

# Removal Of Selenium From Polluted Water By Fexoy-Sucrose Foams

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**Abstract** A series of iron-based carbon foams were evaluated as adsorbents for selenium removal from aqueous solutions. The carbon foams were prepared using sucrose as a precursor and then impregnated with different iron oxides/hydroxides. The efficiency of iron-based sucrose foams was compared to that achieved with a commercial activated carbon impregnated by the same method. The sucrose foams showed removal percentages of 10-90% depending on the synthesis process and pH (2-7). Acidic pH enhanced the adsorption of Se increasing the removal percentages up to 80-90%. The chemical and textural properties of the carbon support play a fundamental role in the type of iron species loaded, and hence in the adsorption of selenium. The morphology and dispersion of the iron nanoparticles can also influence the adsorption processes. Furthermore, the sucrose foams developed in this study could be an efficient and sustainable method to remove other metalloids from wastewater.

**Keywords:** adsorption; inorganic selenium; carbon foams; sucrose; iron nanoparticles

## 1. Introduction

Selenium (Se) is a naturally occurring metalloid element, which is essential to human and other animal health in trace amounts, but is harmful in excess (Fordyce, 2013). Its deficiency or overabundance may cause serious health problems (Lenz and Lens, 2009). Selenium has emerged as an important contaminant in aqueous medium. Once in the aquatic environment, it can rapidly attain levels that are toxic to fish and wildlife because of bioaccumulation in food chains and resultant dietary exposure (Lemly, 2004). Anthropogenic activities, such as mining, agricultural and metal processing industries are the main sources of Se released to the environment (Santos et al., 2015).

Technologies used in the treatment of wastewater include membrane filtration, ion-exchange, coagulation-flocculation precipitation, electrocoagulation and adsorption (Okonji et al., 2021). These methods have disadvantages such as high cost, operational complexity and large volumes of Se-containing sludge from the post-treatment (Okonji et al., 2021). However, adsorption is currently receiving great attention because it is considered a promising technique for the industrial application in terms of high efficiency, low-cost of implementation and easy operational design (Howarth et al., 2015; Okonji et al., 2020).

Although numerous materials such as zerovalent iron (ZVI), metal-organic frameworks, zeolites and graphene oxide composites have been found to be effective for Se adsorption from aqueous media (Fu et al., 2014; Halalshah et al., 2022; Howarth et al., 2015; Okonji et al., 2021, 2020), activated carbons are undoubtedly the most used adsorbents for water purification. However, they may present low efficiencies for some inorganic species such as Se(VI) and high costs for production and regeneration (Okonji et al., 2021). The capacity for Se removal enhances when activated carbons are loaded with Fe species (Ying et al., 2020; Zhang et al., 2018, 2008).

This study proposes the use of Fe/carbon foams-based composites as an attractive and novel alternative to the adsorbents studied so far for the removal of Se from the aqueous medium. Carbon foams are materials highly versatile in terms of design, texture and chemical properties (Inagaki et al., 2014). They are characterized by their macroporosity with interconnected open pores, but they can also present micro- and mesoporosity depending on the synthesis process. If the microporous and macroporous structure are properly combined these materials can become excellent adsorbents (Stojanovska et al., 2018). The interconnected porous framework provides not only an excellent support for the anchoring of iron oxides/hydroxides on the surface but also may increase mass transfer and reduce pressure drop in fixed-beds. In addition, the carbon foams developed in this study were prepared using sucrose as sustainable precursor. The results were compared with an activated carbon impregnated with iron species.

## 2. Experimental part

### 2.1. Materials

Two materials were selected as supports for the iron oxides/hydroxides: an activated carbon (AC) and sucrose-based carbon foams (SFs). The AC was the commercial activated carbon Norit RB3. The SFs were elaborated using commercial sucrose as carbon precursor, and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (0.3 wt% Fe) or phytic acid (25 wt%) as additives.

