

## Article

# Techno-Economic Evaluation of Iron and Aluminum Coagulants on Se(IV) Removal

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**Abstract:** Research on selenium pollution in natural waters is continuous and discouraging. In this study, coagulation/precipitation was applied with the use of Fe(II), Fe(III), and poly-aluminum chloride (PACl) salts for Se(IV) removal at concentration range 10–100 µg Se(IV)/L that is commonly found in drinking waters. Prehydrolyzed Fe(III)-FeCl<sub>3</sub> delivered the best uptake capacity ( $Q_{10}$  = 8.9 mg Se(IV)/g Fe(III) at pH 6) at the residual concentration equal to the drinking water regulation limit of 10 µg/L. This was much higher than the efficiencies achieved when applying the other coagulants: i.e.,  $Q_{10}$  = 7.3 mg Se(IV)/g Fe<sup>3+</sup>-FeClSO<sub>4</sub>,  $Q_{10}$  = 6.4 mg Se(IV)/g prehydrolyzed Fe(III)-Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and 0.7 mg Se(IV)/g Al-PACl at pH 6, and  $Q_{10}$  = 0.45 mg Se(IV)/g Fe(II) at pH 7.2. Comparing the different sources of Fe(III), it is apparent that Se(IV) uptake capacity is inhibited by the presence of SO<sub>4</sub><sup>2-</sup> in crystal structure of prehydrolyzed Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, while prehydrolyzed FeCl<sub>3</sub> favors Se(IV) uptake. Temperature effect data showed that coagulation/precipitation is exothermic. In techno-economic terms, the optimal conditions for Se(IV) removal are coagulation/precipitation at pH values lower than 7 using prehydrolyzed Fe(III)-FeCl<sub>3</sub>, which provides a combination of minimum sludge production and lower operating cost.

**Keywords:** tetravalent selenium Se(IV); Fe-based coagulants; PACl; polluted waters; cost estimation

## 1. Introduction

Water quality degradation is a crucial matter of global concern. Long-term consumption of drinking water that contains high concentrations of toxic elements is related to carcinogenesis, chronic diseases, vital organ destruction, and increased mortality [1]. The presence of selenium in aquatic environments is gradually increasing and although selenium is an essential element for cellular growth, when consumed in excess it can lead to selenosis and other neurological and gastrointestinal implications [2,3]. Weathering of minerals alongside the high variety of human activities that involve selenium usages, such as industrial wastewaters, mining, and oil refinery activities, agricultural runoff, photosensitive materials, semiconductors, and insecticides, contribute massively to selenium pollution in aquifers [4,5]. Increasing reports of polluted drinking water sources obliged the European Commission to set the Drinking Water Regulation Limit (DWRL) for selenium to 10 µg/L [6].

Selenium in water is mainly present as two inorganic anionic species: SeO<sub>3</sub><sup>2-</sup> (Se(IV)-selenite) and SeO<sub>4</sub><sup>2-</sup> (Se(VI)-selenate). Geogenic selenium in natural waters is present in both species with Se(IV) being the dominant one since the Eh of natural waters at pH range 6–8 is commonly lower than 0.5 V (Figure S1) [7], while in high oxidizing environments the Se(VI) species dominate [8]. Total selenium concentrations in groundwater have been reported in the range of 0.06–400 µg/L, while in some cases concentrations can reach 6000 µg/L [9,10]. The existence of these high concentrations emphasizes the requirement of an effective treatment process for the removal of selenium from potable water.

Purification of polluted waters has been studied by applying various treatment processes, such as physical, biological, and chemical, including adsorption with inorganic [11,12] or organic adsorbents [13] that mostly demonstrate low sorption capacities or weak chemical affinity. Biological removal [14] is a time-consuming process and not compatible with potable water. Reductive precipitation [15] results in high removal costs due to posttreatment processes necessary to remove residual reductants. Constructed wetlands [16] are time and space consuming, and nanofiltration and reverse osmosis [17] are non-selective processes and modify the physicochemical characteristics of water.

