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## DIFFERENT TYPES OF ADSORBENTS FOR SELENIUM (Se) REMOVAL FROM WATER: A REVIEW

### Abstract

*Development of adsorption materials based on metal oxides, silicon dioxide, carbon, bio-sorbents and adsorbents, obtained from natural waste, can be used to remove selenium from water. Research on some of these materials is at the laboratory level, while the others were tested in the pilot plants, and a few have found a commercial application. The high adsorption capacities show a possibility of their application for selenium removal from water. This paper presents a literature review of different types of adsorbents for the removal of selenium (Se) from water.*

**Keywords:** selenium, adsorption, adsorbents, adsorption capacity

### 1 INTRODUCTION

Selenium (Se) is naturally present in rocks and soils in the environment in the form of selenite, selenate, selenide, and elemental Se. It is a trace element in the natural ore deposits that contain minerals, such as heavy metal sulfides [1]. In addition to the naturally occurring Se, its increase of concentration in the environment is caused by human activities, especially mining, coal combustion, pesticide production, agricultural use, etc. [2]. Selenium occurs in water and wastewater from natural sources, but also due to anthropogenic activities, such as agriculture, mining, oil refineries, and coal combustion, the concentrations range from a few micrograms per liter to 30 mg L<sup>-1</sup>.

Selenium is nutritionally important in small amounts, but higher amounts are associated with certain diseases and potential side effects in humans, and can also be toxic to aquatic organisms, birds, and other animals, which is shown to be a worldwide problem.

In accordance with the principles of green chemistry, it is necessary to take preventive measures to reduce the release of selenium, and then the necessary methods for removal from water should be considered and evaluated. Various methods for the treatment of selenium-containing water and wastewater have been investigated [3,4]. Some are still in the laboratory research phase, others have already been tested in the pilot plants, and a few have been applied on a commercial scale. It is difficult to define the best cost-effective option, given the different characteristics of water and wastewater that need to be treated, which requires specific approaches and different costs. The impact of any technology should be assessed, optimized and demonstrated on the basis of a case study [5]. Selenium removal can be achieved by application physical, chemical, and biological methods. Therefore, the prevention, control and removal of selenium from water are very important.

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## 2 ADSORPTION

Special attention is paid to the removal of selenium in the scientific literature, where the application of adsorption, development and efficiency of different types of adsorbents having a special significance. Conventional and alternative materials have been explored as the potential adsorbents for Se, in order to find the cheap strategies for water and wastewater treatment. Until now, the scientific literature has mostly published series of laboratory tests, using the standard selenium solutions. The adsorption materials are classified into organic resins, oxides and minerals (including single and mixed oxides and hydroxides), carbon-based adsorbents (activated carbon and graphene), biosorbents and adsorbents derived from the natural waste.

The obtained experimental data are modeled by the well-known Langmuir and Freundlich isotherms. The parameters, obtained by the Langmuir isotherm (especially  $Q_m$ ), can be directly correlated with the adsorption properties of an adsorbent. The maximum adsorption capacity ( $Q_m$ ) represents the maximum amount of adsorbate that a solid can retain to achieve a single layer coverage. In addition, the Langmuir isotherm also provides a qualitative agreement with the experimental data obtained for the values ( $Q_m$ ) [6].

It is important to note that the adsorbed amounts of Se depend on the experimental conditions (pH, concentration, ionic strength of solution, temperature, ions in solution, etc.). It is clear that the maximum adsorption capacity ( $Q_m$ ) is not the only criterion to estimate the adsorbent potential, but it may be the first. Many other aspects must be considered such as the adsorption kinetics, effect of various factors on adsorbent performance, suitability for continuous treatment, separation

of solid and liquid phases, leaching results, availability and cost of procurement, regeneration and disposal after use.

