

Article

A New Approach for Retaining Mercury in Energy Generation Processes: Regenerable Carbonaceous Sorbents

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Abstract: The energy production processes from fossil fuels represent the first anthropogenic source of mercury emissions in Europe and the second in the world. Among the different possibilities that can be posed to reduce these emissions, this work focuses on the use of regenerable sorbents based on gold nanoparticles dispersed on activated carbon foam. The use of regenerable sorbents would not only allow the objective of reducing mercury emissions, but also avoiding the generation of new toxic wastes. The results showed a retention efficiency of 100% and a retention capacity close to $600 \mu\text{g}\cdot\text{g}^{-1}$ over several cycles of regeneration. Moreover, acid gases did not poison the support. It was observed that mercury capture in this simulated oxy-combustion atmosphere was a consequence of two mechanisms: (1) the amalgamation of elemental mercury and elemental gold and (2) the oxidation of elemental mercury in the presence of HCl, with the subsequent retention of the oxidized mercury on the surface of the activated carbon foam. The nanodispersion of gold on such supports involves a high initial investment. However, this would be counterbalanced by the remarkable regeneration capacity of the sorbent and the possibility of recovering all the materials used.

Keywords: mercury; regenerable sorbent; combustion; energy generation

1. Introduction

Solving environmental problems is a challenge for society, but having an energy supply is also a challenge. Therefore, it is necessary to develop clean energy generation technologies. Coal combustion will be maintained at least until 2030 and could be used even longer, if hazardous emissions are avoided [1,2]. Efforts to reduce many of the pollutants in coal combustion have paid off, but Hg emissions remain worrying [3–5]. Combustion plants account for 54.5% of Hg air emissions in Europe and the United Nations Environment Programme (UNEP) considers their reduction one of its priority objectives [6,7].

It is well-known that the chemical properties of elemental mercury (Hg^0) such as its high volatility and water insolubility, limit the benefits that flue gas cleaning systems, installed in the coal combustion power plants for other pollutants, could contribute to the retention of mercury. Whereas oxidized mercury (Hg^{2+}) can be captured in such systems, Hg^0 remains in the gas stream and is mostly emitted to the atmosphere. For this reason, there is special interest in the development of specific technologies for the capture of Hg^0 [8–11]. If coal-fired power generation is to cease to be the main anthropogenic source of mercury emissions into the air and if the UNEP mandates proposed in the last meeting of the Minamata Group are to be fulfilled [12], the emissions of Hg^0 from power plants need to be reduced.

Of the options currently available, the most advanced technology capable of capturing Hg^0 , involves injecting solid sorbents into the flue gas stream before the particle control devices. Although the efficiency of solid sorbents depends on their characteristics, temperature, flue gas composition and other conditions, the retention of Hg^0 by this technology could be substantial [13,14]. However, there are some drawbacks, such as the huge amount of sorbent that would be needed just for one single use and the fact that after retention the solid material would have to be collected together with the fly ash, compromising recovery or disposal of both [15–17]. Therefore, the use of solids capable of being regenerated would be an attractive alternative to injection technology [18,19]. Moreover, regenerable sorbents are designed for use at the end of the cycle where most flue gas impurities have already been reduced, making this process versatile enough to be used not only in conventional coal combustion and oxy-combustion plants, but also in other processes such as CO_2 or natural gas purification.

Some of the regenerable materials developed for Hg^0 capture have been obtained by the dispersion of a noble metal or metal oxide on an inorganic or carbonaceous support of high surface area [20–25]. The mechanism of Hg^0 retention by regenerable sorbents impregnated with noble metals, such as gold, silver, copper, palladium or platinum, is based on the formation of a metal-Hg amalgam [26–28]. For this to occur, both the metal and the mercury have to be in an elemental state. The amalgam is then decomposed at a temperature between 400 °C and 500 °C to release the mercury and leave the sorbent ready for the next adsorption cycle. The efficiency of this process mainly depends on the type of metal used, the size and distribution of the metal on the sorbent and the possible degradation of the metal as a consequence of regeneration or when it comes into contact with acid gases, such as SO_2 or HCl [18,29–32]. The effectiveness of this type of sorbent over several cycles of capture and regeneration has been demonstrated in a previous study carried out by the authors using a commercial activated carbon impregnated with gold. It has also been demonstrated that, after regeneration, it is possible to recover and collect the mercury [33,34]. An additional advantage of using a carbonaceous material as support is that, after the depletion of the sorbent, it is possible to recover the gold by burning the support. In this way a residue containing gold ready to be purified is obtained [34].

