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Selenite Removal from Water †

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Abstract: The present study aims at comparing the two most promising water treatment technologies for selenium removal. A techno-economical comparison of Se(IV) uptake between the laboratory synthesized iron oxy hydroxide (FeOOH/2.5) with the highest positive surface density of 3.25 mmol [OH$^-$]/g and adsorption capacity 4.3 µg Se(IV)/mg FeOOH/2.5 at pH 7, and coagulation/precipitation with the use of Fe(III) presenting an uptake capacity 3.2 µg Se(IV)/mg Fe was attempted based on the laboratory scale results. The evaluation showed that coagulation/precipitation treatment appears to be economically advantageous in comparison to adsorption process that was applied in Rapid Small Scale Column Tests (RSSCTs) with the FeOOH/2.5. It must be pointed out that for selection of the optimum removal method, other criteria should also be considered, such as post treatment requirements, water flow, labor cost, and maintenance requirements.

Keywords: Se(IV); adsorption; coagulation/precipitation; iron oxy-hydroxides; Fe-based coagulants; cost comparison

1. Introduction

Several works of research have pointed out that though selenium is a micronutrient of vital importance for human growth and reproducibility, it bears numerous health hazards when bioaccumulated in the human body [1]. Unfortunately, there is a narrow range between daily necessary selenium uptake and intake quantities that result, in some cases, to fatal toxicity [2]. Although selenium is a micronutrient, when surpassing homeostatic levels, it becomes toxic for living organisms [3]. Selenate (SeO$_4^-$) predominates in oxidizing conditions and is very soluble with low adsorption and precipitation capacities, while selenite (SeO$_3^{2-}$) is present in moderate redox potential ranges and neutral pH environments [4]. Increasing reports on water pollution by selenium verify that excess consumption leads to the potential of bioaccumulation to humans and causes adverse health effects, such as selenosis and cancer, which has forced the European Commission to set a Drinking Water Regulation Limit (DWRL) for selenium at 10 µg/L [5,6].

Both Se(IV) and Se(VI) are toxic, with the first species being more toxic than the second one. The dominant species of selenium in water depends on physicochemical factors, including redox conditions and pH. SeO$_3^{2-}$ (Se(IV)) is presented as the dominant species, since moderate redox potential ranges and neutral pH environments are mostly met in nature [7,8]. Research on selenium removal is ongoing, with a variety of treatment methods being examined that include: chemical reduction techniques either with nanoparticles such as zero valent iron [9] and inorganic sulfur reductants such as Na$_2$S and Na$_2$S$_2$O$_4$ [10,11]; co-precipitation with barite during the crystallization

phase [12]; coagulation-flocculation with Fe/Al based inorganic coagulants [13]; adsorption with inorganic adsorbents such as natural or synthesized iron-based adsorbents [14,15], apatites [16], layered double hydroxides [17], activated carbon [18], graphene oxide [19], and organic-based adsorbents such as chitosan [20] and conjugate adsorbents [21,22]; ion-exchange with resins [23]; membrane technologies [24]; bioremediation with thauera selenatis [25]; and phytoremediation using ashydrilla, duckweed, swamp lily, cattail and phragmites [26]. In order to apply the optimum water treatment process for selenium removal—apart from the removal effectiveness criteria such as the removal capacity at C_e = 10 µg/L (Q_{10} value), maintaining (not modification) the physicochemical characteristics of the water, and estimation of treatment cost—the water flow rate and specific requirements of treatment process should be also considered.

The majority of selenium removal treatment technologies are suitable for wastewater treatment rather than treatment of potable water. Research focuses on acidic conditions with high initial selenium concentrations that do not correspond to the physicochemical characteristics of natural waters. Acidic conditions and membrane processes lead to the deterioration of the physicochemical characteristics of the treated water. Among the water treatment processes, the most promising methods are considered to be the adsorption and coagulation/precipitation, because they fulfil the above mentioned criteria of processes evaluation along with economic benefits.

This study aims at the evaluation of Se(IV) removal from a techno–economic point of view by comparing the optimum uptake capacity shown by adsorption onto iron oxy hydroxides (FeOOH/2.5) and by coagulation/precipitation with Fe(III). These two treatment technologies take advantage of the Se(IV) affinity to Fe(III). Conditions that simulate natural water matrix, pH 7 and initial concentration of 100 µg Se(IV)/L were used at the laboratory experiments. The techno economic evaluation was based on the removal efficiency that was determined according to the uptake capacity at a residual concentration equal to DWRL of 10 µg/L—henceforth abbreviated as Q_{10}.

2. Materials and Methods

2.1. Water Characteristics

For both the adsorption and coagulation experiments, tap water (Table 1) of the city of Thessaloniki, Greece, was used after chlorine removal by filtering through a fixed bed of activated carbon. Water samples were spiked daily with Se(IV) and were used in the experiments after at least 24 h.