### 2.1 Adsorption materials based on organic resins, metal oxides and silicon dioxide

Thiourea-formaldehyde (TUF) chelating resin was synthesized and used in the adsorption of selenite ( $\text{SeO}_3^{2-}$ ) and selenate ( $\text{SeO}_4^{2-}$ ) ions. The effect of the initial acidity of the solution and the initial concentration of selenium on adsorption was investigated. Selenite and selenate ions were found to be adsorbed on TUF resin under strongly acidic conditions (3–5 M HCl). The adsorption capacity of TUF resin was  $833.3 \text{ mg g}^{-1}$  for selenite and  $526.3 \text{ mg g}^{-1}$  for selenate. All the obtained adsorption data for selenite and selenate ions fit well into the Langmuir isotherm. Mechanisms of adsorption are the reduction of selenite or selenate to elemental selenium, Se (0) [7], Table 1.

Oxides of aluminum, iron and silicon dioxide, in natural or synthesized forms, can be used to remove selenium. In addition to the large specific surface area, the oxides generally have a high zero charge point ( $\text{pH}_{\text{ZPC}}$ ), which means that the solid surface will be positively charged over a wide range of pH values, and have a higher affinity for the oxyanion adsorption [25]. Many studies of oxyanions and oxides were conducted to explain the type of interaction between the adsorbate and adsorbent, Table 1. The type of interaction between selenite species and selenate with mineral oxides was studied using the X-ray adsorption spectroscopy (XRD), and it was shown that selenate forms a weakly bound complex with the outer-sphere, and that selenite forms a tightly bound complex with the inner-sphere [26].

**Table 1** Adsorption capacities ( $Q_m$ ) listed in literature for Se (IV) and Se (VI) for oxides, minerals and organic synthetic resin

| Adsorbent  | Se Species | $C_{in}$ (mg L <sup>-1</sup> ) | m/v (g L <sup>-1</sup> ) | pH <sup>a</sup> | T (°C) | $Q_m$ (mg g <sup>-1</sup> ) | Ref. |
|--|------------|--------------------------------|--------------------------|-----------------|--------|-----------------------------|------|
| <i>Organic synthetic resin</i>                               |            |                                |                          |                 |        |                             |      |
| Thiourea-formaldehyde resin                                  | Se (IV)    | 50-1000                        | 0.4                      | *               | -      | 833.2                       | [7]  |
|  | Se (IV)    | 100-500                        | 0.4                      | *               | -      | 526.3                       |      |
| <i>Oxides and minerals</i>                                   |            |                                |                          |                 |        |                             |      |
| Commercial FeOOH   | Se (IV)    | 0.5-20                         | 0.5                      | 5               | 25     | 26.3                        | [8]  |
| Commercial hydroxyapatite                                    | Se (IV)    | 0.005-0.020                    | -                        | 5               | 30     | 0.82 <sup>c</sup>           | [9]  |
| Anatase nanoparticles  | Se (IV)    | 10-54                          | 5.0                      | 5               | 20     | 7.71                        | [10] |
| Magnetite  | Se (IV)    | 0.24-40                        | -                        | 4               | 25     | 0.22                        | [11] |
|  | Se (VI)    | 0.24-40                        | -                        | 4               | 25     | 0.25                        |      |
| Binary oxide Al(III)/SiO <sub>2</sub>                        | Se (IV)    | 0-237                          | -                        | 5               | 25     | 32.7                        | [12] |
|  | Se (VI)    | 0-237                          | -                        | 5               | 25     | 11.3                        |      |
| Binary oxide Fe(III)/SiO <sub>2</sub>                        | Se (IV)    | 0-237                          | -                        | 5               | 25     | 20.4                        |      |
|  | Se (VI)    | 0-237                          | -                        | 5               | 25     | 2.4                         |      |
| Fe-Mn hydride oxides based adsorbents                        | Se (IV)    | 5-500                          | 2                        | 4               | 22     | 41.02                       | [13] |
|  | Se (VI)    | 5-500                          | 2                        | 4               | 22     | 19.84                       |      |
| Mn <sub>3</sub> O <sub>4</sub> (non-microwave-assisted aged) | Se (IV)    | 0.25-10                        | 2.5                      | 4               | 25     | 0.507                       | [14] |
|  | Se (VI)    | 0.25-10                        | 2.5                      | 4               | 25     | 1.00                        |      |
| Mn <sub>3</sub> O <sub>4</sub> (microwave-assisted aged)     | Se (IV)    | 0.25-10                        | 2.5                      | 4               | 25     | 0.800                       |      |
|  | Se (VI)    | 0.25-10                        | 2.5                      | 4               | 25     | 0.909                       |      |
| Magnetic Fe/Mn oxide nanomaterial                            | Se (IV)    | 0.25-10                        | 2.5                      | 4               | 25     | 6.57                        | [15] |
|  | Se (VI)    | 0.25-10                        | 2.5                      | 4               | 25     | 0.769                       |      |
| Mg-Al LDH  | Se (IV)    | 0-1000                         | 4                        | 9 <sup>a</sup>  | 25     | 120                         | [16] |
| Zn-Al LDH  | Se (IV)    | 0-1000                         | 4                        | 9 <sup>a</sup>  | 25     | 99                          |      |
| Mg/Fe HTlc   | Se (IV)    | ~0-80 <sup>b</sup>             | 1                        | 6               | 30     | 2.9                         |      |