An alternative to using noble metals is impregnation with metal oxides, which makes the sorbent cheaper [25]. Moreover, with some of these materials, it is possible to capture mercury at higher temperatures (200–400 °C) [35]. Despite the promising results achieved so far, they are still under development and their evaluation in real conditions requires further investigation.

In the present work, a new regenerable sorbent for Hg^0 capture designed to be used at the end of the cycle in an oxy-combustion plant, has been developed and evaluated. An activated carbon foam with a negligible ash content was prepared to allow the recovery of the gold after sorbent depletion. This support was impregnated with 1.8% of nanodispersed gold. Activated carbon foams offer a number of advantages as gold supports for the application pursued in this work. Of these, their enhanced mechanical strength and easy manageability that make it possible to manufacture carbon structures of any monolithic shape are the most important. Moreover, the physical and chemical characteristics of their surfaces can be modified according to the needs of the industrial processes for which they are designed.

2. Experimental

2.1. Preparation of the Carbon Support

The activated coal-based carbon foam (CF) was synthesized by chemical activation of a carbon foam with ZnCl_2 , following a method previously reported by the authors of this paper [36]. Briefly, this procedure involves: (1) the preparation of a foam precursor (coal/ ZnCl_2 mixture), (2) the manufacture of a “green foam” by a foaming process and (3) the thermal treatment of the “green foam” to remove any volatile matter and to develop microporosity in the resultant activated carbon foam (activation step).

A bituminous coal with a high fluidity (12,401 ddp_m) and a maximum fluidity temperature of 443 °C was selected as precursor of the carbon foam. Firstly, the coal was exposed to different acid treatments to remove its mineral matter (HCl 5 M, HF 22 M and HCl 12 M) [37], as a result of which an ash reduction of more than 90% was achieved. Afterwards, the demineralized coal was impregnated with 100 mL of a solution of ZnCl₂ in ethanol at 65 °C under constant stirring for 2 h, with a coal: ZnCl₂ mass ratio of 1:1. The mixture was then dried at 105 °C for 2 days for the evaporation of ethanol and the dried mixture was subjected to a foaming process at 450 °C for 2 h. During this step, the coal undergoes a plastic state where the volatile matter causes a pressure increase acting as foaming agent over the softened coal. The resultant “green foam” was then carbonized in a horizontal tubular furnace under an Ar flow (200 mL/min) at 500 °C for 2 h. Finally, the resulting foam was washed with a 3 M HCl solution and distilled water to remove any remaining residue.

2.2. Impregnation with Gold

The Au-loaded CF (CF-Au) was obtained by impregnating the carbon support with a solution of Au nanoparticles stabilized as a colloid (Au sol). The Au sol was prepared by means of a procedure described elsewhere [33].

As gold precursor, an aqueous solution of chloroauric acid (HAuCl₄·3H₂O, 0.127 M) was used with tetrakis(hydroxymethyl) phosphonium chloride (THPC, 78 wt %) as reducing agent. The amount of reagent used was that necessary to obtain a sorbent with 3 wt % Au.

Once the Au sol was prepared, a suspension made up of 150 mg of CF (ground to a size of 0.2 nm–0.5 nm) and 8 mL of distilled water, which was previously treated in an ultrasonic bath for 15 min, was added to the gold sol. The mixture was stirred for 2 h and kept at ambient temperature for 2 days to allow the Au nanoparticles to deposit in the porous structure. Next, the sample was filtered, washed with hot distilled water and dried. Finally, the sample was carbonized under Ar (100 mL·min^{−1}) at 350 °C for 3 h to remove any organic compound from the support.

2.3. Characterization of the Sorbent

The Brunauer-Emmett-Teller (BET) surface areas of the samples were measured by N₂ adsorption at −196 °C. The total pore volumes of the samples (V_T) were calculated from the amount of N₂ adsorbed at a relative pressure of 0.98, and the micropore volumes were estimated using the Dubinin-Radushkevich (DR) equation (V_{DR-N2}). The volume of mesopores (V_{Meso}) was calculated from the difference between the V_T and V_{DR-N2}. The morphology of the gold nanoparticles was examined using a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectroscope (EDX). Speciation of the gold on the CF-Au was carried out by X-ray photoelectron spectroscopy (XPS). The quantity of Au retained in the support was determined by means of inductively coupled plasma mass spectrometry (ICP-MS), via indirect analysis of the Au remaining in the solution after impregnation.

