



## Full Length Article

# Potential of iron-based composites derived from sucrose foam for mercury removal and safe recovery

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## ABSTRACT

Although various methods for removal of elemental mercury from gas streams have been proposed, the control of mercury emissions to the environment from anthropogenic sources, mainly coal-fired power plants, remains unresolved in many countries worldwide. Meanwhile, the Minamata Convention and the IED of the European Commission continue to impose restrictions for its control and mitigation. In this work, a new material based on a sucrose foam impregnated with iron oxide nanoparticles has been developed for the adsorption of elemental mercury from flue gases allowing the regeneration of the material and the recovery of elemental mercury. Of the different iron oxides supported on the sucrose foam,  $\alpha\text{Fe}_2\text{O}_3$  nanoneedles were found to be the most efficient in capturing mercury through a Mars-Maessen mechanism and the forming of  $\text{HgO}$ . The adsorbents developed proved to be effective in the presence of  $\text{SO}_2$  and  $\text{H}_2\text{O}$ , with the  $\text{O}_2$  present in the gas playing a key role in the regeneration of the material. From the results found sucrose foam-based  $\alpha\text{Fe}_2\text{O}_3$  composite could be an attractive alternative to traditional non-regenerable activated carbons, reducing costs and being environmentally sustainable.

## 1. Introduction

Mercury is emitted from different natural and anthropogenic sources, travelling short or long distances depending on its chemical forms, to finally be locally and globally deposited. High levels of mercury exposure can produce harmful effects on the nervous, digestive and immune systems [1]. Therefore, mercury reduction is an essential step for a global environmental protection. This concern is reflected in the so-called Minamata Convention on Mercury, which came into force in 2017 [2]. All parties ratifying the Convention are required to control and reduce mercury emissions from the main anthropogenic sources (fossil fuel combustion, non-ferrous metal smelting, cement production, wastes incineration, etc). Although the Convention does not specify reduction amounts nor control technologies, several measures, such as the best available techniques (BAT) and multipollutant control technologies, are required. The necessary levels of reduction of mercury emissions from the main anthropogenic sources are included in a directive of the European Parliament [3] and in the US Environmental Protection Agency [4].

Mercury is a trace impurity in coal that, when burned, can be released into the environment. Although different economic and

technological scenarios are contemplated by countries around the world, the global consumption of coal in the coal-fired power plants does not seem to decrease greatly during 2020–2030 [5–7]. Global coal consumption was estimated considering the development of power industry and clean energy production and the standard coal consumption for electric power production worldwide.

It is estimated that the distribution of mercury species in the total mercury emission to the air from power plants is: 87% elemental mercury ( $\text{Hg}^0$ ), 5% oxidized mercury ( $\text{Hg}^{2+}$ ) and 8% mercury bound to particulate matter ( $\text{Hg}_p$ ) [8,9]. The removal of  $\text{Hg}^0$  is the main unsolved concern.

The use of certain sorbents and catalysts that oxidize mercury is an efficient technology for the retention of  $\text{Hg}^0$  from coal-fired power plants [10]. Many researchers have studied  $\text{Hg}^0$  oxidation by several catalysts and different mechanisms have been proposed [11,12]. Nowadays, the highly volatile and water-insoluble  $\text{Hg}^0$  is mostly reduced by activated carbon injection and selective catalytic reduction (SCR) coupled with flue gas desulphurization (FGD) units [13,14]. However, the injection of activated carbon can limit the use of fly ash in concrete production due to an increase in its carbon content [13,15]. The incorporation of magnetic materials ( $\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$ ) in a sorbent

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would allow the separation of the fly ashes by applying an external magnetic field [16,17]. Efficiencies close to 90% have been achieved using magnetic-based attapulgite sorbents depending on the gases present in the gas stream [18,19]. On the other hand, activated carbon injection has other drawbacks in terms of environmental protection, such as the regeneration process. Traditional sulfur- or halogen-impregnated activated carbons [20], in which  $\text{Hg}^0$  is mainly retained through chemical adsorption, are not regenerable sorbents, leading to the generation of new mercury-contaminated waste after depletion.

The most studied regenerable sorbents to date are: 1) noble metals-based materials and 2) metal oxides-based materials [21–23]. Metals and metal oxides are deposited on supports with the appropriate physical, chemical and textural properties for an adequate dispersion of the additive, as well as for gas circulation. Activated carbons, carbon monoliths and carbon foams, among others, have been used as carbonaceous supports [24–26]. However, and taking into account the new environmental policies [27], the precursors used as supports for new carbon materials will have to be not only economically viable but also environmentally sustainable and remain within the framework of a circular economy. In many cases, this is not an easy task to accomplish.

Noble metals such as gold (Au), silver (Ag), and palladium (Pd) have the ability to amalgamate with  $\text{Hg}^0$ . A sorbent loaded with any of them, can be easily regenerated after use by heating, with the concomitant condensation and isolation of  $\text{Hg}^0$  [28–30]. In order to reduce the costs associated with the use of noble metals, materials doped with metal oxides have also been developed as regenerable sorbents, most of them based on manganese oxides ( $\text{MnOx}$ ) [31–33]. Recently, biochars doped with magnetite ( $\text{Fe}_3\text{O}_4$ ) have been proven to be effective for the capture of  $\text{Hg}^0$  in flue gas [34]. However, the possibility of regenerating the sorbent was not evaluated.