$C_{in}$  - initial concentration range; m/v – adsorbent dosage; T - temperature, <sup>a</sup>initial pH; <sup>b</sup>equilibrium concentrations (estimated from the graphs); <sup>c</sup>maximum adsorption amount obtained experimentally, at the higher equilibrium concentration (20 µg L<sup>-1</sup>); \*3 mol L<sup>-1</sup> HCl; \*\*5 mol L<sup>-1</sup> HCl.

The studies have confirmed the observations [27, 28, 13], that the activated alumina (AA), mainly composed of aluminum-oxide (Al<sub>2</sub>O<sub>3</sub>), is a good material for adsorption and catalysis. It is prepared by dehydration of aluminum hydroxide at high temperatures and has the good physi-

cal properties, well-developed macro and meso porous structure, and a large specific surface area. The pH<sub>ZPC</sub> value of activated alumina ranges from 8.4 to 9.1 [29, 30]. AA has been shown to be ineffective for Se (VI), and adsorption and performance for Se (IV) depend on pH, and are affected

by silicon dioxide, arsenic, and vanadium in solution [30, 31]. For the initial Se (IV) concentrations in the range of 10–94 mg L<sup>-1</sup>, the maximum adsorption is between pH 2 - 7, with a significant decrease above pH 7 [30]. The maximum adsorption efficiency was observed at pH values of 2.5 to 4 for a Se (IV) concentration of 440 mg L<sup>-1</sup>. However, this dependence on pH is not a problem for the wastewater from flue gas desulfurization (FGD) and mine wastewater due to their typically acidic pH, but is not suitable for the agricultural water because its pH is around 8 [32].

Oxyhydroxides and iron oxides, such as magnetite (Fe<sub>3</sub>O<sub>4</sub>) [33, 34, 11, 35], hematite (α-Fe<sub>2</sub>O<sub>3</sub>) [36], maghemite (γ-Fe<sub>2</sub>O<sub>3</sub>) [37], FeOOH commercial adsorbent [8] and iron nanoparticles oxides/hydroxides [38] have been studied as selenium adsorbents. The adsorption of Se (VI) to maghemite was found to be dependent on the pH and ionic strength of solution [36]. Examination of the influence of pH value was done in the range of 3.5 - 8.0, and the best degree of removal is at pH 3.5; complete removal is at an ionic strength of 0.01 M NaCl and about 70% for 0.1 M NaCl (from an initial concentration of approximately 790 mg L<sup>-1</sup> and using a 1 g L<sup>-1</sup> dose of adsorbent).