The most coagulation/precipitation treatment processes are based on the reduction of selenite to elemental selenium using mostly sulfur-based reductants or zero-valent iron (ZVI) [4,15,18]. However, this method requires posttreatment to completely remove the residual reductant. Moreover, research has focused on low (acidic) pH values and high selenium concentrations like those encountered in industrial wastewaters rather than potable water [17]. Research on drinking water treatment mostly incorporates the use of relatively low-cost ferric or aluminum salts for the coagulation/precipitation process [19,20]. Hu et al. (2015) showed that iron-based coagulant can reduce an initial selenium concentration of 250  $\mu\text{g/L}$  by 98%, when a coagulant dosage of 0.4 mmol  $\text{Fe}^{3+}/\text{L}$  is applied in weakly acidic conditions [19]. High coagulant dosages and acidic pH conditions were also reported as the crucial parameters that influence selenium coagulation by Adio et al. (2017) when studying the precipitation of selenium by nZVI (nano zero-valent iron) [21]. Almost all studies have focused on high initial concentrations in a distilled water matrix without evaluating other co-existing ions. In addition, these proposed treatment techniques are efficient only at acidic pH ranges, therefore, requiring a posttreatment process, strongly modify water quality, and do not achieve residual concentrations below the DWRL of 10  $\mu\text{g/L}$ .

Coagulation/precipitation is traditionally applied for drinking water treatment since it offers significant advantages such as high removal efficiencies using low-cost coagulants and is effective at a wide range of pH values [22]. However, the main disadvantage of applying this process for selenite removal is that the relatively high coagulant dose required results in the production of large quantities of sludge that must be managed and safely disposed of.

The present work focuses on the evaluation of selenite removal by applying coagulation/precipitation with Fe and Al coagulants to a tap water matrix. The criteria of coagulant evaluation were: the ability to achieve residual concentrations ( $C_e$ ) lower than the current DWRL of 10  $\mu\text{g/L}$ , the removal capacity at  $C_e = 10 \mu\text{g/L}$  ( $Q_{10}$  value), and maintaining (not modifying) the physicochemical characteristics of the water. The data obtained can be utilized when designing a full-scale treatment process for selenite removal only since the experiments were conducted at pH range 6–8 and initial selenium concentrations were 10–100  $\mu\text{g Se(IV)/L}$  similar to those commonly encountered in natural waters. To the best of our knowledge, no previous research has estimated the  $Q_{10}$  value at the pH range of 6–8, which would provide realistic data applicable for the scale-up of the coagulation/precipitation process and to estimate the treatment cost for selenite removal.

## 2. Materials and Methods

### 2.1. Water Characteristics

The tap water of the city of Thessaloniki, Greece, was used in this study, following chlorine removal by filtering through a fixed bed of activated carbon. The physicochemical characteristics of the tap water used are presented in Table 1. Water samples were spiked daily with Se(IV) and were used in the experiments at least 24 h after Se(IV) addition to allow sufficient time for incorporation into the water matrix.

### 2.2. Reagents and Materials

Deionized water was used to prepare stock solutions of all used reagents. All glassware, polyethylene bottles, and sample vessels were immersed in 15%  $\text{HNO}_3$  solution and rinsed three times with deionized water before use. The 100 mg/L stock solutions of Se(IV) were prepared by the

dissolution of analytical grade  $\text{Na}_2\text{SeO}_3$ . The initial selenite concentrations for the removal experiments ranged between 25 and 100  $\mu\text{g/L}$ .

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

| Parameter                         | Value         |
|-----------------------------------|---------------|
| pH                                | $7.4 \pm 0.1$ |
| Conductivity ( $\mu\text{S/cm}$ ) | $590 \pm 30$  |
| $\text{Na}^+$ (mg/L)              | $35 \pm 5$    |
| $\text{Ca}^{2+}$ (mg/L)           | $80 \pm 10$   |
| $\text{Mg}^{2+}$ (mg/L)           | $24 \pm 3$    |
| $\text{HCO}_3^-$ (mg/L)           | $342 \pm 20$  |
| Fe (mg/L)                         | $<0.02$       |
| Mn (mg/L)                         | $<0.005$      |
| $\text{NO}_3^-$ (mg/L)            | $9 \pm 3$     |
| $\text{SO}_4^{2-}$ (mg/L)         | $10 \pm 4$    |
| $\text{Cl}^-$ (mg/L)              | $15 \pm 5$    |
| TOC (mg/L)                        | $0.5 \pm 0.2$ |

Commercial ferric salts ( $\text{FeClSO}_4$ ,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) were used to prepare stock solutions of the Fe-based coagulants. The stock solutions of 1500 mg  $\text{Fe}^{3+}/\text{L}$  were prepared by dilution in 1 L distilled water: 12 g of 12.5% w/w  $\text{FeClSO}_4$  solution, 7.53 g of  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ , and 7.25 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ . To prepare the 1500 mg  $\text{Fe}^{2+}/\text{L}$  stock solution, 7.45 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was diluted in deionized water following oxygen removal with  $\text{N}_2$ . The pH of the stock solutions was adjusted to within the range of 1–1.5 by the addition of either concentrate  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$ . The Fe concentrations ( $1500 \pm 50$  mg/L) were verified by flame atomic absorption spectrophotometry. Prehydrolyzed stock solutions of 1500 mg  $\text{Fe(III)}/\text{L}$  were prepared daily by the reaction of proper quantities of  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  at  $\text{pH } 2.5 \pm 0.2$  with the addition of 1M  $\text{NaOH}$ . The coagulant of poly-aluminum chloride (PACl) contained 111.3 g  $\text{Al}/\text{L}$ , 20% degree of basicity, and had a density of 1.52 g/mL.