In order to solve some of the aforementioned drawbacks associated with the main sorbents used to date for  $\text{Hg}^0$  removal, in this work, a new material based on carbon foam was developed. The carbon material was impregnated with iron oxides ( $\text{FexOy}$ ) to improve the mercury adsorption capacity and to allow the regeneration of the sorbent. In addition, sucrose was used as a precursor for the carbon foam leading to an economically and environmentally sustainable sorbent. The iron-based sorbent derived from sucrose foam is developed with the intention of being regenerated and used in the flue gas stream at the end of the coal combustion cycle where most of  $\text{Hg}^{2+}$  may already have been retained, assuming that it will be used in a power plant in where DeNox, particles control and desulfurization devices are operating.

## 2. Materials and methods

### 2.1. Carbon foam preparation and characterization

A carbon foam (SF) was elaborated using commercial sucrose as precursor and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.3% wt Fe) as foaming enhancer and activating agent. The first step to obtain the foam consists of the preparation of a caramel by heating sucrose up to 170 °C. After cooling, the caramel was placed in an oven with air circulation for the actual foaming process, which was performed in two successive steps: (i) heating up to 150 °C at 2 °C  $\text{min}^{-1}$  and (ii) heating up to 250 °C at 2 °C  $\text{min}^{-1}$ . The residence times at each temperature were 2.5 and 3 h, respectively. The resultant foam was carbonized for 2 h at 800 °C in a horizontal tubular furnace, under an argon flow of 50  $\text{mL min}^{-1}$  and a heating rate of 5 °C  $\text{min}^{-1}$ .

Two impregnation methods, involving different thermal treatments, were used to obtain SFs loaded with different iron species: (A)  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{CH}_3\text{COONa}$  in water [35] and (B)  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in ethanol [36]. The resultant SFs were named according to the iron species present: SF- $\text{FeOOH}$  (method A), SF- $\alpha\text{Fe}_2\text{O}_3$  (method A followed by thermal treatment at 300 °C), SF- $\text{FexOy}$  (method B with carbonization at 500 °C) and SF- $\text{Fe-FexOy}$  (method B with carbonization at 800 °C). At first, the SFs were loaded with 20 wt% Fe. Afterwards, the SF displaying higher

mercury retention capacity was also loaded with 5, 10 and 30 wt% Fe, in order to evaluate the effect of iron concentration.

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).

The magnetic properties of the SFs were determined using a Microsense EV9 vibrating sample magnetometer (VSM), measuring the magnetization of the SF versus the magnetic field applied between 22 and –22 kOe at 300 K. The variation of the magnetization versus temperature was also determined for an applied magnetic field of 1 kOe.

The specific surface area of carbon foams was determined by the standard BET method using  $\text{N}_2$  adsorption data. The total pore volume,  $V_t$ , was obtained from the amount of  $\text{N}_2$  adsorbed at a relative pressure of 0.975, and the micropore volume,  $V_{\text{micro}}$ , was determined by fitting the Dubinin-Radushkevich (DR) equation to the  $\text{N}_2$  adsorption isotherm. The mesopore volume,  $V_{\text{meso}}$ , was calculated as the difference between  $V_t$  and  $V_{\text{micro}}$ . The macroporous texture of the carbon foams was determined by Hg intrusion analysis performed on Micromeritics AutoPore IV apparatus, operating at a maximum pressure of 227 MPa. The samples were outgassed at 120 °C overnight before analysis.

The surface chemical composition of the SFs was investigated by X-ray photoelectron spectroscopy (XPS). XPS analyses were carried out on a Specs spectrometer, using  $\text{MgK}\alpha$  (1253.6 eV) radiation from a double anode at 50 w. Binding energies for the high-resolution spectra were calibrated by setting C 1 s to 284.6 eV.

### 2.2. Experimental design

The mercury retention capacity of the carbon foam composites was evaluated in a fixed-bed reactor (Fig. 1), which is heated in a vertical furnace at 80 °C. The simulated flue gas consists of 15%  $\text{CO}_2$ , 6%  $\text{O}_2$ , 8%  $\text{H}_2\text{O}$  and 100 ppm  $\text{SO}_2$  in  $\text{N}_2$  (i.e., in an atmosphere relatively free of acid gases after SCR, ESP and FGD units). Elemental mercury ( $\text{Hg}^0$ ) is incorporated into the gaseous stream from a commercial permeation tube, with a concentration of 100  $\mu\text{g m}^{-3}$ . The  $\text{Hg}^0$  in the gas phase that is not retained in the fixed-bed is registered in the VM-3000 analyzer. The oxidized mercury ( $\text{Hg}^{2+}$ ) that is not retained in the sorbent is captured in an ionic exchanger resin (Dowex® 1x8), developed to selectively capture  $\text{Hg}^{2+}$  [37] and placed at the outlet of the fixed-bed. The  $\text{Hg}^{2+}$  captured in the resin was measured by using an automatic mercury analyser AMA 254. Once the adsorption cycle has finished, the sorbent is heated up to 450 °C at 2 °C  $\text{min}^{-1}$  in an inert  $\text{N}_2$  atmosphere, to regenerate the carbon foam composite. After the  $\text{Hg}^0$  adsorption–desorption cycle,  $\text{Hg}^0$  is recovered by condensation and collected in a container [28] (Fig. 1), leaving the carbon foam composite free of  $\text{Hg}^0$  and ready to be reused.

Possible mercury oxidation is also evaluated by temperature programmed desorption ( $\text{HgTPD}$ ) by comparing the mercury desorption profile of the spent adsorbent with that obtained using a reference material ( $\text{HgO}$ ). The desorption profiles are obtained by heating the sample at a rate of 50 °C  $\text{min}^{-1}$  under a  $\text{N}_2$  flow of 500  $\text{mL min}^{-1}$  [38].