The preparation of SFs involves three steps: (i) the preparation of a caramel by heating sucrose with the additive up to 170 °C; (ii) after cooling, the caramel was foamed in an oven with air circulation heating up to 250

°C, and (iii) carbonization of the green foams. The experimental conditions employed during foaming will depend on the additive. Briefly, the caramel was heated up to 150 °C for 2.5 h and then the temperature was increased to 250 °C for 3 h. Subsequently, the green foam was carbonized at 800 °C for 2 h under an Ar flow or subjected to a CO<sub>2</sub>-physical activation at 900 °C. The latter consisted of heating from room temperature to 800 °C under Ar and then switching to CO<sub>2</sub> stream, heating up to 900 °C and holding this temperature for 2 h. The heating rate was set at 5 °C min<sup>-1</sup> throughout both thermal treatments. The products were labelled as SF and SF<sub>CO<sub>2</sub></sub>. Foam SF was also subjected to an oxidative treatment by means of a 2M solution of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in H<sub>2</sub>SO<sub>4</sub> (1M) during 5h under reflux. The resultant foam was collected by filtration and washed with abundant Milli-Q water. The oxidized sample was denoted SF<sub>ox</sub>. When phytic acid was used as additive, foaming was performed in a similar way, but the residence time at 250 °C was increased to 20 h. After that, the foam was subjected to the CO<sub>2</sub>-physical activation at 900 °C. Finally, the resultant foam was washed with hot Milli-Q water to remove any phosphorous residue. The sample was denoted SF<sub>phy-CO<sub>2</sub></sub>. Carbon supports were impregnated with 10 wt% Fe by means of a solution of iron sulfate heptahydrate (FeSO<sub>4</sub>·7H<sub>2</sub>O) and sodium acetate (CH<sub>3</sub>COONa) in MilliQ water, according to a method detailed in a previous study (López-Toyos et al., 2023). The iron-carbon composites prepared were designated as XFe, where X is the carbon support (AC, SF, SF<sub>ox</sub>, SF<sub>CO<sub>2</sub></sub>, SF<sub>phy-CO<sub>2</sub></sub>). For comparison purposes, both sucrose foams and the activated carbon were ground to a size of 0.2- 0.5 mm before the impregnation step.

### 2.2. Characterization of carbon foams and activated carbon

Elemental analysis of the carbon supports was carried out using a LECO CNH-2000 for C, H and N, and a LECO VTF-900 for direct determination of oxygen. Temperature programmed desorption (TPD) experiments were carried out on a chemisorption analyzer equipped with a mass spectrometer. The textural properties of the materials were analyzed using a volumetric adsorption system. The specific surface area was determined by the standard BET method, using N<sub>2</sub> adsorption data at -196 °C. The total pore volume, V<sub>t</sub>, was obtained from the amount of N<sub>2</sub> adsorbed at a relative pressure of 0.985, and the micropore volume, V<sub>micro</sub>, was determined by fitting the Dubinin-Radushkevich (DR) equation to the N<sub>2</sub> adsorption isotherm. The mesopore volume, V<sub>meso</sub>, was calculated as the difference between V<sub>t</sub> and V<sub>micro</sub>. The distribution and morphology of the iron nanoparticles was studied by scanning electron microscopy (SEM), whereas the iron species were identified by X-ray diffraction (XRD).

### 2.3. Batch adsorption experiments

The adsorbents AC and SFs (0.4 g, dosage 10 g L<sup>-1</sup>) were added into a Se standard solution. An initial Se

concentration of 25 mg L<sup>-1</sup> was used for the experiments to evaluate the pH effect (2 and 7). All the experiments were conducted using glass bottles of 50 mL capacity and the pH was measured using a Seven Multi pHmeter (Mettler Toledo). Mixing was maintained using a temperature-controlled orbital shaker at ambient temperature and a constant shaking speed of 100 rpm during 72 h. The initial pH of the solution was adjusted by adding HCl or NaOH (0.1M). The collected samples were filtered using a 0.45 μm nylon syringe filter and further stored at 4 °C prior to analysis by inductively coupled plasma mass spectrometry (ICP-MS). All the experiments were conducted in duplicate. The overall error for each observation was lower than 5%.