2.4. Hg Retention/Regeneration Device

The tests for evaluating the retention of mercury by the sorbent were carried out in an experimental laboratory scale device described elsewhere [38] (Figure 1). The device consists of: (1) a gas blending station equipped with mass flow controllers to prepare the gas composition (73% CO₂, 27% N₂, 100 ppm SO₂ and 25 ppm HCl), (2) a calibrated permeation tube (VICI Metronics, VICI, Poughkeepsie, NY, USA) placed inside a glass “U” tube, immersed in a water bath, to obtain 100 µg·m^{−3} of Hg⁰ in gas phase, (3) a glass reactor, with a sorbent bed of 0.1 g of CF-Au, kept at 40 °C (the total volume of the flow gases through the sorbent was 500 mL·min^{−1}), and (4) a continuous mercury analyzer (VM 3000, Mercury Instruments, Littleton, CO, USA) to monitor the Hg⁰. A Dowex[®] 1 × 8 ion exchanger resin was used to determine the oxidized mercury (Hg²⁺) [39,40]. The total amount of Hg retained in the sorbent and the Hg²⁺ captured in the resin were analyzed using AMA equipment (LECO Corporation, Saint Joseph, MO, USA). The mercury retention experiments were conducted for a period of 1440 min.

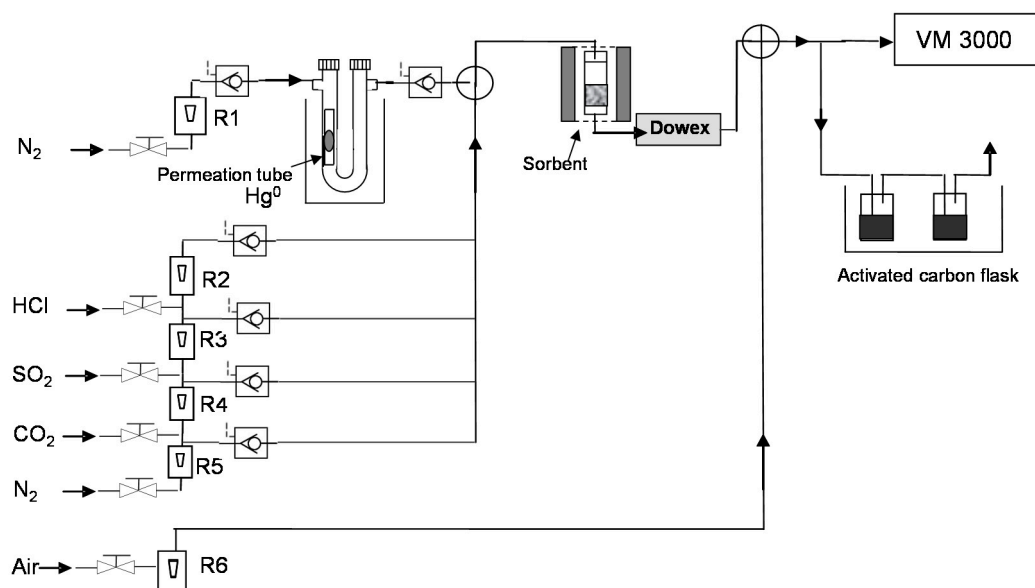


Figure 1. Schematic diagram of the experimental device used for mercury retention.

The regeneration was carried out by heating the post-retention sorbents in the same experimental device, from 40 °C to 450 °C, at a heating rate of 3 °C·min⁻¹, under a N₂ flow of 500 mL·min⁻¹. The desorbed mercury was monitored as a function of temperature using the VM3000 analyser. The gold-doped regenerated sorbent was then re-used to capture mercury.

3. Results and Discussion

3.1. Characterization of the Sorbent

Table 1 shows the results obtained from the textural characterization of the support (CF) and the impregnated-support (CF-Au) together with the gold content in CF-Au. As can be observed the textural parameters hardly varied in either material indicating that no textural changes occurred as a result of the deposition of the Au (Figure 2). The amount of Au deposited on the foam was 1.8%, i.e., 60% of the added Au (3 wt %).