## 3. Results and discussion

### 3.1. Characterization of carbon foam composites

The morphologies and microstructures of the SFs impregnated with 20 wt% Fe using different methods were first investigated by SEM. As shown in Fig. 2a, SF possesses an interconnected porous framework, which can serve as a support for the anchoring of iron oxides on the surface (Fig. 2b–f). All the SFs have a multimodal porosity, with pores ranging from micro/mesopores to macropores. The presence of macropores (Figure S1) can be beneficial for gas passing through, whereas micro/mesopores can increase mercury adsorption due to their larger contact area (Table 1). An enhanced BET surface area means more exposed active sites available for mercury adsorption. Therefore, a

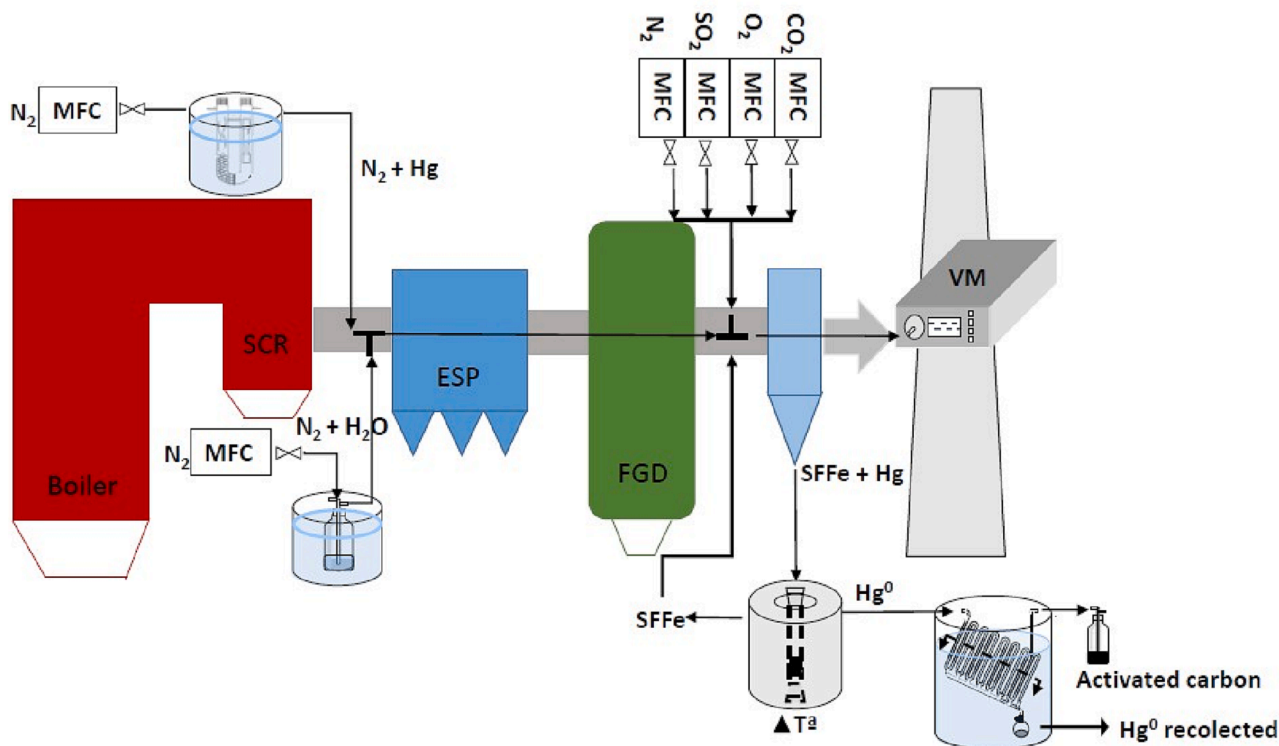


Fig. 1. Schematic diagram of the process for  $\text{Hg}^0$  removal using SFs in coal combustion flue gases.

well-developed pore structure of sorbent will presumably favor mercury removal.

SF has a BET surface area of  $306 \text{ m}^2 \text{ g}^{-1}$  and  $V_t$  of  $0.24 \text{ cm}^3 \text{ g}^{-1}$ , with a textural porosity composed of both micro and mesopores at similar ratios, 46 and 54%, respectively. The iron oxides/hydroxides are deposited coating the carbon structure of the foam (Fig. 2b-f), so it is expected that the composite foams show a reduction in their textural parameters. The results presented in Table 1 confirm slightly reductions in the BET surface area and the pore volume of the composites in comparison with the parent foam, being more pronounced in the sample impregnated with the method B and carbonized at  $500 \text{ }^\circ\text{C}$  (SF-FeOy:  $200 \text{ m}^2 \text{ g}^{-1}$  and  $0.08 \text{ cm}^3 \text{ g}^{-1}$ ) (Table 1). In SEM image (Fig. 2e) is clearly visible, that iron oxide nanoparticles tend to agglomerate in sample SF-FeOy, which may lead to blockage of mayor number of pores. When the carbonization temperature was increased to  $800 \text{ }^\circ\text{C}$  the agglomerates tend to disappear and the sample SF-Fe-FeOy showed comparable BET surface to those obtained by method A (Table 1).