### 2.3. Experimental Procedure

The treatment tests were performed on a Wisestir JT-M6C jar tester with six paddle stirrers at  $20 \pm 1^\circ\text{C}$ . The water pH was adjusted to 6, 7, and 8 via the addition of either 0.1 M  $\text{HCl}$  or 0.1 M  $\text{NaOH}$ . 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  $0.45 \mu\text{m}$  membrane filter, and acidified at  $\text{pH} \leq 2$  to determine the residual selenium concentration. Data at pH 7 and temperatures 5, 20, and  $35^\circ\text{C}$  were also obtained and used to evaluate the influence of temperature on selenite removal.

### 2.4. Analytical Procedure

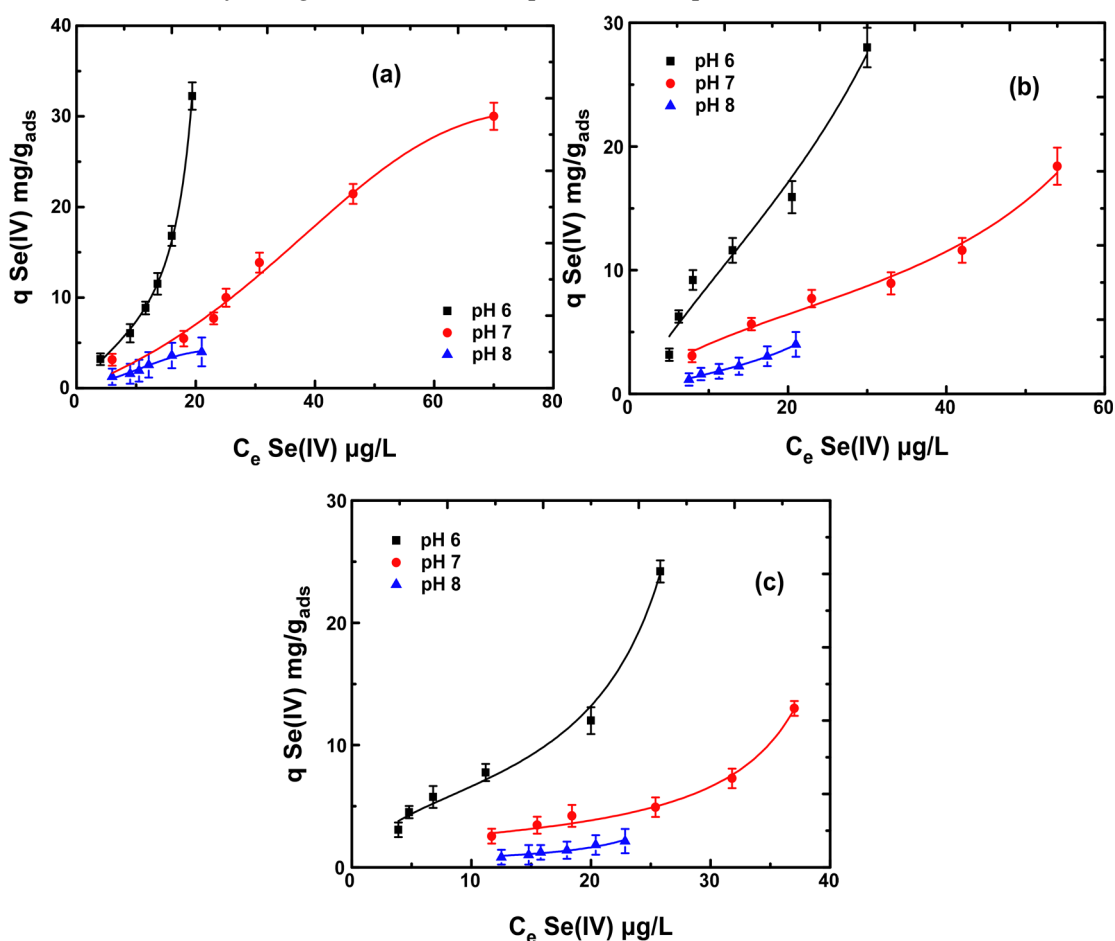
Initial and residual selenium concentrations were determined by graphite atomic absorption spectrophotometry using a Perkin–Elmer AAnalyst 800 instrument. The method's detection limit (DL) for selenium was 1  $\mu\text{g Se}/\text{L}$ . The removal efficiency was evaluated according to adsorption capacity at a residual concentration equal to DWRL of 10  $\mu\text{g}/\text{L}$ , abbreviated as  $Q_{10}$  henceforth. The initial concentrations of iron and aluminum were determined by flame atomic absorption spectrophotometry, while the residual concentration of iron at water samples treated by the qualified coagulant was determined by graphite atomic absorption spectrophotometry (DL = 2  $\mu\text{g Fe}/\text{L}$ ), using a Perkin–Elmer AAnalyst 800 instrument.