Table 1. BET surface area, total pore volume (V_T), micropore volume (V_{DR-N_2}), mesopore volume (V_{Meso}) and gold content in the support (carbon foam (CF)) and impregnated support (CF-Au).

Method of Analysis	Parameters	CF	CF-Au
Adsorption N ₂	S_{BET} (m ² ·g ⁻¹)	880	850
	V_T (cm ³ ·g ⁻¹)	0.39	0.37
	V_{DR-N_2} (cm ³ ·g ⁻¹)	0.36	0.35
	V_{Meso} (cm ³ ·g ⁻¹)	0.03	0.02
ICP-MS	Au (wt %)	-	1.8

The micrographs obtained by SEM show a morphology characteristic of activated carbon foams before (Figure 3a,b) and after gold treatment (Figure 3c) and the distribution of Au particles on the surface of the CF-Au sorbent as ranging from 2 nm to 30 nm (Figure 3d).

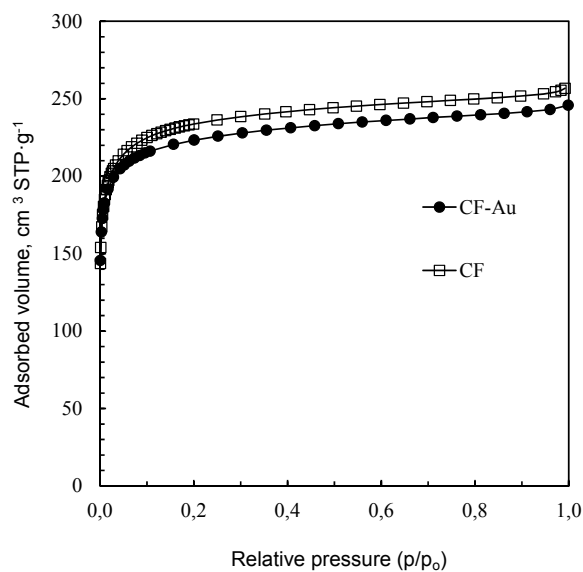


Figure 2. N_2 adsorption isotherms at -196°C of CF and CF-Au.