Titanium dioxide (TiO<sub>2</sub>) has been shown to adsorb different types of selenium [27, 39, 10]. Anatase is one of the polymorphic forms of titanium dioxide, which is a non-toxic mineral, with the high chemical stability, large specific surface area and ability to oxidize and reduce the absence of numerous pollutants. The isoelectric point of anatase p*H*<sub>ZPC</sub> was found to be 6.3 (at 25°C) [36] and the adsorption of both selenium species on anatase gradually decreased with increasing pH [27, 37, 39, 10], with less efficient removal of selenates [39], with adsorption becoming negligible for the pH value above 6 [27, 37].

The kinetics of selenium (IV) adsorption on anatase is described by a pseudo-

second order kinetic model, with the rate constants depending on pH and sorbate concentration [39, 18]. Ionic strength did not affect the adsorption of Se (IV) [39], but its increase caused a decrease in the removal of Se (VI) [27]. At pH 5 and temperatures in the range 273–313 K, the maximum adsorption capacities, according to the Langmuir model, were between 7.3 and 8.5 mg g<sup>-1</sup> [10]. At pH 3.5, more than 90% of selenate was removed from an initial concentration of 0.8 mg L<sup>-1</sup>, using an anatase dose of 0.46 g L<sup>-1</sup>, and NaCl concentration of 0.01 mol L<sup>-1</sup> [27], removal of Se (VI) selenate using anatase is not effective. The binary metal oxides, Al(III)/SiO<sub>2</sub> and Fe(III)/SiO<sub>2</sub>, were prepared in order to improve the adsorption capacity of SiO<sub>2</sub> for anionic species [40]. The binary oxide Al(III)/SiO<sub>2</sub> showed the adsorption capacities for Se (IV) and Se (VI), 32.7 and 11.3 mg g<sup>-1</sup>, respectively; higher than Fe(III)/SiO<sub>2</sub>, 20.4 and 2.4 mg g<sup>-1</sup>, respectively, due to a stronger association between Al(III) and surface of SiO<sub>2</sub> and its total specific surface area which is positively charged. After a contact time of 2 hours, more than 95% of Se (IV) was adsorbed and equilibrium was reached.

Szlachta and Chubar (2013) [13] developed an ion exchange adsorbent based on the oxides of hydrate Fe(III) and Mn(III) (ratio 1:1). The adsorption equilibrium isotherms were performed at 22°C and different pH values, which had a constant value during the experiments. The maximum adsorption capacity (single layer), calculated according to the Langmuir isotherm for Se (IV), was 41.02, 26.71 and 18.45 mg g<sup>-1</sup>, at pH 4, 6 and 8, respectively. The predicted maximum adsorption capacity for Se (VI) is 19–20 mg g<sup>-1</sup>.

## 2.2 Carbon-based adsorbents

Activated carbon (AC) is the most commonly used commercial adsorbent for water treatment. Its efficiency in removing

numerous organic pollutants is well known, but its adsorption capacity for metals is not always satisfactory. Granular Activated Carbon (GAC) is used in continuous processes. The treatment of AC with iron has been investigated to improve its ability to remove oxyanions, although the iron treatment usually reduces the specific surface area and volume of pores [41, 42, 43, 18]. The  $pH_{ZPC}$  of modified AC and iron content itself have been shown to be determinants of AC performance for the arsenic oxyanion adsorption [44].

Zhang et al. (2008) [18] synthesized the granular activated carbon (Fe-GAC) and reported significant removal of selenite in a

wide pH range (2–8) and reduction in removal efficiency at pH values greater than 8. The adsorption kinetics followed the second-order pseudo model and it took 48 hours to reach the equilibrium (more than 90% is adsorbed in 6 h). The adsorption isotherms are generally well described by the Langmuir model. The adsorption capacities ranged from 2.5–2.9  $mg\ g^{-1}$  with different ionic strengths and temperatures (25–45°C). Phosphate, at a concentration of 5  $mmol\ L^{-1}$ , completely suppressed the adsorption of selenite on the Fe-GAC. At concentrations between 0.1 and 5  $mmol\ L^{-1}$ , sulfate did not show a significant effect on selenite adsorption on the Fe-GAC, Table 2.