### 3. Results and Discussion

#### 3.1. Se(IV) Removal by Fe(III) and Fe(II) Coagulation

##### 3.1.1. Fe(III) Addition

The adsorption isotherms of Se(IV) removal by coagulation/precipitation with iron coagulants addition were conducted in the pH range of natural waters, i.e., 6–8. The experimental results are shown in Figure 1 and the derived data are presented in Table 2. The fitting attempts showed that the results obtained are best described by the Brunauer-Emmett-Teller (BET) model, similar to the studies of Mitrakas et al. (2018) [20] on Sb(V) removal and Ouzounis et al. (2015) [23] on As(III) removal by coagulation/precipitation using iron-based coagulants. The BET model suggests weak multilayer physisorption of Se(IV), where the adsorption enthalpy is the same for each layer and the formation of a new layer begins before the completion of the previous one.



**Figure 1.** Adsorption isotherms for the addition of: (a)  $\text{Fe}^{3+}$ - $\text{FeClSO}_4$ , (b) prehydrolyzed  $\text{FeCl}_3$ , and (c) prehydrolyzed  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  for Se(IV) are fitted to the BET model. Experimental conditions: 20 °C, pH 6, 7, and 8, Fe(III) dose range 1–15 mg/L, initial Se(IV) concentration range 25–100 µg/L.

The results are in accordance with the literature and show that selenite removal is favored at lower pH values (Table 2). More specifically, uptake capacity fell by more than 50% when the pH was raised from 6 to 7 (i.e., 56% by  $\text{Fe}^{3+}$ - $\text{FeClSO}_4$ , 53% by prehydrolyzed  $\text{Fe(III)-FeCl}_3$ , and 58% by prehydrolyzed  $\text{Fe(III)-Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ ), while the reduction of uptake capacities recorded at pH 8 compared to those recorded at pH 6 were 73%, 82%, and 87%, respectively. The prehydrolysis of  $\text{FeCl}_3$  at  $\text{pH } 2.5 \pm 0.2$  results in higher density of bivalent  $\text{Fe(OH)}^{2+}$  cationic species (Fig. 2S). In contrast, at pH range 6–8, the  $\text{Fe}^{3+}$  is modified to monovalent  $\text{Fe(OH)}^{2+}$  and non-charged  $\text{Fe(OH)}_3$ . Therefore, it was deemed worthwhile to verify the influence of Fe(III) prehydrolysis on Se(IV) adsorption due to higher density of cationic species at the iron doses.

**Table 2.** 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 <sup>2</sup> | Q <sub>10</sub><br>mg Se(IV)/<br>g Fe | Coagulant<br>Cost,<br>€/kg Se(IV) |
|---|----|---------|---------|---------|----------------|---------------------------------------|-----------------------------------|
| Fe <sup>3+</sup> -FeClSO <sub>4</sub>   | 6  | 0.7548  | 0.0368  | −0.0034 | 0.999          | 7.3                                   | 205 ± 4                           |
| Fe <sup>3+</sup> -FeClSO <sub>4</sub>   | 7  | 0.2598  | −0.0174 | −0.0002 | 0.987          | 3.2                                   | 469 ± 3 2                         |
| Fe <sup>3+</sup> -FeClSO <sub>4</sub>   | 8  | 0.1123  | −0.0642 | −0.0021 | 0.963          | 2.0                                   | 750 ± 50                          |
| prehydrolyzed<br>FeCl <sub>3</sub> ·6H <sub>2</sub> O                                       | 6  | 1.3442  | −0.0683 | −0.018  | 0.966          | 8.9                                   | 169 ± 12                          |
| prehydrolyzed<br>Fe(III)-FeCl <sub>3</sub> ·6H <sub>2</sub> O                               | 7  | 0.7706  | −0.1000 | −0.0014 | 0.987          | 4.2                                   | 357 ± 24                          |
| prehydrolyzed<br>Fe(III)-FeCl <sub>3</sub> ·6H <sub>2</sub> O                               | 8  | 0.1953  | −0.0361 | −0.0017 | 0.993          | 1.6                                   | 938 ± 63                          |
| prehydrolyzed<br>Fe(III)-Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·9H <sub>2</sub> O | 6  | 2.4445  | −0.4178 | −0.0138 | 0.987          | 6.4                                   | 234 ± 16                          |
| prehydrolyzed<br>Fe(III)-Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·9H <sub>2</sub> O | 7  | 28.0367 | −13.059 | −0.2951 | 0.987          | 2.7                                   | 556 ± 37                          |
| prehydrolyzed<br>Fe(III)-Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·9H <sub>2</sub> O | 8  | −81.995 | −146.32 | 4.7852  | 0.918          | 0.8                                   | 1875 ± 125                        |