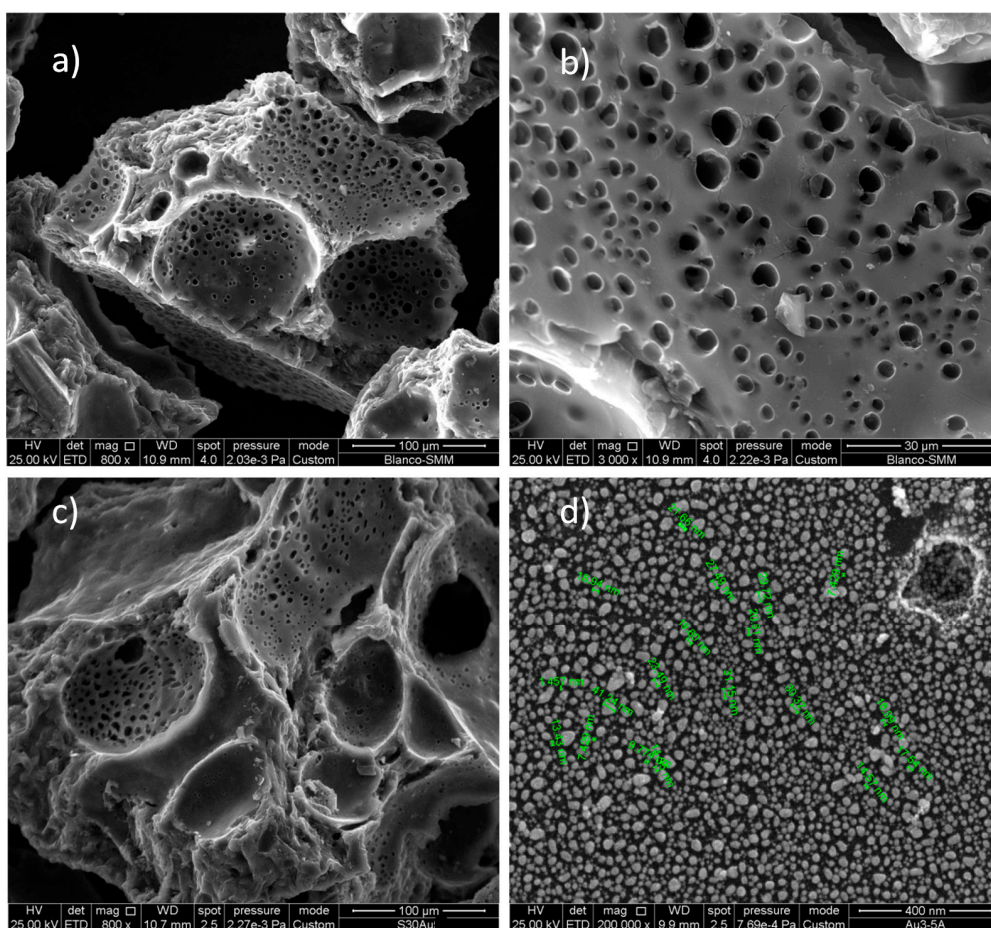


Figure 3. Scanning electron microscope (SEM) micrographs of CF at lower (a) and higher (b) magnification where a macroporous structure is observed and CF-Au at lower (c) and higher (d) magnification. Note: (d) micrograph allows the identification of the gold particles on the surface.

An analysis of the Au-loaded carbon foam by XPS showed two Au 4f peaks corresponding to the binding energy of metallic Au (84.0 eV and 87.7 eV) (Figure 4). The absence of oxidized Au, at least within the detection limit of XPS, makes the method of impregnation suitable for the deposition of elemental gold which is necessary for its amalgamation with elemental mercury.

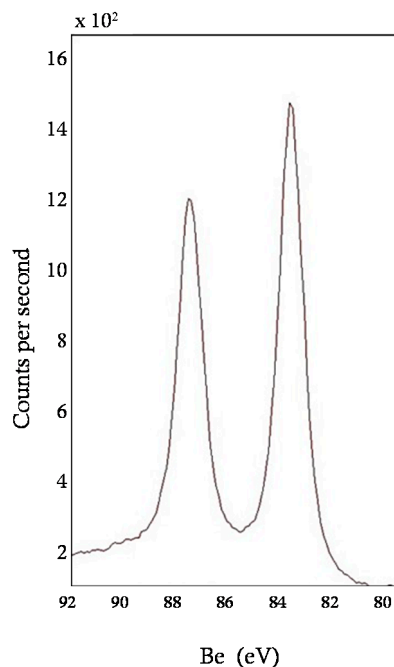


Figure 4. X-ray photoelectron spectroscopy (XPS) spectrogram of CF-Au. Au 4f with peaks corresponding to Au(0).

3.2. Hg Retention

The mercury retention capacity of the CF-Au sorbent was evaluated in an atmosphere containing 27% N₂, 73% CO₂, 100 ppm SO₂ and 25 ppm HCl. This composition is similar to what one would expect just before the stack in an oxy-combustion power plant (i.e., a predominance of CO₂ with low amounts of sulphur and halogen species). It is at this point where it is intended to use the sorbents developed i.e., after the mercury has passed through all the gas cleaning systems installed in an oxy-combustion coal power plant.

Figure 5 shows the mercury adsorption profiles obtained with the CF-Au foam in the oxy-combustion atmosphere over five regeneration cycles. No changes were observed in the morphology of the CF-Au or the oxidation state of gold after regeneration of the sorbent. Each cycle was carried out during 1440 min, the experimental time chosen for comparing the behaviour of the different sorbents under similar conditions. The curves represent the mercury concentration ratio (C/C_0) versus time, where C is the concentration of mercury not retained (registered after the sorbent bed), and C_0 is the inlet mercury concentration. In the particular case of Figure 5, saturation of the sorbent was not reached in the 1440 min period. As can be observed, an efficiency of 100% was attained in all the cycles, with approximately 600 $\mu\text{g}\cdot\text{g}^{-1}$ of mercury being retained (Table 2).

According to previous results obtained with similar materials, the mercury capture achieved with the sorbent could be a consequence of two possible mechanisms: (1) the formation of an amalgam between Au⁰ (Figure 4) and Hg⁰ and/or (2) the adsorption of oxidized mercury produced on the foam surface with the participation of the HCl present in the gas stream [34,41–43]. In order to confirm these mechanisms, a series of experiments were carried out, in which the mercury retention capacity of CF and CF-Au was evaluated in an atmosphere free of acid gases.