Table 1. Main (yearly) physicochemical characteristics of Thessaloniki tap water.

Parameter	Value
pH	7.4 ± 0.1
Conductivity (µS/cm)	590 ± 30
Na^+ (mg/L)	35 ± 5
Ca^{2+} (mg/L)	80 ± 10
Fe (mg/L)	<0.02
Mg^{2+} (mg/L)	24 ± 3
HCO_3^- (mg/L)	342 ± 20
NO_3^- (mg/L)	9 ± 3
SO_4^{2-} (mg/L)	10 ± 4
Cl^- (mg/L)	15 ± 5
Mn (mg/L)	<0.005
TOC (mg/L)	0.5 ± 0.2

2.2. Reagents and Adsorbents

The 10 mg/L stock solutions of Se(IV) were prepared by the dissolution of analytical grade Na_2SeO_3. Then, 12 g of 12.5% *w/w* $FeClSO_4$ solution was used to prepare a stock solution of 1500 mg

Fe(III)/L by dilution in 1 L distilled water. The pH of the stock solution was adjusted to 1–1.5 by the addition of 6 M HCl. The Fe concentrations (1500 ± 50 mg/L) were verified by flame atomic absorption spectrophotometry. The FeOOH adsorbents evaluated were laboratory synthesized following the procedure of Tresintsi et al., 2012, by the oxidation-hydrolysis of $FeSO_4 \cdot H_2O$ at pH values 2.5 [27]. The main physicochemical characteristics of the qualified adsorbents [14] are shown in Table 2.

Table 2. Main physicochemical characteristics of laboratory synthesized FeOOH/2.5.

Synthesis Parameters			Fe, wt. %	Surface Area, m²/g	IEP [1]	ZPC [2]	PSCD [3] mmol [OH⁻]/g
Materials	pH	ORP (mV)					
$FeSO_4/H_2O_2$	2.5	600	44.8	48	6.9	2.7	3.25

[1] Isoelectric point. [2] Point of zero charge. [3] Positive surface charge density.

2.3. Coagulation Tests

The treatment tests were performed on a Wisestir JT-M6C jar tester with six paddle stirrers at 20 ± 1 °C. The water pH was adjusted to 7 via the addition of either 0.1 M HCl or 0.1 M NaOH. A 1500 mL water sample was transferred into a 2000 mL glass beaker. Under initial rapid stirring at 230 rpm, the predetermined coagulant dose ranging between 1 and 30 mg/L was added. After 2 min of rapid mixing, the stirring speed was reduced to 80 rpm and the solution was stirred continuously for 60 min. A 100 mL sample was collected, filtered through a 0.45 μm membrane filter and acidified at pH ≤ 2 to determine the residual selenium concentration.

2.4. Adsorption Tests

For the evaluation of the adsorbent rapid small-scale column tests (RSSCTs) were applied in glass columns of 1.1 cm diameter and 50 cm height with polytetrafluoroethylene (PTFE) valves and caps, and a glass frit at the base of each column. The columns were filled with FeOOH/2.5 adsorbent of particle size 0.25–0.50 mm to the height of 23.6 cm and were fed from the top with 100 μg Se(IV)/L solution in tap water of Thessaloniki at pH 7 ± 0.1 via a dosing pump. Effluent samples were collected periodically and analyzed for residual selenium concentration. The laboratory experiment simulates full-scale processes and was designed to achieve an Empty Bed Contact Time (EBCT) of 3–4 min at 20 °C which corresponds to 5–6.5 min of EBCT of the respective large scale column (Table 3).

Table 3. Experimental conditions of RSSCTs for evaluation of FeOOH/2.5 adsorption capacity.

Parameter	FeOOH/2.5
EBCT small scale, min	4.3
Equivalent EBCT of large scale, min	6.5
Hydraulic loading rate, m/h	1.2
Media height (L), cm	23.6
Particle size range, mm	0.25–0.5
Geometric mean of particles (d_P), mm	0.35
L/d_P	67.4
Column media diameter (D), cm	1.1
D/d_P	31
Column cross sectional area, cm²	0.95
Media mass, g	12.2
Bed volume, mL	22.4
Bed Volume per hour	22.3
Flow rate, L/h	0.31
Backwash flowrate, L/h	0.8
$R_e \cdot S_c$	~2000
pH	7
Temperature °C	20 ± 1

2.5. Analytical Procedure

Initial and residual selenium concentrations were determined by graphite atomic absorption spectrophotometry using a Perkin-Elmer Analyst 800 instrument. The method's detection limit for selenium was 1 µg Se/L.