As can be observed in Fig. 2b-f, the iron oxide/hydroxide nanoparticles are deposited in a wide range of morphologies, depending on the synthesis conditions (method and temperature). The method of oxidative hydrolysis with  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{CH}_3\text{COONa}$  in water favors the formation of nanoneedles (Fig. 2b-d), whereas the method with  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in ethanol promotes the formation of peanut-shaped nanoparticles (Fig. 2e-f). In addition, the iron species were different depending on the thermal treatment. The analysis by XRD (Fig. 3) revealed the presence of goethite in the sample synthesized by oxidative hydrolysis, along with other oxide phases, more specifically, oxides with spinel structure (magnetite or maghemite) (SF-FeOOH). The subsequent heat treatment of the sample at  $300 \text{ }^\circ\text{C}$  caused a transformation of the iron oxide species into hematite (Fig. 3), although their original morphology of nanoneedles was preserved (SF- $\alpha\text{Fe}_2\text{O}_3$ ) (Fig. 2c-d). Nevertheless, the presence of magnetite and/or maghemite cannot be ruled out. In the detail of the SEM image at  $5 \mu\text{m}$  (Fig. 2b) it can be observed that polyhedrons have also been formed. The iron species identified in the SFs impregnated with  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in ethanol were

the iron oxides with spinel structure, magnetite and/or maghemite (SF-FeOy), with the presence of elemental iron when the temperature of carbonization increased from  $500$  to  $800 \text{ }^\circ\text{C}$  (SF-Fe-FeOy).

A magnetic characterization was also carried out to confirm the presence of magnetite and/or maghemite in the samples. Fig. 4 shows the variation of magnetization versus temperature. A low-temperature phase transition is observed in the SFs. This corresponds to the Verwey transition, which is associated to magnetite. The presence of magnetite particles is more significant when the magnetization ( $\text{emu/g}$ ) is higher (Figure S2). It must be taken into account that the presence of elemental iron also increases the saturation magnetization. This occurs in SF-Fe-FeOy (Figure S2), in which, elemental iron has already been identified by XRD (Fig. 3). The sample SF-FeOOH shows a higher hysteresis than SF- $\alpha\text{Fe}_2\text{O}_3$  (Figure S2), indicating a higher proportion of magnetite particles in SF-FeOOH. In Fig. 4, it can also be observed that sample SF-Fe-FeOy, unlike SF-FeOy, does not show a slight drop as the temperature increases. This behavior is characteristic when the material contains elemental iron. All these results agree with those found by XRD.

The results mentioned above reveal a successful synthesis of sucrose foam with different iron species incorporated into the carbon matrix with abundant active sites for the effective adsorption of mercury. The different morphology of the iron species on the SF surface can have a significant influence on the mercury adsorption performance and the subsequent regeneration of the sorbent.

### 3.2. Effect of iron species on mercury adsorption

Fig. 5 shows the mercury adsorption curves for the SFs. As explained in the previous section, the SFs contain different iron species depending on the impregnation method and the heat treatment. The curves represent the outlet/inlet Hg concentration ratio ( $C/C_0$ ) versus time. The mercury adsorption capacities fell into the following increasing order: SF-FeOOH  $\leq$  SF-Fe-FeOy  $<$  SF-FeOy  $<$  SF- $\alpha\text{Fe}_2\text{O}_3$ , the later achieving an efficiency of 100% ( $C/C_0 = 0$ ) and a mercury retention capacity of  $90 \pm 10 \mu\text{g g}^{-1}$ .