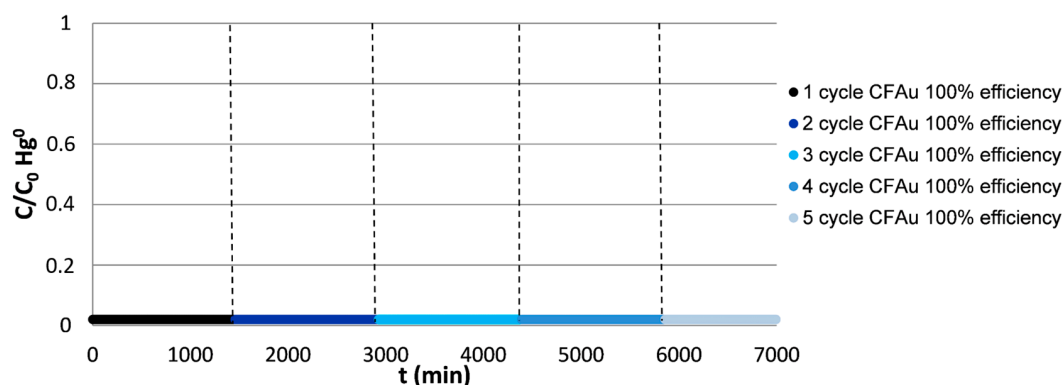


Figure 5. Mercury adsorption on CF-Au in an atmosphere containing CO₂, N₂, SO₂ and HCl.

Table 2. Absolute mercury retention (*R*) and percentages of mercury retained (% Hg_{ret}) and oxidized (% Hg²⁺) in CF-Au in each cycle in an atmosphere containing CO₂, N₂, SO₂ and HCl, over 1440 min.

No. Cycle	<i>R</i> (μg g ^{−1})	% Hg _{ret}	% Hg ²⁺
1	637	99.7	0.3
2	601	99.7	0.3
3	627	98.2	1.8
4	594	95.7	4.3
5	615	93.7	6.3

3.2.1. Effect of Impregnation with Gold

Figure 6a shows the mercury adsorption curve obtained with the CF foam in an atmosphere composed of 80% CO₂ and 20% N₂. The saturation of the sorbent ($C/C_0 = 1$) was quickly reached with no efficiency of 100% taking place. Analysis of the sorbent post-retention at the saturation point showed a mercury retention capacity of 106 μg·g^{−1}, i.e., approximately 15% of all the mercury emitted. No oxidized mercury was detected at the exit of the reactor from an analysis of the Dowex resin. When the experiments were carried out in the same atmosphere with the carbon foam impregnated with gold (CF-Au), the mercury retention capacity was greater (Figure 6b). An efficiency of 100% over approximately 9 h was achieved with 287 μg·g^{−1} of mercury being retained during this time. The amount of oxidized mercury detected in these conditions was again negligible. In summary, the higher mercury capture achieved by CF-Au than by CF was a consequence of the amalgamation between Au⁰ and Hg⁰ in the atmosphere containing 80% CO₂ and 20% N₂.

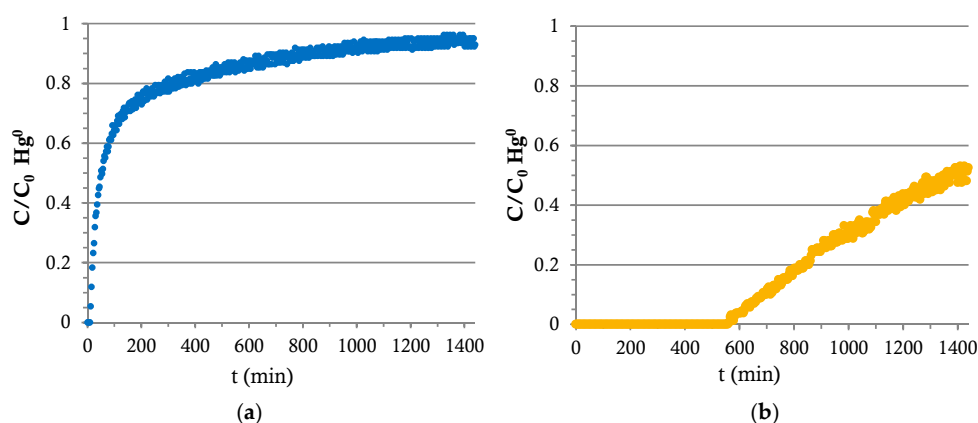
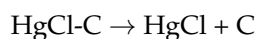
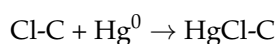
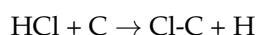


Figure 6. Mercury adsorption curves for: (a) CF and (b) CF-Au in an atmosphere containing CO₂ and N₂.