3. Results and Discussion

3.1. Coagulation Tests

The experimental results (Figure 1) for Se(IV) coagulation/precipitation by Fe(III) at pH 7 delivered a Q_{10} value of 3.2 µg Se(IV)/mg Fe(III) with the data best fitted in a BET adsorption model (Table 4) that indicated the Se(IV) removal by a physisorption process [28]. In order to estimate the cost of treatment, the Fe(III) dose required for the removal of Se(IV) from natural water at an initial concentration of 100 µg Se(IV)/L and pH 7 can be calculated as follows:

$$\text{Fe(III) dose} = [(100 \times 10 \text{ µg Se(IV)/L})/[3.2 \text{ µg Se(IV)/mg Fe(III)}] = 28.1 \text{ mg Fe(III)/L} \quad (1)$$

Since the current commercial cost of Fe(III) coagulants in Greece is 1.5 ± 0.1 EUR/kg Fe(III), the cost of the reagent required for the removal of 1 kg Se(IV) and treatment 10^3 m^3 using FeClSO$_4$ solution at pH 7 can be calculated as follows:

Fe(III) consumption for removal 1 kg Se(IV):

$$[1 \text{ kg Se(IV)}/3.2 \text{ µg Se(IV)/mg Fe(III)}] = [1000 \text{ g Se(IV)}/3.2 \text{ g Se(IV)/kg Fe(III)}] = \\ 312.5 \text{ kg Fe(III)/kg Se(IV)} \quad (2)$$

$$\text{Reagent cost} = [312.5 \text{ kg Fe(III)/kg Se(IV)}] \times [1.5 \pm 0.1 \text{ EUR/kg Fe(III)}] = \\ 469 \pm 32 \text{ EUR/kg Se(IV)} \quad (3)$$

Fe(III) consumption for treatment 10^3 m^3:

$$[10^3 \text{ m}^3 \times (100 - 10) \text{ mg Se(IV)/m}^3]/[3.2 \times 10^3 \text{ mg Se(IV)/kg Fe(III)}] = \\ 28.1 \text{ kg Fe(III)}/10^3 \text{ m}^3 \quad (4)$$

$$\text{Reagent cost}/10^3 \text{ m}^3 = [28.1 \text{ kg Fe(III)}/10^3 \text{ m}^3] \times [1.5 \pm 0.1 \text{ EUR/kg Fe(III)}] = \\ 42.1 \pm 2.8 \text{ EUR}/10^3 \text{ m}^3 \quad (5)$$
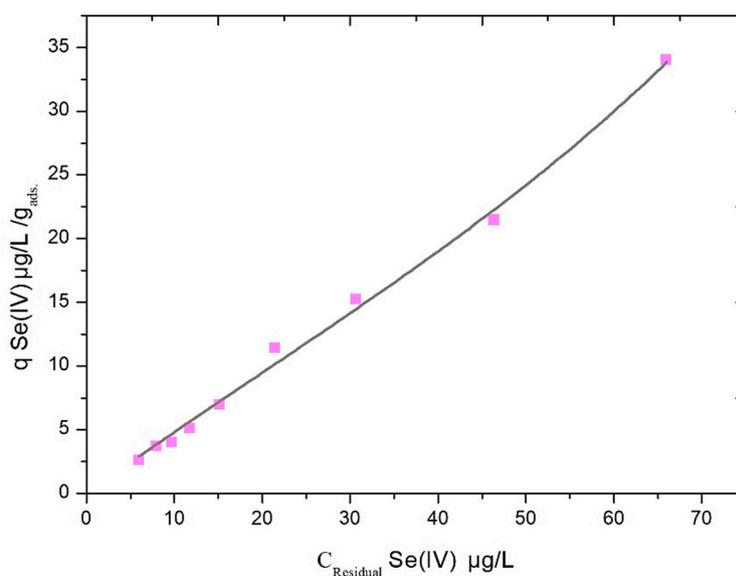

Figure 1. Se(IV) adsorption isotherm by Fe(III) coagulant. Experimental conditions: pH 7, Fe(III) dose range 1–15 mg/L, initial Se(IV) concentration range 25–100 µg/L.

Table 4. BET fitting parameters for Se(IV) adsorption isotherms with Fe(III) (according to the equation: $Q = aC/(1 + bC + dC^2)$).

Coagulant	pH	A	b	d	R^2	Q_{10} μg Se(IV)/mg Fe	Reagent Cost, EUR/kg Se(IV)
Fe^{3+}-FeClSO$_4$	7	0.2598	−0.0174	−0.0002	0.987	3.2	469 ± 32

Energy and labor costs of the treatment process do not depend on initial Se(IV) concentrations, but rather the water quantity and energy/labor prices of each individual country/state. An approximation of the energy and labor cost based on current Greek market prices is estimated to be 50 ± 20 EUR/10^3 m^3 treated water.