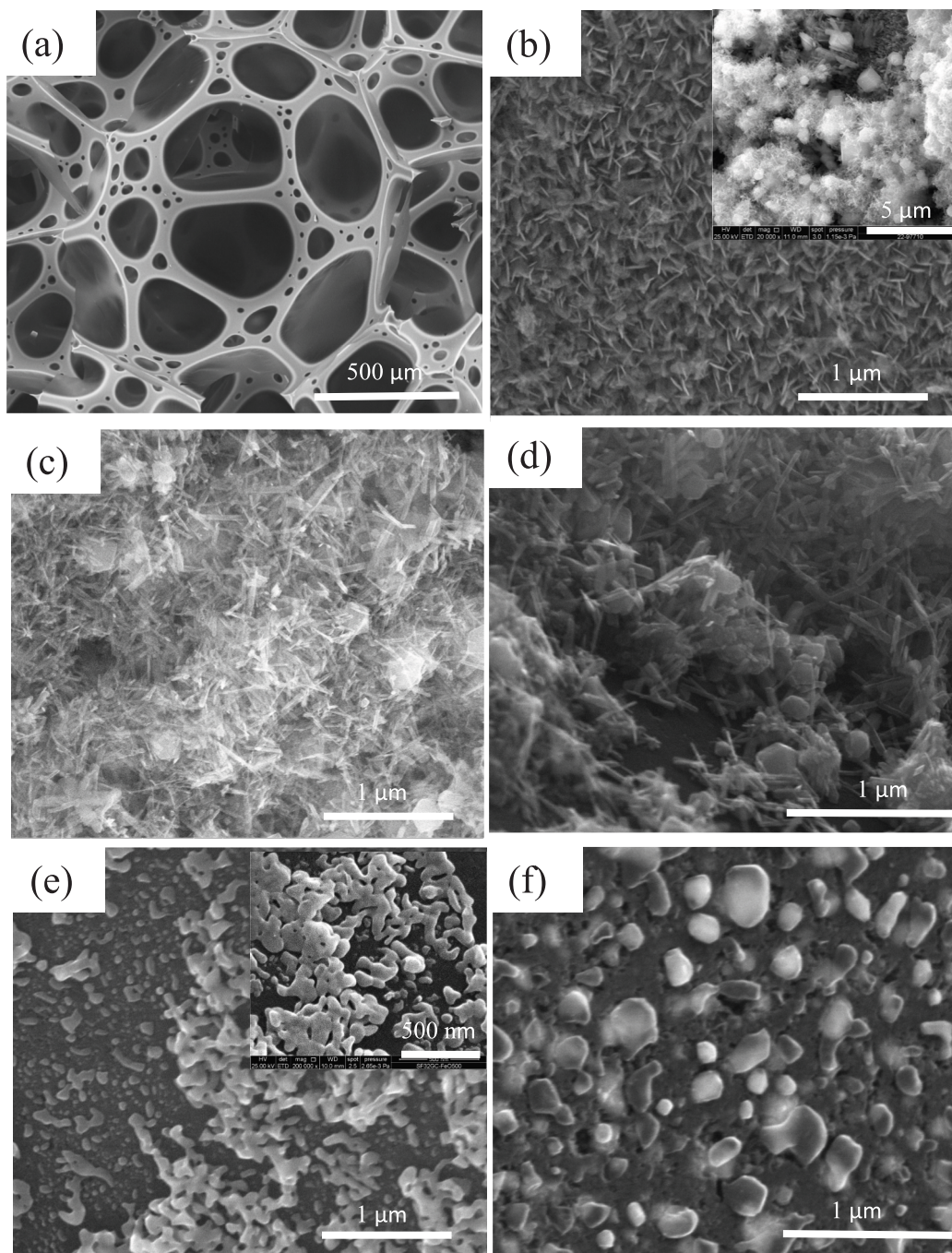


Fig. 2. SEM images of a) SF, b) SF-FeOOH, c) and d) SF- $\alpha$ Fe<sub>2</sub>O<sub>3</sub>, e) SF-FexOy and f) SF-Fe-FexOy.

**Table 1**  
Textural properties of the carbon foams.

	$S_{BET}$ (m <sup>2</sup> g <sup>-1</sup> )	$V_t$ (cm <sup>3</sup> g <sup>-1</sup> )	$V_{micro}$ (cm <sup>3</sup> g <sup>-1</sup> )	$V_{meso}$ (cm <sup>3</sup> g <sup>-1</sup> )
SF	306	0.24	0.13	0.11
SF-FeOOH	266	0.22	0.11	0.11
SF- $\alpha$ Fe <sub>2</sub> O <sub>3</sub>	253	0.22	0.10	0.12
SF-FexOy	200	0.16	0.08	0.08
SF-Fe-FexOy	275	0.24	0.11	0.13

On the one hand, when the SFs impregnated with method A (FeSO<sub>4</sub> 7H<sub>2</sub>O and CH<sub>3</sub>COONa in water) are compared, the mercury retention capacity is much higher in SF- $\alpha$ Fe<sub>2</sub>O<sub>3</sub> than SF-FeOOH, displaying both the same iron morphology in the form of nanoneedles (Fig. 2b-d) and similar textural properties (Table 1). The outer layer of Fe<sup>3+</sup> presents an empty orbital structure in the iron oxide ( $\alpha$ Fe<sub>2</sub>O<sub>3</sub>), which could be beneficial for the Fe/Hg<sup>0</sup> interaction [39]. On the other hand, when the SFs impregnated with method B (Fe(NO<sub>3</sub>)<sub>3</sub> 9H<sub>2</sub>O in ethanol) are compared, the SF treated at 800 °C resulting in the formation of elemental iron (SF-Fe-FexOy) shows a lower mercury retention capacity than the SF treated at 500 °C (SF-FexOy). Although the foam treated at a higher temperature has greater BET surface area and total pore volume (Table 1), the formation of elemental iron does not favour the retention

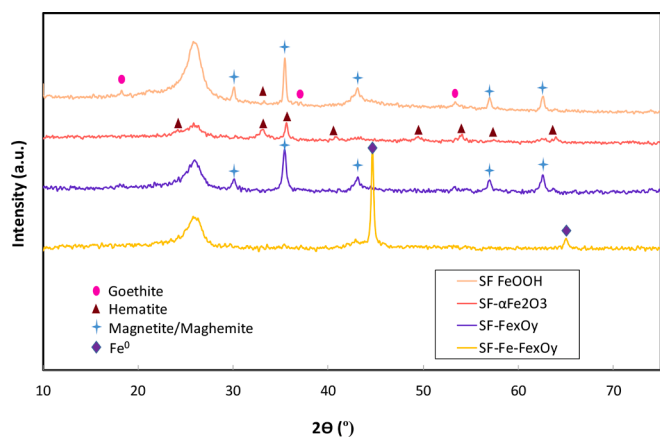


Fig. 3. XRD pattern of the resulting carbon foam composites SF-FeOOH, SF- $\alpha$ Fe<sub>2</sub>O<sub>3</sub>, SF-FexOy and SF-Fe-FexOy.

of elemental mercury. In addition, the formation of the nanoparticles is less uniform in SF-Fe-FexOy (Fig. 2f).

These results suggest that: 1) the formation of  $\alpha$ Fe<sub>2</sub>O<sub>3</sub> on the surface of the sucrose foam creates active sites for chemisorption/oxidization of the elemental mercury in the support (Fig. 5), and 2) a large number of needle-shaped nanoparticles with uniform size (Fig. 2c-d) improves the mercury adsorption as compared with peanut-shaped nanoparticles (Fig. 2 e-f).

### 3.3. Effect of iron concentration on mercury adsorption

The effect of iron concentration on mercury adsorption is examined through the comparative experiments in which the SF with the highest mercury retention (SF- $\alpha$ Fe<sub>2</sub>O<sub>3</sub>) was impregnated with different iron amounts (5, 10, 20 and 30 %wt) (Fig. 6a). It must be taken into account that the Fe coating was not quantitative. The efficiency of the impregnation ranged between 40 and 70%, using 5–20% Fe, whereas the efficiency decreased to 25% for 30% Fe (Table S1).