Indeed, the Q<sub>10</sub> values of 8.9 and 4.2 mg Se(IV)/g Fe(III) or µg Se(IV)/mg Fe(III) of prehydrolyzed Fe(III)-FeCl<sub>3</sub> at pH values 6 and 7 were the highest of the Fe(III)-based coagulants (Table 2). In contrast, the prehydrolyzed Fe(III)-Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·9H<sub>2</sub>O showed the lowest efficiency due to incorporation of sulfates in crystal structure of oxy-hydroxide (FeOH-SO<sub>4</sub>) that decreased the density of cationic species [Fe(OH)<sup>2+</sup>] and in turn the adsorption capacity [11,24,25]. Determination of the Q<sub>10</sub> value is fundamental for estimating the coagulant dose and the cost (Table 2) required for Se(IV) removal from water. For example, using prehydrolyzed Fe(III)-FeCl<sub>3</sub>·6H<sub>2</sub>O, the Fe(III) dose required for the removal of Se(IV) of initial concentration 50 µg/L at pH 7 can be calculated as follows:

$$\text{Fe(III) dose} = [(50 - 10 \text{ µg Se(IV)/L}) / [4.2 \text{ mg Se(IV)/mg Fe(III)}]] = 9.5 \text{ mg Fe(III)/L}$$

Since the current commercial cost of Fe(III) coagulants in Greece is 1.5±0.1 €/kg Fe(III), the cost of the coagulant required (Table 2) for the removal of 1 kg Se(IV) using prehydrolyzed Fe(III)-FeCl<sub>3</sub>·6H<sub>2</sub>O at pH 7 can be calculated as follows:

Fe(III) consumption:

$$[1 \text{ kg Se(IV)} / 4.2 \text{ mg Se(IV)/g Fe(III)}] = [1,000 \text{ g Se(IV)} / 4.2 \text{ g Se(IV)/kg Fe(III)}] = 238.1 \text{ kg F(III)/kg Se(IV)}$$

$$\text{Coagulant cost} = [238.1 \text{ kg F(III)/kg Se(IV)}] \times [1.5 \pm 0.1 \text{ €/kg Fe(III)}] = 357 \pm 24 \text{ €/kg Se(IV)}$$

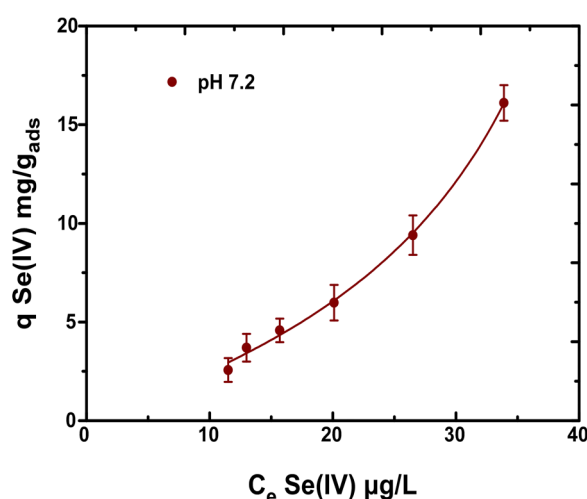
Due to low affinity, the spent iron doses for Se(IV) removal below DWRL are relatively high, resulting in treated water pH lower than the saturation one (pH<sub>s</sub>). In order to modify the water pH at pH ≥ pH<sub>s</sub> to eliminate the corrosion of distribution network, an alkaline reagent should be added depending on the chemistry of the water. So, in reagents' cost, the cost of alkaline reagent dose along with coagulant's one must be incorporated.