3.2. Adsorption Tests

According to Kalaitzidou et al. 2019, the implementation of the RSSCTs breakthrough curve for an initial concentration of 100 μg Se(IV)/L resulted in a Q_{10} value of 4.3 μg Se(IV)/mg FeOOH/2.5 [14]. The commercial cost of adsorbents is estimated to 8 EUR/kg. The estimated cost of adsorbents according to adsorption capacities estimated by the RSSCTs (Figure 2), which simulate the full-scale adsorption process, for Se(IV) removal from natural water at an initial concentration of 100 μg Se(IV)/L and pH 7 were calculated as follows:

FeOOH/2.5 consumption for removal 1 kg Se(IV):

$$[1 \text{ kg Se (IV)}/(4.3 \text{ μg Se(IV)/mg FeOOH/2.5})] = [1000 \text{ g Se(IV)}/(4.3 \text{ g Se(IV)/kg FeOOH/2.5})] = 232.6 \text{ kg FeOOH/2.5/kg Se(IV)} \tag{6}$$

Cost of FeOOH/2.5 adsorbent:

$$\text{Adsorbent cost} = [232.6 \text{ kg FeOOH/2.5/kg Se(IV)}] \times [8.0 \text{ EUR/kg FeOOH/2.5}] = 1860.8 \text{ EUR/kg Se(IV)} \tag{7}$$

Furthermore, the adsorbent cost, e.g., for treatment 10^3 m^3: natural water, with an initial concentration of 100 μg/L at pH 7.0 ± 0.1 is:

$$\text{Spent FeOOH/2.5}/10^3 \text{ m}^3 = [10^3 \text{ m}^3 \times (100 - 10) \text{ mg Se(IV)/m}^3]/[4.3 \times 10^3 \text{ mg Se(IV)/kg FeOOH/2.5}] = 20.9 \text{ kg FeOOH/2.5} \tag{8}$$

$$\text{Adsorbent cost} = (20.9 \text{ kg FeOOH/2.5}/10^3 \text{ m}^3) \times (8.0 \text{ EUR/kg FeOOH/2.5}) = 167.2 \text{ EUR/}10^3 \text{ m}^3 \tag{9}$$
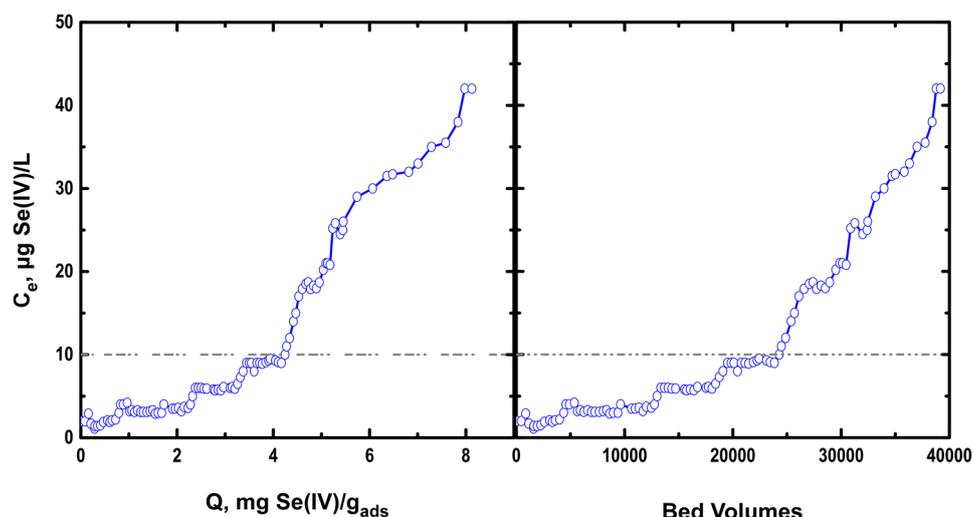
Figure 2. Breakthrough curves of: Se(IV) adsorption by FeOOH/2.5 in RSSCTs (initial concentrations: 100 µg Se(IV)/L, pH = 7, T = 20 °C).

4. Conclusions

Coagulation/precipitation with the application of Fe(III) and adsorption onto FeOOH water treatment processes are both effective and techno–economically viable for selenite removal. Adsorption has many advantages that include the reusability of the adsorbent, safe disposal and low labor cost, with the main disadvantage being the significantly higher treatment cost. Although uptake capacities (Q_{10}) were similar for both processes, the comparison between the coagulation/ precipitation and the adsorption water treatment process indicated the superiority of the first method to reduce Se(IV) below the regulated drinking water limit of 10 µg/L in terms of economic aspects. However, for the installation of the optimum drinking water treatment process, sludge production, post treatment requirements, water flow rate, and initial selenite concentration, along with labor and maintenance requirements, should also be considered. The major disadvantage of the coagulation/precipitation process is the production and management of a high amount of sludge.

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