The highest amount of iron deposited was reached using 20 wt% Fe (Table S1), which favoured the mercury retention as a consequence of the greater number of active sites on the sorbent surface. It is also remarkable that the sample SF- $\alpha$ Fe<sub>2</sub>O<sub>3</sub> 30 wt% Fe, unlike SF- $\alpha$ Fe<sub>2</sub>O<sub>3</sub> 20 wt% Fe, showed a proportion of polyhedrons (Fig. 6b) higher than that of nanoneedles (Fig. 2c-d). The different morphology can be attributed to different synthesis conditions (pH) [40]. Taking into account that both samples showed the same iron species, the results suggest that nanoneedles are more beneficial for the adsorption/oxidation of elemental mercury than polyhedrons (Fig. 5).

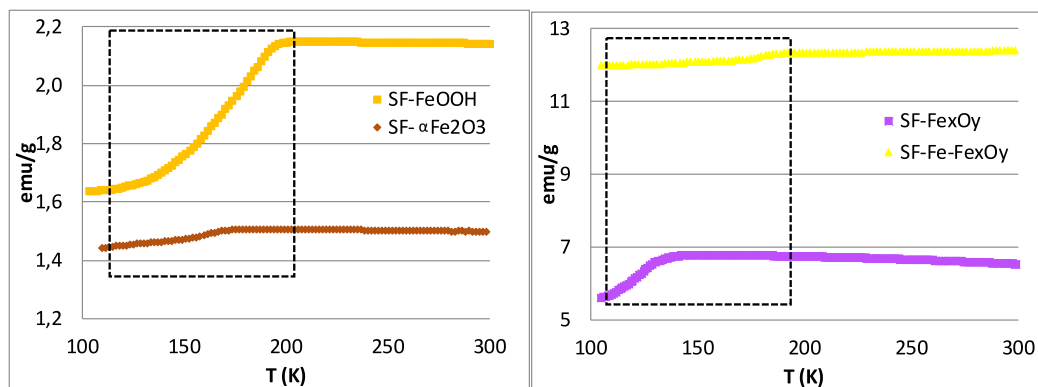


Fig. 4. Verwey transition of the resulting carbon foam composites impregnated with 20 wt% Fe using FeSO<sub>4</sub> 7H<sub>2</sub>O and CH<sub>3</sub>COONa in water (SF-FeOOH and SF- $\alpha$ Fe<sub>2</sub>O<sub>3</sub>) and Fe(NO<sub>3</sub>)<sub>3</sub> 9H<sub>2</sub>O in ethanol (SF-FexOy and SF-Fe-FexOy).

### 3.4. Adsorption-Desorption cycles: The role of O<sub>2</sub>

It is well-known that the O<sub>2</sub> present in the flue gas may play a key role in the mercury adsorption and regeneration process [36]. The mercury retention capacity of SF- $\alpha$ Fe<sub>2</sub>O<sub>3</sub> with 20 wt% Fe was evaluated in the flue gas containing various concentrations of O<sub>2</sub>. As can be observed in Fig. 7a, the mercury retention capacity was improved when the O<sub>2</sub> content in the flue gas increased from 6 to 16%. O<sub>2</sub> had a promotion effect on mercury removal over SF- $\alpha$ Fe<sub>2</sub>O<sub>3</sub>, probably as a consequence of the generation of active oxygen species and the regeneration of the oxygen consumed on the carbon foam surface [41], which favours the adsorption and oxidation process of elemental mercury.

Fig. 7a also shows the mercury retention capacity of SF- $\alpha$ Fe<sub>2</sub>O<sub>3</sub> with

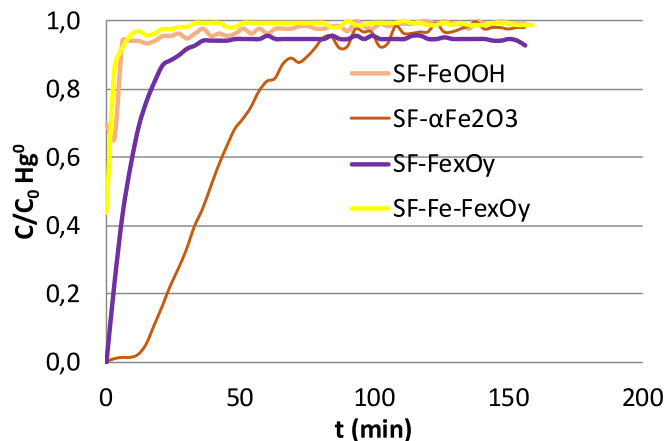


Fig. 5. Mercury adsorption curves of the SFs impregnated with 20 wt% Fe using FeSO<sub>4</sub> 7H<sub>2</sub>O and CH<sub>3</sub>COONa in water (SF-FeOOH and SF- $\alpha$ Fe<sub>2</sub>O<sub>3</sub>) and Fe(NO<sub>3</sub>)<sub>3</sub> 9H<sub>2</sub>O in ethanol (SF-FexOy and SF-Fe-FexOy).

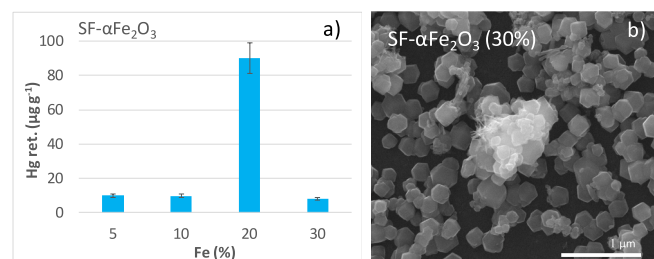


Fig. 6. (a) Mercury retention capacity of SF- $\alpha$ Fe<sub>2</sub>O<sub>3</sub> with 5, 10, 20 and 30 wt% Fe, and (b) SEM imagen of SF- $\alpha$ Fe<sub>2</sub>O<sub>3</sub> with 30 wt% Fe.