## 3. Results and discussion

### 3.1. Characteristics of the sucrose foams versus the activated carbon

The carbon materials used as starting materials for supporting iron nanoparticles have different chemical and structural properties. The textural parameters are summarized in Table 1. The reference material AC is an essential microporous material with a high BET surface area (1183 m<sup>2</sup> g<sup>-1</sup>). Unlike activated carbons, carbon foams may exhibit a multimodal porosity (macro-, meso- and microporosity). The support SF shows a lower BET surface (306 m<sup>2</sup> g<sup>-1</sup>) with a similar fraction of micro- and mesopores. The presence of macropores in SF foams can be beneficial for fixed-bed, as micro/mesopores can increase selenium adsorption due to their larger contact area. The oxidation of SF (SF<sub>ox</sub>) led to a degradation in its textural parameters, decreasing the S<sub>BET</sub> by 30% (214 m<sup>2</sup> g<sup>-1</sup>). By contrast, the physical activation with CO<sub>2</sub> produced an increase in the specific BET surface area (742 m<sup>2</sup> g<sup>-1</sup>), as well as in micro- and mesopore volume.

**Table 1.** Textural properties of the raw activated carbon and the sucrose foams.

Sample	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	V <sub>t</sub> (cm <sup>3</sup> g <sup>-1</sup> )	V <sub>micro</sub> (cm <sup>3</sup> g <sup>-1</sup> )	V <sub>meso</sub> (cm <sup>3</sup> g <sup>-1</sup> )
AC	1183	0.53	0.45	0.08
SF	306	0.24	0.13	0.11
SF <sub>ox</sub>	214	0.13	0.09	0.04
SF <sub>CO<sub>2</sub></sub>	742	0.72	0.31	0.41
SF <sub>phy-CO<sub>2</sub></sub>	1042	0.43	0.43	-

The presence of oxygen functionalities on the surface of the carbon supports can enhance the anchoring of iron oxides. Sample AC has a moderate oxygen content (14%). TPD experiments reveal that most of this oxygen corresponds to basic and thermally stable groups, such as carbonyls and/or quinone-like structures, with a minor fraction of acidic carboxyl groups. The oxygen percentage for the foam SF was much lower (1.6%), but the oxidation

treatment led to a remarkable increase in its content, giving rise to values up to 10.3%. The oxygen groups incorporated correspond mainly to lactones and anhydrides. Physical activation does not produce significant changes in the oxygen functional groups in sample SF<sub>CO2</sub> (1.2%), but a slight increase was observed for SF<sub>phy-CO2</sub> (2.5%), probably due to the incorporation of a small amount of phosphate groups (Shi et al., 2019).

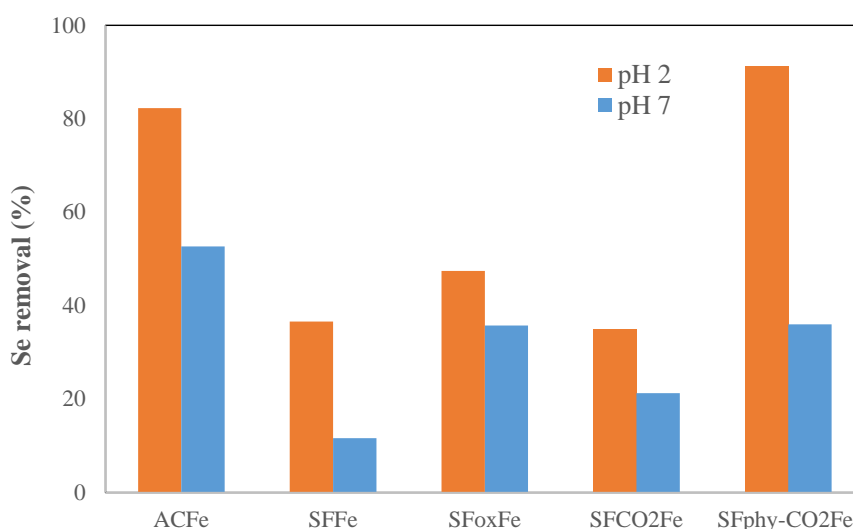
Iron was found mainly in the form of nanoneedles, nanorods and pseudocubic crystals. The iron composition (i.e., iron hydroxides and/or iron oxides) plays a fundamental role in Se adsorption (Zhang et al., 2018). Therefore, iron species were evaluated in this preliminary study by XRD. A mix of hydroxides (goethite ( $\alpha$ -FeOOH) /lepidocrocite ( $\gamma$ -FeOOH)) and oxides with a spinel structure (magnetite (Fe<sub>3</sub>O<sub>4</sub>)/maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>)) were deposited on sample ACFe, whereas for sample SFFe, the main contribution corresponded to iron oxides (magnetite/maghemite). In the case of sample SF<sub>ox</sub>Fe, the oxidative treatment caused a transformation of the iron oxide species to hematite. A small amount of goethite was also observed in the oxidized sample. On the other hand, the gasification process mainly led to the formation of lepidocrocite in samples SF<sub>CO2</sub>Fe and SF<sub>phy-CO2</sub>Fe. From these results, it can be inferred that the iron species deposited on the carbon supports will be determined by their chemical surface.