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. Based on current Greek market prices, the energy and labor costs required are estimated to be approximately 60 ± 30 €/10<sup>3</sup> m<sup>3</sup> for treated water in the range 25–250 m<sup>3</sup>/h (Supplementary, Text S1). Furthermore, the total cost of treatment incorporates also the maintenance cost, which is estimated by the depreciation cost of the mechanical equipment at 5 years operation, which according to our experience is estimated around 20 ± 5 €/10<sup>3</sup> m<sup>3</sup> treated water. Therefore, from a techno-economic point of view, Se(IV) removal is a viable treatment process only when using prehydrolyzed Fe(III)-FeCl<sub>3</sub> and pH values lower than 7.

In addition, the residual iron concentration in almost all treated water samples was determined below 10 µg Fe/L, when the regulation limit for drinking water is 200 µg Fe/L, due to extremely low solubility of  $\text{Fe}(\text{OH})_3$  ( $K_{\text{sp}} \text{Fe}(\text{OH})_3 = 6 \times 10^{-38}$ ).

### 3.1.2. Fe(II) Addition

The oxidation time of Fe(II) at pH < 7 for doses > 2 mg Fe(II)/L overpasses 1 h (Figure S3) [26]. Therefore, the pH 7.2 was selected for total oxidation of any Fe(II) dose within 1 h, in order to study the influence on Se(IV) removal of the gradual oxidation of Fe(II) to Fe(III) and the hydrolysis of the latter to  $\text{Fe}(\text{OH})_3$  with the in situ formed oligomeric and polymeric species  $[\text{Fe}(\text{OH})_y]^{z+}$ . However, the experimental results showed a negative influence of the long-term oxidation/hydrolysis of iron on Se(IV) uptake capacity (Figure 2, Table 3). The adsorption data were also best fitted to the BET multilayer model, verifying the weak multilayer physisorption of Se(IV). The commercial cost of Fe(II) is  $0.9 \pm 0.1$  €/kg Fe(II) thus resulting in a coagulant cost of  $360 \pm 40$  € (Table 3) for the removal of 1 kg Se(IV). The  $Q_{10}$  values of Fe(II) and prehydrolyzed  $\text{Fe}(\text{Cl})_3$  are 4.2 and 2.5 mg Se(IV)/g Fe, respectively, which means that for diminishing the same initial Se(IV) concentration at  $C_e = 10$  µg/L it must spent:  $[(4.2 - 2.5)/2.5] \times 100 = 68$  % greater Fe(II) dose, resulting, in turn, in 68 wt.% more  $[\text{Fe}(\text{OH})_3]$  sludge production. The same coagulant cost is attributed to the almost 70% higher cost of Fe(III) [ $1.5 \pm 0.1$  €/kg Fe(III)] in comparison to Fe(II) [ $0.9 \pm 0.1$  €/kg Fe(II)]. The residual iron concentration in treated water samples was also determined below 10 µg Fe/L.



**Figure 2.** Adsorption isotherm with Fe(II) addition for Se(IV) uptake fitted to the BET model. Experimental conditions: 20 °C, pH 7.2, Fe(II) dose 1–15 mg/L, initial Se(IV) concentration 50 µg/L.

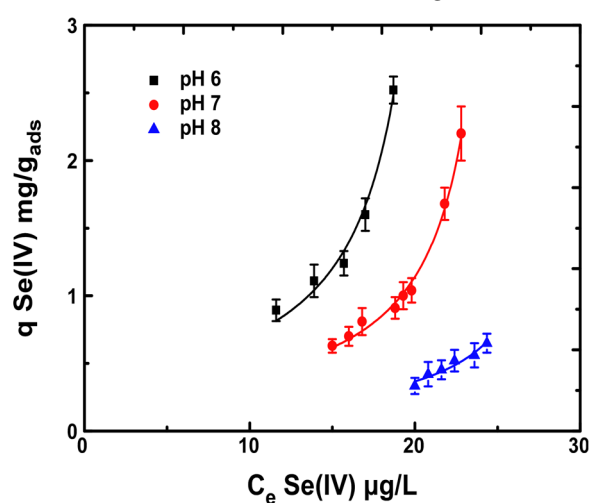
**Table 3.** BET fitting parameters for Se(IV) adsorption isotherm with Fe(II) at pH 7.2 (according to the equation:  $Q = aC/(1 + bC + dC^2)$ ).

