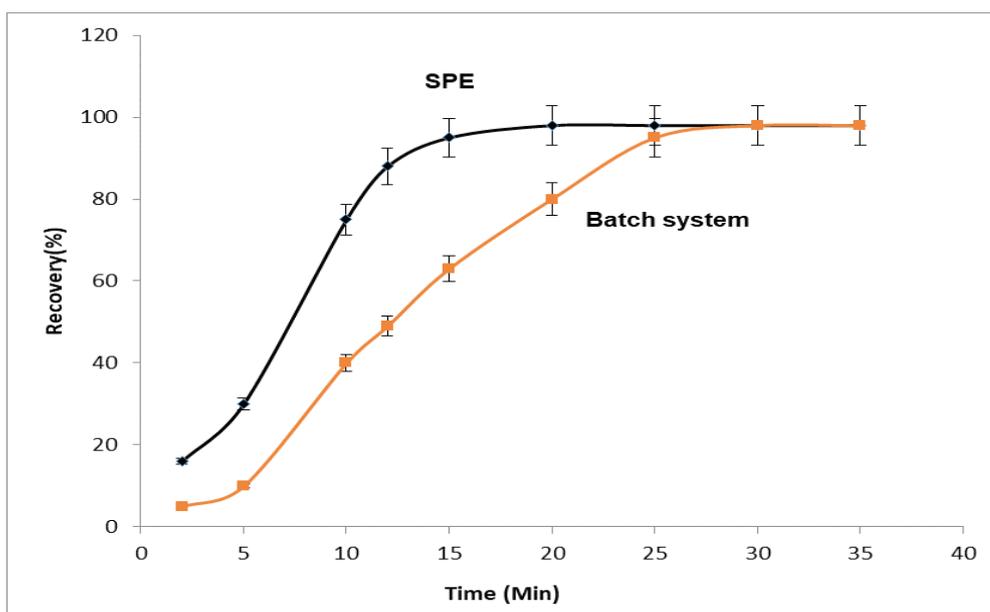


Fig.3. The effect of contact time for removal of Se(IV) from water and wastewater by DAS

### 3.4. Effect of amount of biosorbent

The effect of amount of biosorbent was investigated under optimized conditions (pH=5 and contact time: 30 min.). As shown in Figure 4, the selenium biosorption increased slowly with the DAS amount up to 2 g for batch system. The DAS surface becomes saturated with the extra Se(IV) ions in

optimized amount of DAS. Therefore, a number of Se(IV) ions remain in solution and biosorption yield decreased. At higher amount of DAS, biosorption yield is almost unchanged. Because most of Se(IV) ions interact with DAS surface. For SPE, the 0.5 g of DAS is favorite mass for removal of Se (IV) in water samples with high recovery more than 95%.