**Table 2** Adsorption capacities ( $Q_m$ ) listed in literature for Se (IV) and Se (VI) for carbon-based adsorbents

| Adsorbent  | Se Species | $C_{in}$ ( $mg\ L^{-1}$ ) | $m/v$ ( $g\ L^{-1}$ ) | $pH^a$ | T ( $^{\circ}C$ ) | $Q_m$ ( $mg\ g^{-1}$ ) | Ref. |
|--|------------|---------------------------|-----------------------|--------|-------------------|------------------------|------|
| <i>Carbon-based adsorbents</i>                   |            |                           |                       |        |                   |                        |      |
| Fe-GAC   | Se (IV)    | 2                         | 0.3-2.8               | 5      | 25                | 2.58                   | [18] |
| Magnetic nano-particle-graphene oxide composites | Se (IV)    | 0-100                     | 1                     | 6-9    | 25                | 23.81                  | [19] |
|  | Se (VI)    | 0-100                     | 1                     | 6-9    | 25                | 25.51                  |      |

$C_{in}$  - initial concentration range;  $m/v$  – adsorbent dosage; T - temperature, <sup>a</sup>initial pH

Different graphene-based adsorbents were studied for different types of pollutants, including heavy metals, anions, dyes, and other organic pollutants [45, 46, 47]. The hydrophilic monolayer graphene oxide has a large specific surface area, so that it is easy to change the hydroxyl and carboxyl functional groups on the surface.

Modification of graphene oxide sheets with magnetic iron oxide nanoparticles was performed and this material (magnetic nanocomposite of graphene oxide) was used to remove selenium (IV) and (VI) from water [19]. The adsorbent is dosed in the amount of 1  $g\ of\ L^{-1}$ , the percentage of removal is from 80% to almost 100% at concentration of 300  $mg\ of\ L^{-1}$  Se (IV) and Se (VI) in solution. In the pH range of

2–10, it did not have a significant effect on Se (IV) adsorption, but at pH 11, a drastic drop in percentage of removal was observed. However, in the adsorption of Se (VI), a gradual decrease in the percentage of removal with increasing pH value along the entire studied range was observed. By the equilibrium tests performed at pH values from 6 to 9, the adsorption capacity of 23.8  $mg\ g^{-1}$  and 15.1  $mg\ g^{-1}$  for Se (IV) and Se (VI), respectively, was shown. Important advantages of adsorption by the magnetic nanocomposite graphene oxide are a high percentage of removal for both Se oxyanions, high rate of desorption and rapid separation of solid / liquid components (external magnetic field),k Table 2

### 3 BIOSORBENTS AND ADSORBENTS OBTAINED FROM NATURAL WASTE

In addition to the commercial and synthetic adsorbents, many other materials were investigated as the unconventional adsorbents to remove contaminants from water. The aim of this research is to find a cheap (low-cost) alternative to the traditional adsorbents, avoiding the costs of their preparation (and regeneration) and taking advantage of waste and natural readily available materials. Some studies have reported the use of raw materials, but further treatments were carried out to produce the adsorbents with improved properties [48].