| Coagulant                            | pH  | a      | b       | d       | R <sup>2</sup> | Q <sub>10</sub><br>mg Se(IV)/g Fe | Coagulant Cost,<br>€/kg Se(IV) |
|--------------------------------------|-----|--------|---------|---------|----------------|-----------------------------------|--------------------------------|
| FeSO <sub>4</sub> ·7H <sub>2</sub> O | 7.2 | 0.2317 | −0.0063 | −0.0003 | 0.996          | 2.5                               | 360 ± 40                       |

### 3.2. Se(IV) Removal by PACl Coagulation

The most commonly used coagulant for water treatment processes is poly-aluminum chloride (PACl). The adsorption isotherms of Se(IV) removal with PACl were conducted at pH range 6–8 (Figure 3). The fitting of adsorption data to the BET multilayer model verifies the weak multilayer physisorption of Se(IV) by Al-PACl. The uptake capacities of Se(IV) by Al-PACl are discouraging for further investigation. The maximum uptake capacity, as expected, was achieved in the most acidic conditions at pH 6 (0.7 mg Se(IV)/g Al-PACl), which is almost 13 times lower than the corresponding Fe(III) from prehydrolyzed  $\text{FeCl}_3$  (8.9 mg Se(IV)/g Fe). The much better efficiency of Fe-based

coagulants was also reported by Hu et al. (2015) [19]. Conclusively, coagulation/precipitation is not an attractive process for Se(IV) removal using Al-PACl. The current commercial cost of Al-PACl is  $2.5 \pm 0.2$  €/kg Al, resulting in an extremely high coagulant cost required for the removal of 1 kg Se(IV) (Table 4). The coagulant cost of Al-PACl is almost 20 times higher than that of prehydrolyzed FeCl<sub>3</sub>.



**Figure 3.** Adsorption isotherms with poly-aluminum chloride (PACl) addition for Se(IV) uptake fitted to the BET model. Experimental conditions: 20 °C, pH 6–8, PACl dose 1–15 mg Al/L, initial Se(IV) concentration 25 µg/L.

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

| Coagulant | pH | a        | b        | d       | R <sup>2</sup> | Q <sub>10</sub><br>mg Se(IV)/g Al | Coagulant<br>Cost,<br>€/kg Se(IV) |
|-----------|----|----------|----------|---------|----------------|-----------------------------------|-----------------------------------|
| PACl      | 6  | 33.9371  | −87.8062 | −3.9688 | 0.969          | 0.7                               | 3571 ± 285                        |
| PACl      | 7  | −12.3455 | −46.9791 | 1.819   | 0.983          | 0.4                               | 6250 ± 500                        |
| PACl      | 8  | −164.12  | −1301.1  | 43.081  | 0.914          | 0.2                               | 12,500 ± 1,000                    |

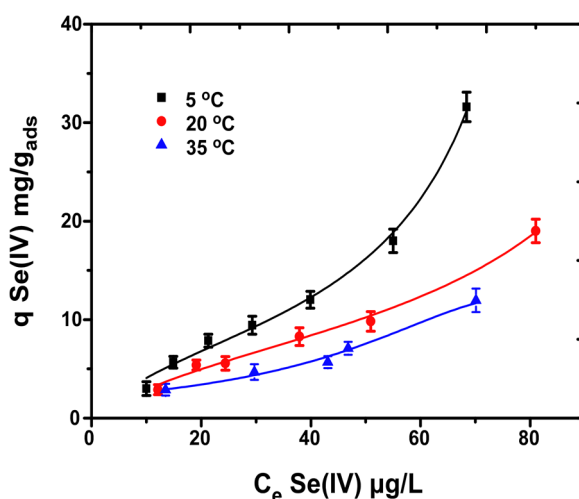
### 3.3. Temperature Effect on Se(IV) Removal by Addition of Fe<sup>3+</sup>-FeCl<sub>3</sub>

As mentioned above, Se(IV) uptake is described by the BET adsorption model that indicates multilayer physisorption. To determine whether the adsorption process is endothermic or exothermic, the temperature effect was examined at temperatures of 5, 20, and 35 °C at pH 7. Figure 4 shows that adsorption is favored at lower temperatures since the respective Q<sub>10</sub> values recorded for temperatures of 5, 20, and 35 °C (Table 5) were 4.1 mg Se(IV)/g Fe(III), 3.2 mg Se(IV)/g Fe(III), and 2.4 mg Se(IV)/g Fe(III), respectively.