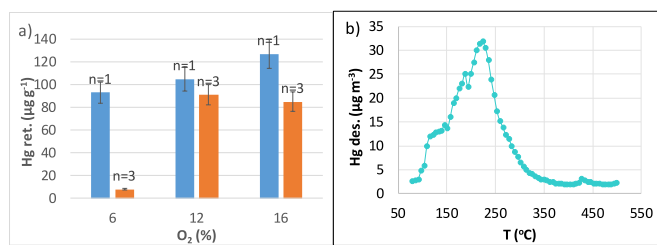


Fig. 7. (a) Mercury retention capacity of SF- $\alpha\text{Fe}_2\text{O}_3$  with 20 wt% Fe in cycles 1 and 3, and (b) mercury desorption curve.

20 wt% Fe after several cycles of adsorption–desorption with different concentration of  $\text{O}_2$  in the flue gas. After the first adsorption cycle, the mercury retention capacity of SF- $\alpha\text{Fe}_2\text{O}_3$  decreased sharply with 6%  $\text{O}_2$ , suggesting that the hematite active sites were consumed during the retention experiments. However, the removal efficiency of the regenerated sucrose foams is still 67–90% when 12–16%  $\text{O}_2$  is present in the flue gas after the third cycle. Therefore, the deactivation can be counteracted by adding  $\text{O}_2$  to the gas stream to regenerate the sorbents.

These hypotheses were supported by XPS results. Fig. 8 shows the O 1s and C 1s core-level spectra of the fresh sorbent SF- $\alpha\text{Fe}_2\text{O}_3$  20 wt% Fe, and after the second adsorption cycle (flue gas of 12%  $\text{O}_2$ ). The C1s spectrum can be deconvoluted into three peaks at 533.1, 531.8 and 530.1 eV (Fig. 8a). The first peak at 533.1 eV corresponds to Si-O, which derived from the sand employed in the sorbent bed. In addition, this peak can be assigned to oxygen atoms in -O-C. The peak at 531.8 eV corresponds to O = C groups and also to chemisorbed oxygen in metal oxides. The peak at 530.1 eV lower binding energy is related to lattice oxygen in metal oxides groups [42,43]. As can be observed in Fig. 8a the lattice oxygen is reduced drastically after the adsorption cycle, thus its consumption may be related to the loss of mercury retention efficiency along cycles. By other hand, an increase of oxygen groups can be inferred from the C1s spectrum (Fig. 8b) after retention experiments. The fresh sorbent shows a main peak at 284.6 eV assigned to carbon group C-C and a little contribution from C-O (285.7 eV) and C-OOR groups (289.8 eV), whereas for the used sorbent an increase of these oxygen related peaks was observed. Therefore, the  $\text{O}_2$  presence in the flue gas seems to promote creation of oxygen functionalities, which can be beneficial for mercury adsorption/oxidation reactions [44]. No significant differences were found in the Fe 2p spectra (Figure S3). The peaks at 709.5 and 710.8 eV were assigned to  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions, in agreement with XRD results. A satellite peak at 718.1 eV also corroborate the present of  $\text{Fe}^{3+}$  species (Figure S3).

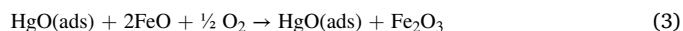
It should also be taken into account that the GHSV in real conditions ranges between 2000 and 6000  $\text{h}^{-1}$  [45], while in the experimental conditions of this study it is approximately 100000  $\text{h}^{-1}$ . Therefore, the efficiency of mercury retention by the developed adsorbent would be improved, because a lower GHSV leads to higher residence times that favour mercury removal.

The mercury adsorbed on the spent SF- $\alpha\text{Fe}_2\text{O}_3$  was evaporated by thermal treatment at 450  $^{\circ}\text{C}$  in an  $\text{N}_2$  atmosphere to subsequently reuse the adsorbent (Fig. 7b). The highest peak of mercury desorption occurs at approximately 225  $^{\circ}\text{C}$ , a remarkable result for sorbent regeneration at such low temperature. A low activation energy in the desorption process could be profitable for regeneration.

From this perspective and considering that SF- $\alpha\text{Fe}_2\text{O}_3$  showed good resistance to  $\text{SO}_2$  and  $\text{H}_2\text{O}$ , which can compete with elemental mercury for active sites and lead to sorbent deactivation,  $\alpha\text{Fe}_2\text{O}_3$ -based sucrose foams could be an attractive alternative to traditional non-regenerable activated carbons, reducing costs and being environmentally sustainable.

### 3.5. Mechanism of mercury adsorption

Several studies have already shown that Fe<sub>x</sub>O<sub>y</sub> on carbon surface could supply lattice oxygen for elemental mercury adsorption and oxidation [36,46,47]. The elemental mercury removal could be explained by the Mars–Maessen mechanism, which is described by the following reactions [48]:



The first step is a physisorption process in which elemental mercury is adsorbed on the surface of the sucrose foam with a BET surface area of 253  $\text{m}^2 \text{g}^{-1}$  (Table 1) (I). The second step is the reaction between the adsorbed mercury with hematite to oxidize mercury, by combination with chemisorbed oxygen and lattice oxygen, and reduce the sucrose foam surface (II). The adsorbent is then reoxidized by the oxygen present in the flue gas regenerating the consumed chemisorbed oxygen and lattice oxygen (III) and the binary oxide is finally formed (IV).

The formation of oxidized mercury is confirmed by the analysis of the mercury captured in the Dowex resin at the gas outlet of the fixed-bed. The percentage of oxidized mercury retained in the resin ranged between 15 and 20% of the total amount of elemental mercury that passed through the adsorbent. The results of HgTPD also suggest the formation and retention of oxidized mercury by the material developed here (Figure S4). The thermal desorption profile of commercial HgO that appears at 200–350  $^{\circ}\text{C}$  (Figure S4) can be associated with that obtained for the mercury retained in the spent adsorbent (Fig. 7b), both showing similar decomposition temperatures.