Agricultural waste, used to prepare the carbon sorbent by treatment with hot sulfuric acid are: peanut shell [20, 21] and rice shell. This treatment partially oxidizes cellulose and hemicellulose and creates functional groups (-COOH and -OH) on the surface of

adsorbent. Increasing the pH value from 1.5 to 7, leads to a gradual decrease in the adsorption of Se (IV) in both adsorbents. The maximum sorption capacities were in the range of 24 - 43 mg g<sup>-1</sup> for adsorbent obtained from peanut shell and 26 - 41 mg g<sup>-1</sup> for adsorbent obtained from rice shell [20, 21], at pH 1.5 and different temperatures (25-45°C), with higher adsorption at higher temperatures. The scanning electron microscopy (SEM) and XRD analysis showed the presence of elemental selenium as particles on the sorbent surface, indicating the reduction of Se (IV) to Se (0), which is developed on the sorbent surface. The physico-chemical tests indicate that the carbon oxidation has occurred on the surface of peanut shells and rice shells treated with sulfuric acid, Table 3.

**Table 3** Adsorption capacities ( $Q_m$ ) listed in literature for Se (IV) and Se (VI), on waste materials and biosorbents

| Adsorbent                                 | Se Species | $C_{in}$ (mg L <sup>-1</sup> ) | m/v (g L <sup>-1</sup> ) | pH <sup>a</sup> | T (°C) | $Q_m$ (mg g <sup>-1</sup> ) | Ref. |
|---|------------|--------------------------------|--------------------------|-----------------|--------|-----------------------------|------|
| <i>Waste materials and biosorbents</i>    |            |                                |                          |                 |        |                             |      |
| Sulfuric acid-treated peanut shells (dry) | Se (IV)    | 25-250                         | 2                        | 1.5             | 25     | 23.76                       | [20] |
| Sulfuric acid-treated rice husk (dry)     | Se (IV)    | 25-250                         | 2                        | 1.5             | 25     | 25.51                       | [21] |
| Cladophora hutchinsiae (green algae)      | Se (IV)    | ~0-300 <sup>b</sup>            | 8                        | 5               | 20     | 74.9                        | [22] |
| S. cerevisiae dried biomass               | Se (IV)    | ~0-120 <sup>b</sup>            | 2                        | 5               | 25     | 39.02                       | [23] |
| Fish scales                               | Se (IV)    | 0.005-0.02                     | -                        | 5               | 30     | 0.67                        | [9]  |
| Hydroxyapatite (fish-scale)               | Se (IV)    | 0.005-0.02                     | -                        | 5               | 30     | 1.58 <sup>c</sup>           |      |
| G. lucidum mushroom                       | Se (IV)    | ~0-40 <sup>b</sup>             | 7                        | 5               | 20     | 127                         | [24] |
| Chitosan                                  | Se (IV)    | 0.005-0.02                     | -                        | 5               | 30     | 1.92 <sup>c</sup>           | [9]  |

$C_{in}$  - initial concentration range; m/v – adsorbent dosage; T - temperature, <sup>a</sup>initial pH; <sup>b</sup>equilibrium concentrations (estimated from the graphs); <sup>c</sup>maximum adsorption amount obtained experimentally, at the higher equilibrium concentration (20 µg L<sup>-1</sup>).

Another natural waste, fish scales, was used as a precursor for the preparation of hydroxyapatite nanocrystals by the alkaline heat treatment [9]. This material showed  $\text{pH}_{\text{ZPC}}$  of 7.86 and a higher specific surface area and pore volume than commercial hydroxyapatite. Selenite adsorption was favored in the pH range between 3 and 6. The maximum adsorption capacity is  $1.94 \text{ mg g}^{-1}$  at  $30^\circ\text{C}$ , according to the Langmuir model. The results of studies concerning the use of fish scales (untreated), chitosan and commercial hydroxyapatite showed that for these adsorbents the adsorption equilibrium is better described by the Freundlich model than by the Langmuir model. However, the Freundlich model did not give very good matches for chitosan and fish scales.