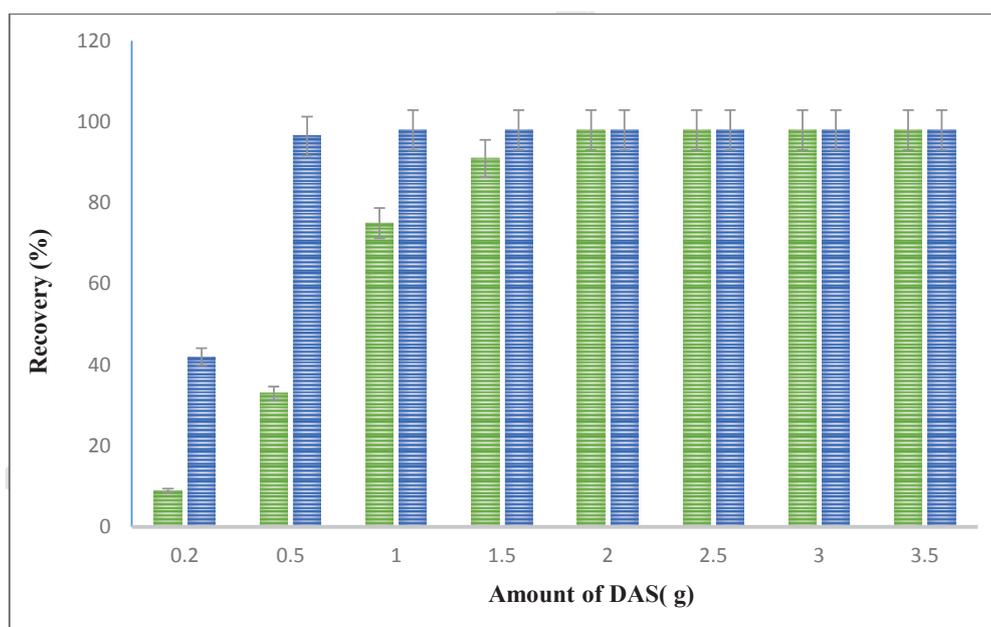


Fig. 4. The effect of biosorbent amount on Se(IV) removal in batch system (green) and SPE procedure(blue) in water and wastewater by DAS

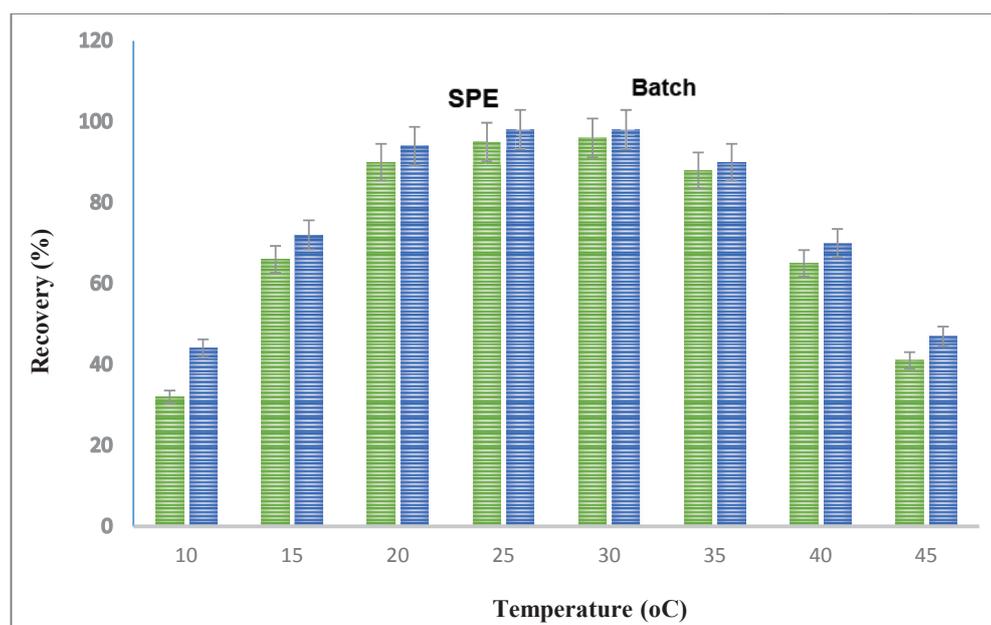


Fig. 5. The effect of temperature on Se(IV) removal in batch system (blue) and SPE procedure(green)from water and wastewater samples by DAS

### 3.5. Effect of temperature

The effect of temperature on selenium biosorption was investigated between 10-45°C in optimized condition. The results showed us, the optimum temperature was achieved 30°C in optimized condition (pH, contact time and amount of biosorbent DAS were 5, 30 minute and 2 g, respectively). Due to Figure 5, by increasing temperature, the selenium biosorption decreased. It indicated the biosorption by DAS is an exothermic reaction. The best temperature for SPE procedure for DAS was 25-30°C.

### 3.6. Effect of initial concentration of selenium

Effect of initial concentration of selenium in the range of 20-250 ppm was investigated for absorption capacity. The results indicated that increasing selenium concentration caused to more absorb of the selenium on DAS and decreased the selenium concentration in the solution. The number of sites on DAS were interacted with Se(IV) ions and can be saturated at high concentrations of selenium ions. According to obtained results, the adsorption capacity of Se(IV) ions on DAS increased up to 124.2 mg g<sup>-1</sup> [AC; mg per gram]. The results have presented in Figure 6.