**Table 5.** BET fitting parameters for Se(IV) adsorption isotherms with Fe<sup>3+</sup>-FeCl<sub>3</sub> at temperatures of 5, 20, and 35 °C and pH 7 (according to the equation:  $Q = aC/(1 + bC + dC^2)$ ).

| Temperature (°C) | a       | b       | d        | R <sup>2</sup> | Q <sub>10</sub><br>mg Se(IV)/g Fe | Coagulant Cost,<br>€/kg Se(IV) |
|------------------|---------|---------|----------|----------------|-----------------------------------|--------------------------------|
| 5                | 0.61229 | 0.05569 | −0.00074 | 0.993          | 4.1                               | 366 ± 25                       |
| 20               | 0.43191 | 0.03832 | −0.00036 | 0.990          | 3.2                               | 469 ± 32                       |
| 35               | 0.41063 | 0.08066 | −0.00086 | 0.983          | 2.4                               | 625 ± 42                       |





**Figure 4.** Adsorption isotherms at temperatures of 5, 20, and 35 °C with  $\text{Fe}^{3+}$ - $\text{FeCl}_3$  addition for Se(IV) uptake fitted to the BET model. Experimental conditions: pH 7,  $\text{Fe}^{3+}$  dose 1–15 mg/L, initial Se(IV) concentrations 50–100 µg/L.

The decrease in uptake capacity observed when increasing the temperature verifies that the adsorption process is exothermic. Furthermore, the lower uptake capacity ( $Q_{10} = 3.2$  mg Se(IV)/g Fe(III)) of  $\text{Fe}^{3+}$ - $\text{FeCl}_3$  at pH 7 and 20 °C compared to that of the prehydrolyzed  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  ( $Q_{10} = 4.2$  mg Se(IV)/g Fe(III)) verifies the positive contribution of the hydrolyzed process to uptake capacity.

#### 4. Conclusions

The experimental data of this study focused on initial Se(IV) concentrations lower than 100 µg/L commonly encountered in polluted natural waters. The adsorption capacities of the coagulation/precipitation process at the drinking water regulation limit ( $Q_{10}$ ) were calculated to produce realistic data information that can be implemented in full-scale water treatment plants. The adsorption isotherms data were better fitted to the BET model for all the coagulants tested, suggesting weak multilayer physisorption of Se(IV). The parameters that affect uptake capacity are pH, with Se(IV) removal being techno-economically viable at pH values lower than 7, coagulant type, and the iron valence for the Fe-based coagulants. The uptake capacity is related to coagulant cost, while energy and labor costs do not depend on initial Se(IV) concentrations. Prehydrolyzed Fe(III)- $\text{FeCl}_3$  delivered the best uptake capacity  $Q_{10} = 8.9$  mg Se(IV)/g Fe(III) at pH 6 and  $Q_{10} = 4.2$  mg Se(IV)/g Fe(III) at pH 7, resulting in coagulant costs of  $169 \pm 12$  €/kg Se(IV) and  $357 \pm 24$  €/kg Se(IV), respectively. The cost of the prehydrolyzed Fe(III)  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Fe}^{3+}$ - $\text{FeClSO}_4$  coagulant at the qualified pH range of 6–7 is between 30% and 50% higher than that of the prehydrolyzed Fe(III)- $\text{FeCl}_3$ . The lower uptake capacity of the prehydrolyzed Fe(III)  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  is mainly attributed to incorporated sulfates in crystal structure of iron oxy-hydroxide decreasing the density of cationic species. The coagulant cost ( $360 \pm 40$  €/kg Se(IV)) of Fe(II) at pH 7.2 is similar to that of the prehydrolyzed Fe(III)- $\text{FeCl}_3$ , which, however, results to 68 wt.% more sludge production. The adsorption process using  $\text{Fe}^{3+}$ - $\text{FeCl}_3$  proved to be exothermic and, by increasing the temperature to 15 °C, results in a 30% increase of coagulant cost. Finally, PACl showed close to one order of magnitude lower uptake capacity compared to Fe-based coagulants, resulting in almost 20 times higher coagulant cost.

**Supplementary Materials:** The following is available online at [www.mdpi.com/2073-4441/12/3/672/s1](http://www.mdpi.com/2073-4441/12/3/672/s1): Figure S1. Selenium speciation as a function of Eh vs pH. Figure S2. Fe(III) speciation as a function of pH. Figure S3. Oxidation rate of Fe(II) by oxygen as function of water pH. Text S1. Estimation of energy cost.

**Author Contributions:** K.K. and L.B. conducted the experimental work. K.K. and L.B. conducted the analysis of selenium by GFAAS in aqueous solutions. M.M. conceived, designed, and supervised the experiments and contributed equally to writing the manuscript and analysis of the result. M.M. coordinated the project and is the corresponding author of this paper. All authors have read and agreed to the published version of the manuscript.



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