## 4. Conclusions

In this study, a cost-effective and environmentally sustainable adsorbent was developed for the capture of elemental mercury from flue gases. The adequate porous structure of the sucrose foam allowed the impregnation of different iron species with different morphology. The results showed that the  $\alpha\text{Fe}_2\text{O}_3$  nanoneedles supported on the sucrose foam were the main active sites for the removal of elemental mercury. The sorbent proved to be effective in the presence of  $\text{SO}_2$  and  $\text{H}_2\text{O}$ , being able to be regenerated by heating to 300  $^{\circ}\text{C}$ . The results of mercury speciation confirmed that mercury is retained in the form of HgO through a Mars–Maessen mechanism. The promising results lead to evaluating the efficiency of the adsorbent under real fuel gas conditions in the next step. In addition, the results found using commercial sucrose to synthesize the mercury adsorbent could provide a path for the utilization of waste from the agricultural industry.

### CRedit authorship contribution statement

**L. López-Toyos:** Conceptualization, Investigation. **M.A. López-Antón:** Writing – original draft, Supervision, Project administration, Funding acquisition. **E. Rodríguez:** Investigation, Supervision. **R. García:** Writing – review & editing. **M.R. Martínez-Tarazona:** Writing – review & editing, Funding acquisition.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

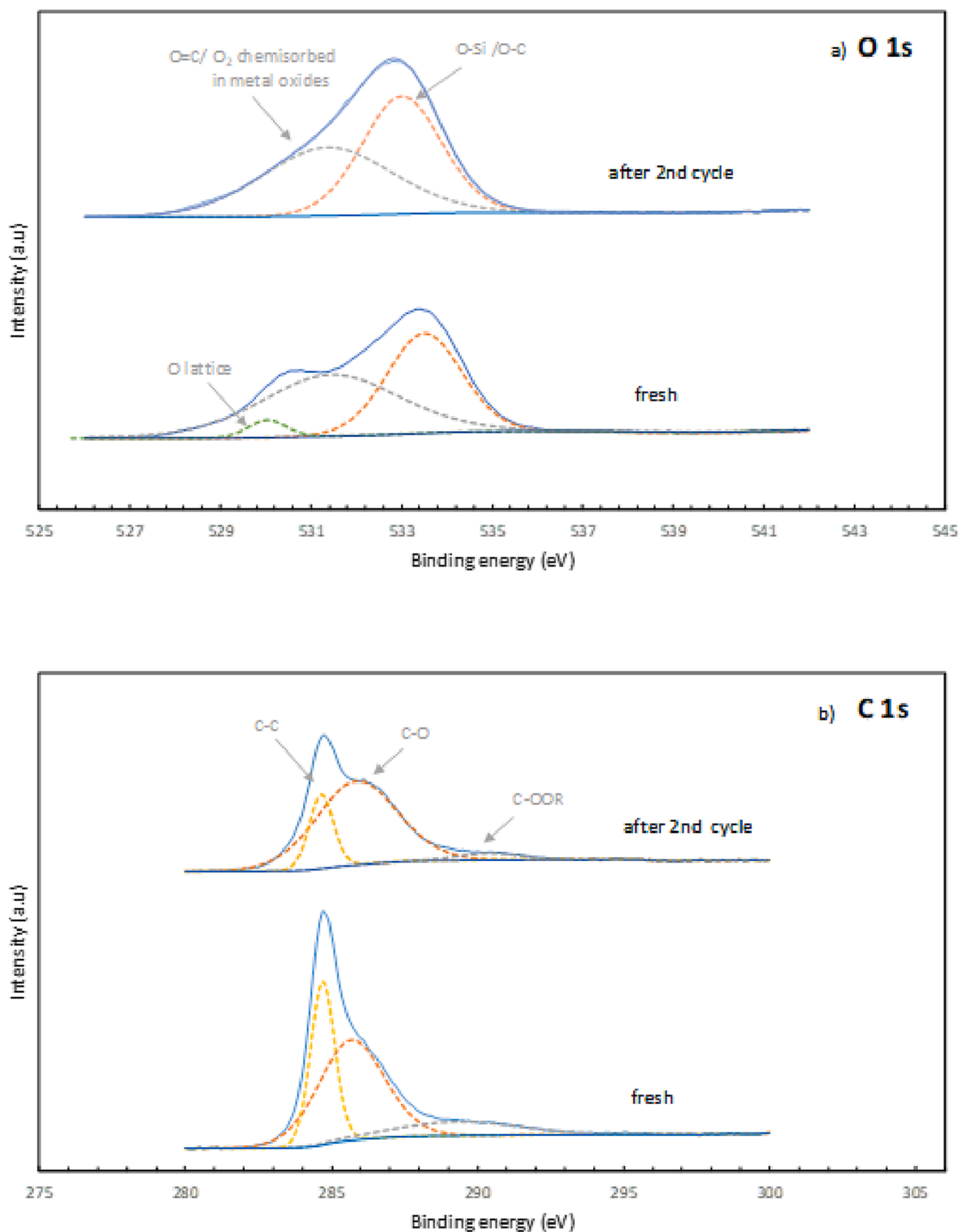


Fig. 8. A) O 1s and b) C 1s core level spectra for the fresh sorbent SF- $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> 20 wt% Fe and after the second adsorption cycle carried out with 12% O<sub>2</sub>.

## Data availability

Data will be made available on request.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuel.2023.128181>.

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