Nettem and Almusallam (2013) [49] studied the adsorption of Se (IV) by red fungus (*Ganoderma lucidum*). Biosorption was rapid (completed in 90 minutes), and the best effect was achieved at pH 5. At the initial Se concentration of  $10 \text{ mg L}^{-1}$ , the adsorbent was dosed in the amount of  $7 \text{ g L}^{-1}$  and optimal pH value of 5, and the removal of Se decreased with increasing temperature by 97% ( $20^\circ\text{C}$ ) at 74% ( $40^\circ\text{C}$ ). The data obtained by the Langmuir and Freundlich models matched well with the experimental data on adsorption equilibrium. The Langmuir model predicted a single-layer and adsorption capacity of  $126.99 \text{ mg g}^{-1}$ , although the maximum experimental adsorbed amount is about  $70\text{--}80 \text{ mg g}^{-1}$  for the studied equilibrium states, Table 3.

The mushroom (*Ascomycota*) was tested for removal the both types of selenium, Se (IV) and Se (VI) [50], where the removal efficiency was 78% for selenite and 28% for selenate.

Biomass obtained from water weeds: water hyacinth (*Eichhornia crassipes*) and small lentils (*Lemna minor*) were tested for the removal of Se (VI) from very dilute solutions ( $20 \text{ mg L}^{-1}$ ) [51]. The maximum adsorption capacity was at pH 4 (estimated

under static conditions). Also, the biosorption capacities of *Eichhornia crassipes* and *Lemna minor*, when tested in the horizontal flow columns, were  $0.135$  and  $0.743 \text{ mg g}^{-1}$ , respectively.

A dried biomass - baker's yeast (*Saccharomyces cerevisiae*) was tested for selenium removal. It is widespread and used in food and beverage production, easy to grow (without complicated fermentation techniques), and also occurs as a by-product from the fermentation industry [51]. Khakpour et al. (2014) tested *Saccharomyces cerevisiae* as an adsorbent for Se (IV) and found that the optimal pH value was 5 (test range 2–8), adsorption capacity  $12.5 \text{ mg g}^{-1}$  (initial Se concentration  $50 \text{ mg L}^{-1}$ , adsorbent dose  $2 \text{ g L}^{-1}$ , temperature  $25^\circ\text{C}$ ). The maximum adsorption capacity was  $39.0 \text{ mg g}^{-1}$ , calculated by the Sips model, which is a combination of the Langmuir - Freundlich isotherm parameters. The authors proposed a two-step process to improve percentage of Se (IV) removal from aqueous solution and improved biomass utilization. On the basis of the initial Se concentration of  $50 \text{ mg L}^{-1}$ , the total removal efficiency of 96% is expected in this two-step process, Table 3.

Algae treatment can be performed by two methods as follows: adsorption on the biomass of inanimate and living algae. The use of algae treatment for selenium biosorption is a promising biotechnology, after obtaining the successful results for heavy metals (such as zinc, lead, cobalt, cadmium, nickel). Tests on green algae (*Ulva rigida* and *Cladophora sericea*) from the Romanian Black Sea coast for Se removal have shown that the removal rate ranges between 80 and 95% within 5–7 h, with the initial Se concentration of  $25 \text{ mg L}^{-1}$  [52]. The adsorption capacity of algae for selenite and selenate is  $0.5 \text{ mg g}^{-1}$  and  $0.2 \text{ mg g}^{-1}$ , respectively.

Green microalgae (*Chlorella vulgaris*) were used in testing the biological treatment of selenate and selenite removal, and showed a high removal efficiency of 89%,

for the initial Se concentration of 1580 mg L<sup>-1</sup>, while the concentration of selenate and selenite in wastewater was 20 and 10 ppb [53].