### 3.7. Kinetic isotherms for Se(IV) and Se(VI)

The most popular isotherms are Langmuir [21,30] and Freundlich [21, 31] models. The Langmuir model describes monolayer adsorption, however Freundlich model show heterogeneous surface. The linear form of Langmuir model is given by following equation I:

$$\frac{C_e}{q_e} = \frac{1}{(K_L q_m)} + \frac{C_e}{q_m} \quad (\text{Eq. I})$$

where  $C_e$  (mg L<sup>-1</sup>) is the equilibrium concentration of the solution,  $q_e$  (mg g<sup>-1</sup>) is the amount of metal adsorbed per specific amount of adsorbent,  $q_m$  (mg g<sup>-1</sup>) is the maximum amount of metal ions required to form monolayer,  $K$  (L mg<sup>-1</sup>) is the adsorption equilibrium constant.

The linear form of Freundlich model is given by following equation II:

$$\log(q_e) = \log(K_F) + \left(\frac{1}{n}\right) \log C_e \quad (\text{Eq. II})$$

where  $n$  is the adsorption intensity and  $K_F$  is the adsorption capacity.

The amount of Se(VI) adsorbed on DAS at equilibrium ( $q_e$ , mg g<sup>-1</sup>) was calculated by Equation (III):

$$q_e = (C_0 - C_e) \times V/m \quad (\text{Eq. III})$$

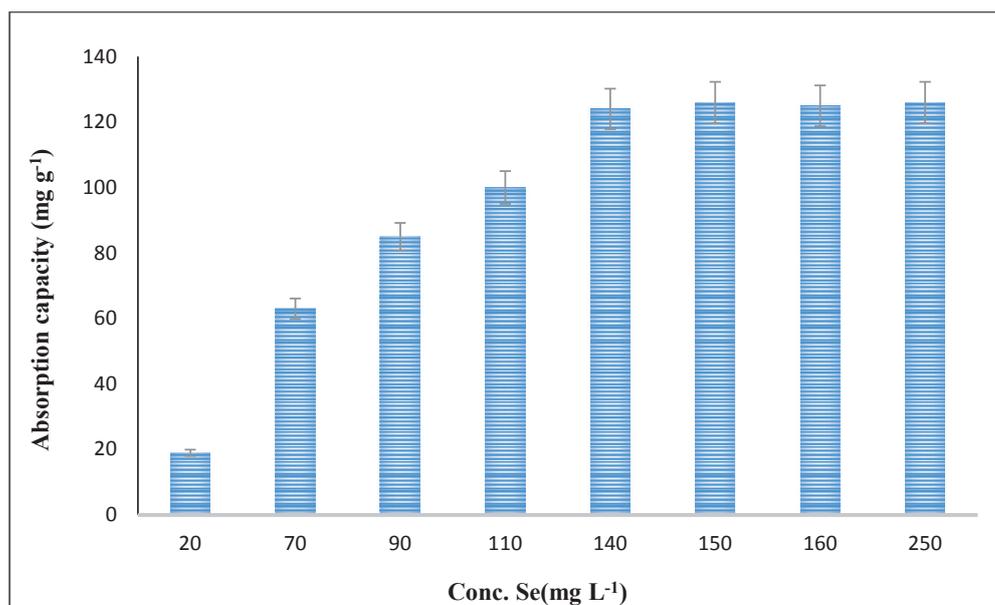


Fig. 6. The effect of initial concentration of Se(IV) ions on absorption capacity of DAS in water and wastewater samples

where  $C_0$  and  $C_e$  ( $\text{mg L}^{-1}$ ) are the initial and equilibrium Se(VI) concentrations, respectively,  $V$  (L) is the volume of the solution and  $m$  (g) is the mass of the adsorbent. ( $C_0 = 10\text{-}250 \text{ mg L}^{-1}$ ,  $C_0 = 250 \text{ mg L}^{-1}$  and  $C_e = 190 \text{ mg L}^{-1}$ ,  $V = 0.1 \text{ L}$ ,  $m = 0.05 \text{ g}$ ). So the  $q_e$ ,  $q_{\text{max}}$  and  $C_e/q_e$  was obtained as  $120 \text{ mg g}^{-1}$ ,  $120 \text{ mg g}^{-1}$  and  $2.08$ , respectively. As different concentrations, the  $C_e/q_e$  were calculated based on Langmuir model between  $0.02\text{-}2.08$ .