### 3.2. Screening of iron-based carbon foams for adsorption of selenium

Figure 1 shows the efficiency of the AC and SFs impregnated with iron for Se removal. ACFe and

SF<sub>phy-CO2</sub>Fe achieved the highest Se removal from a 25 mg L<sup>-1</sup> solution. Indeed, ACFe and SF<sub>phy-CO2</sub>Fe adsorbed between 50-80% and 40-90% of the Se present in the respective solutions, depending on pH. These results confirm that high values of S<sub>BET</sub> (> 1000 m<sup>2</sup> g<sup>-1</sup>) and micropores (> 0.40 cm<sup>3</sup> g<sup>-1</sup>) are beneficial for Se adsorption.

The adsorption of inorganic Se species onto Fe oxides/hydroxides occurs mainly by electrostatic interaction between the negatively charged Se oxyanions and the partially protonated groups of the Fe oxides/hydroxides depending on pH (Okonji et al., 2020). As can be observed in Figure 1, the adsorption of Se was favored by acidic pH for all the adsorbents tested. This effect is the consequence of an increase in the positive charge density of the adsorbent surface at lower pH (Rovira et al., 2008). In acidic conditions, SF<sub>phy-CO2</sub>Fe shows the best performance. The high adsorption capacity can be attributed to a synergic effect of the iron species and the phosphorous functionalities introduced by phytic acid. However, a drastic drop in its efficiency was observed when the pH was increased to neutral conditions. It must be taken into account that, in general, phosphorous-containing carbons show an acidic PZC, so at pH 7 the carbon surface would be negatively charged (Puziy et al., 2020), decreasing the Se adsorption. On the other hand, it should be mentioned that the SF<sub>ox</sub>Fe sample showed a Se removal capacity higher than foams SFFe and SF<sub>CO2</sub>Fe, and comparable to SF<sub>phy-CO2</sub>Fe at pH 7, despite its low S<sub>BET</sub>. These results suggest that hematite is more efficient than iron hydroxides at neutral pH.



**Figure 1.** Effect of pH on Se removal by AC and SFs (all the experiments were conducted at 25 °C with an initial concentration 25 mg L<sup>-1</sup> and dose 10 g L<sup>-1</sup>)

## 4. Conclusions

Carbon foams derived from sucrose and impregnated with iron species may be a sustainable method for Se

removal from aqueous solutions. Carbon supports with appropriated textural properties (micro-, meso- and macroporosity) and chemical characteristics (oxygen or phosphorous groups) were successfully fabricated via a facile route employing low-cost biosustainable resources. The carbon sorbents SF<sub>ox</sub>Fe and SF<sub>phy-CO<sub>2</sub></sub>Fe combined with a homogeneous distribution of iron nanoparticles (FeO(OH) and Fe<sub>x</sub>O<sub>y</sub>) may be promising candidate materials for Se adsorption. Further research will be focused on the effects of adsorbent dosage and Se initial concentration in a wide pH range, their efficiencies to recover Se in different oxidation states and the kinetic of adsorption.

### Acknowledgments

This work was funded by the research projects PID2020-113558RB-C43 (MCIN/ AEI/10.13039/501100011033) and IDI/2021/000031. The authors are grateful for the funding received for the hiring of Lucía López-Toyos through Programa Investigo, Plan de Recuperación, Transformación y Resiliencia, Ministry of Labor and Social Economy (Government of Spain).

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