Marine algae biosorption has shown to be effective in removal the heavy metal cations from wastewater. The high binding capacity of metals to the marine algae is the result of presence the polysaccharides, proteins or lipids on the cell wall surface, which contain functional groups such as amino, hydroxyl, carboxyl and sulfate, which act as binding sites for metals

Marine macroalgae are classified into three species: brown (*Phaeophita*), red (*Rhodophita*) and green (*Cladophora hutchinsiae*) [54]. By studying the biosorption of Se (IV) of green algae (*Cladophora hutchinsiae*), the removal efficiency was obtained between 70 and 96%, the biosorbent was dosed in the amount of 8 g L<sup>-1</sup>, the initial concentration of Se of 10 mg L<sup>-1</sup>, temperature 20°C, the pH value is in the range of 2 to 8, with maximum removal at pH 5. In acidic conditions, low selenium biosorption is explained by the fact that neutral species (H<sub>2</sub>SeO<sub>3</sub>) cannot undergo electrostatic interaction with algae. The increase in temperature showed a decrease in removal efficiency, from 96% (20°C) to 60% (50°C). The kinetics of biosorption were quite well described by a pseudo model elsewhere of the order of different temperatures. The maximum biosorption capacity of this green algae according to Langmuir was calculated to be 74.9 mg g<sup>-1</sup> which corresponded to the steady state. Within the tested concentration range, the maximum adsorption capacity, obtained from the experiments, is about 50–60 mg g<sup>-1</sup>. These values are very important considering that a cheap and easily accessible material was used. Also, these marine algae have been shown to be very stable during the regeneration process, as after ten phases of biosorption - desorption, there is a reduction of about 20% recovery of Se (IV) [22], Table 3.

Selenium and chromium biosorption and interaction with sulfur (S) of marine algae (*Chlorella vulgaris*) were investigated, which showed the highest efficiency of Se removal (95.24%), followed by S (80.01%) and Cr (59.91%). When algae were simultaneously exposed to all elements, the opposite results were obtained with the order of affinity as follows: Cr > S > Se. After exposure, 62.20% of the accumulated Se continuously evaporates into atmosphere, while 34.16% of Cr is released into water [55]. Decreased chlorophyll content and photosynthetic activity indicate the inhibitory effects of Se and Cr on algae, which were apparently worn out over time [56].

## CONCLUSION

Selenium in small quantities is a nutritionally important element, but larger amounts are toxic and have side effects in humans and animals. This problem become very important for environmental protection and therefore prevention, control and removal of selenium from water are very important. Selenium occurs in water and wastewater from natural sources, but also due to the anthropogenic activities such as agriculture, mining, oil refineries and coal combustion, the typical concentrations range from a few micrograms per liter to 30 mg L<sup>-1</sup>. Adsorption is a widely used procedure in water technology for removal the dissolved substances - pollutants. It can be used in drinking water treatment and wastewater treatment systems.

The following can be concluded from the given literature review:

- The adsorption effect is better for acidic and slightly acidic conditions. The typical pH value for wastewater from mining and desulphurization of flue gases is acidic, so the pH is not a worrying and limiting factor for adsorption in the treatment of these types of water. In agricultural water, the adsorption



tion may not be an appropriate method or great care must be taken in a choice of adsorbent. In general, a pre-adjustment of pH value for the adsorption process is expensive and is not in line with the goal of finding an economical method for selenium removal.

- The temperature effect does not have a great influence on the adsorption process.
- The effect of competing ions, such as phosphates and sulfates, can have a major impact on the adsorption process. It has been observed that these ions have a great effect on reduction the selenium adsorption, because they often occur in water and wastewater in high concentrations. Based on this, the practical application of any adsorbent should be carefully studied. If the effect of competing ions is large, the disadvantage can be remedied by introduction the pretreatments to remove sulfates and phosphates by precipitation or a multi-stage adsorption process.
- Some adsorbents (binary metal oxides, single layer hydroxides (LDH), adsorbents based on natural materials) showed the good adsorption capacities and relatively fast adsorption kinetics.
- The natural waste and biosorbents were tested in the laboratory, where it was necessary to prepare these materials to improve the adsorption properties, study the effects of selenium concentration in solution and amount of adsorbent, assess the effect of competitive ions and metals in solution, and finally apply the process in columns with fixed layer and continuous flow.

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