Linear Langmuir equation was considered to gain

isotherm (Fig. 7). The Se(VI) in solutions with different initial concentrations ( $C_0 = 10\text{-}250 \text{ mg L}^{-1}$ ) were used. Langmuir constants,  $K_L$  and  $q_m$  were calculated from the slope and intercept of the plot  $C_e/q_e$  versus  $C_e$ .

As Figure 8, the linear Freundlich isotherm of Se(IV) and Se(VI) is another kinetic model for DAS. Freundlich isotherm parameters,  $K_F$  and  $1/n$  were calculated from the slope and intercept of linear plot.

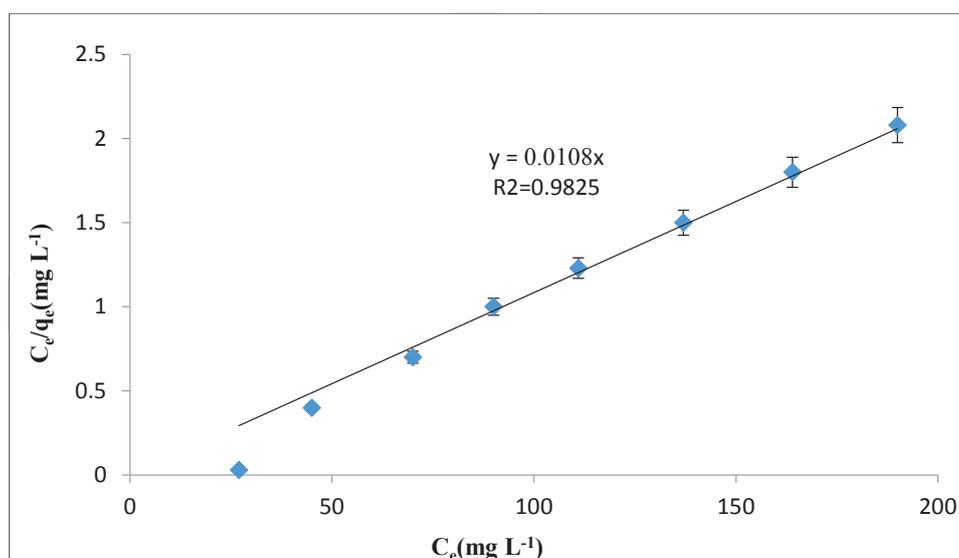


Fig. 7. Linear Langmuir equation for selenium removal by DAS biosorbents from water and wastewater samples

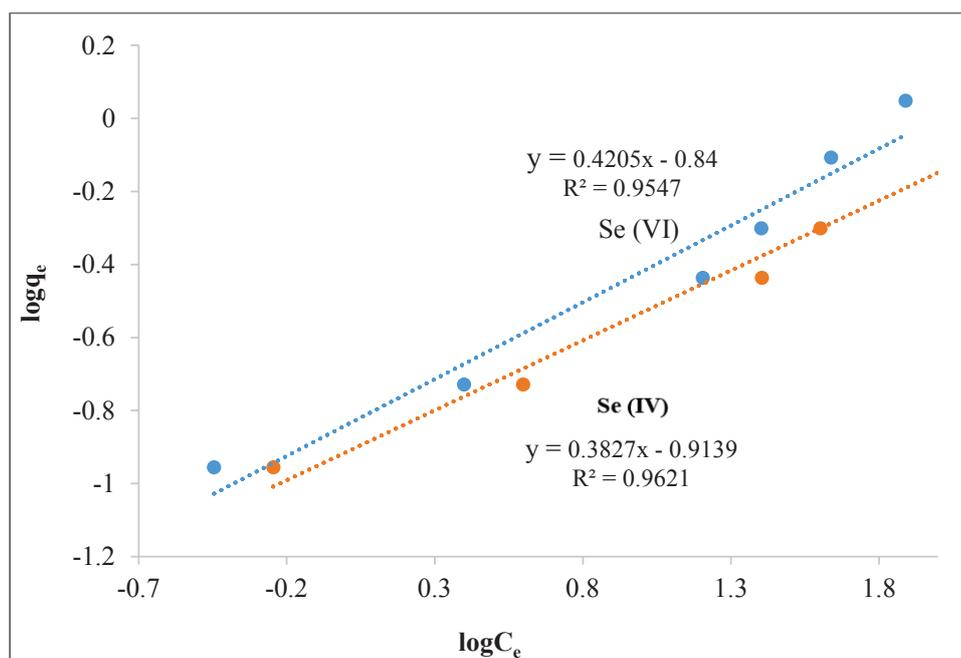


Fig. 8. Linear Freundlich isotherm for selenium removal by DAS biosorbents from water and wastewater samples

### 3.8. Validation of SPE procedure

The selenium was removed and determined in 100 mL of water and wastewater samples based on DAS with SPE procedure at pH=5. The mean concentration of Se(IV) more than Se(VI) in water samples. The spiked water was used to demonstrate the reliability of the method for determination of Se(IV) and Se(VI) in water samples by SPE procedure. The recovery of spiked samples showed

a satisfactory result for determination of Se(IV) and Se(VI) in water samples (Table 1). Moreover, the real water samples were analyzed with HG-AAS/ET-AAS and used for validation of results of SPE/F-AAS procedure. The results showed, the favorite efficiency and reliability of proposed method for determination selenium in water and wastewater sample which was compared to ET-AAS and HG-AAS (Table 2)

**Table 1.** Validation of SPE procedure based on DAS for speciation selenium (VI, IV) in water and wastewater samples (mg L<sup>-1</sup>; n=8)

Sample	Added Se(IV)	Added Se(VI)	*Found Se(IV)	*Found Se(VI)	Total TSe	Recovery Se(IV) (%)	Recovery Se(VI) (%)
Wastewater 1	-----	-----	4.45± 0.19	1.23± 0.05	5.68 ± 0.24	-----	-----
	4.0	0.5	8.29 ± 0.37	1.75 ± 0.07	10.04± 0.45	96.0	104
Wastewater 2	-----	-----	3.86± 0.18	0.56 ± 0.03	4.42 ± 0.22	-----	-----
	4.0	0.5	7.81 ± 0.35	1.03 ± 0.05	8.84 ± 0.42	98.8	94.7
Wastewater 3	-----	-----	1.95 ± 0.14	1.47± 0.08	3.42 ± 0.15	-----	-----
	2.0	1.5	3.98 ± 0.19	2.95 ± 0.14	6.93 ± 0.34	101.5	98.6
River	-----	-----	ND	ND	ND	-----	-----
	2.0	2.0	1.97 ± 0.11	2.07 ± 4.4	4.04 ± 0.21	94.9	103.5

\* $\bar{x} \pm ts / \sqrt{n}$  at 95% confidence (n=8)

Well water prepared from Varamin agricultural

Wastewater 1 prepared from drug company

Wastewater 2 prepared from petrochemical factory

Wastewater 3 prepared from paint factory

River water prepared from Karaj

**Table 2.** Comparing of proposed procedure for selenium determination by F-AAS/DAS with HG-AAS and ET-AAS

Sample	F-AAS/DAS(mg L <sup>-1</sup> )	ET-AAS(µg L <sup>-1</sup> )*	*HG-AAS(µg L <sup>-1</sup> )
Wastewater*	0.55 ± 0.25	ND	5.36 ± 0.52
Water	ND	41.3 ± 13.81	40.9± 13.81

$\bar{x} \pm ts / \sqrt{n}$  at 95% confidence (n=5)

\*Wastewater 1 prepared from drug company, 1 mL of sample diluted with DW up to 100 (1:100)

#### 4. Conclusions

In this study, the results showed tetravalent selenium ions ( $\text{Se}_{\text{IV}}$ ) biosorption were successfully achieved by DAS from contaminated aqueous solutions. The maximum removal of  $\text{Se}(\text{IV})$  ions was 96% at optimized experimental conditions by SPE/F-AAS. The interaction between  $\text{Se}(\text{IV})$  ions and functional groups of DAS surface was exothermic. The experimental data were fitted to Freundlich isotherm. Also the speciation  $\text{Se}(\text{IV})$  and  $\text{Se}(\text{VI})$  ions determined based on DAS by SPE procedure for 0.5 g of DAS at  $\text{pH}=5$ . The method was validated by ET-AAS and HG-AAS. The absorption capacities for  $\text{Se}(\text{IV})$  and  $\text{Se}(\text{VI})$  ions with DAS were achieved  $124.2 \text{ mg g}^{-1}$  and  $121.8 \text{ mg g}^{-1}$ , respectively.

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