3.2.2. Effect of the Gas Composition

If the mercury adsorption obtained with the CF-Au sorbent in the presence of SO₂ and HCl (Figure 5) is compared to that obtained in an atmosphere free of acid gases (Figure 6b), a higher mercury retention in the presence of acid gases is observed. Therefore, in addition to the formation of Hg-Au amalgam, the acid nature of the gas must have an influence on mercury capture.

Although some studies [18,44] suggest that the presence of acid gases, such as SO₂, may poison certain noble metals, decreasing their efficiency for mercury capture, at the levels evaluated in the present work such poisoning did not take place. In fact, in the presence of SO₂ and HCl (Figure 5), the retention capacity increased, and then remained constant over a number of cycles (Figure 5). Some studies [34,41–43] claim that the retention of Hg⁰ in carbon materials is favored by the presence of HCl in the gas stream, which is explained by the following reactions:



where the chlorine atoms bound to the surface of the carbon material (Table 1) react with Hg⁰ to form HgCl and subsequently HgCl₂ by reacting with the HCl present in the atmosphere.

The formation of Hg²⁺ is corroborated by the following results:

- In contrast to what was observed in the atmosphere containing only CO₂ and N₂ where hardly any oxidized mercury was detected at the exit of the reactor, in the atmosphere containing HCl and SO₂ an increase in Hg²⁺ was produced during the regeneration cycles of the CF-Au foam (Table 2).
- In the presence of acid gases, approximately 7% of the desorbed mercury was retained in the Dowex resin evidencing the formation of Hg²⁺.
- Moreover, the mercury desorption profiles of a regeneration cycle of the CF-Au sorbent after adsorption in the atmospheres containing CO₂ and N₂ differ significantly from those obtained with CO₂, N₂, HCl and SO₂ in the gas stream (Figure 7). The profiles obtained in the absence of HCl and SO₂ show a wide band, with mercury desorption taking place in the 60 to 325 °C range, while that obtained in the presence of these gases is narrower (200 °C–350 °C) with a maximum peak of desorption at 275 °C.

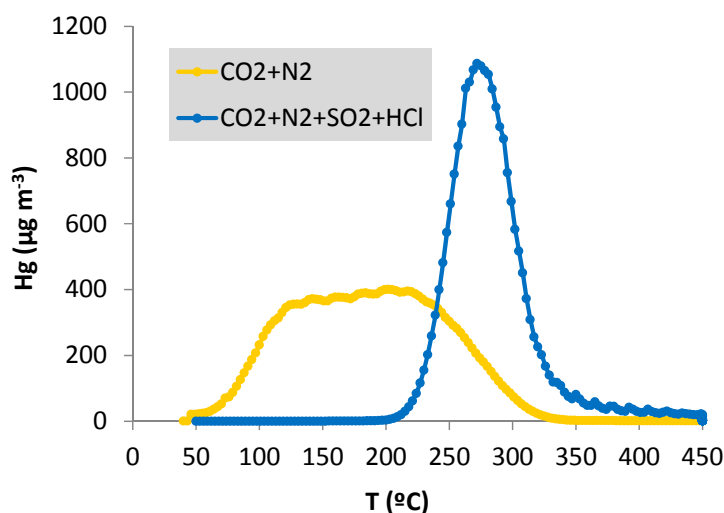


Figure 7. Mercury desorption profiles during the regeneration of CF-Au in different atmospheres.

These results suggest that the mercury species retained in these atmospheres are different indicating that two mercury retention mechanisms might be occurring as a consequence of the simultaneous presence of Au and HCl.

4. Conclusions

The activated coal-based carbon foam impregnated with gold (1.8% Au), showed a 100% efficiency in the capture of Hg^0 during the time of experimentation in an atmosphere enriched in CO_2 with trace amounts of HCl and SO_2 . The capture of mercury occurred as a consequence of: (1) the formation of an amalgam between the gold nanoparticles and Hg^0 and/or (2) the adsorption of Hg^{2+} on the foam surface. The successive cycles of adsorption-desorption demonstrated the ability of the foam to be regenerated without a loss of efficiency in the capture of Hg^0 .

The coal foam is easily manageable, making it possible to manufacture carbon structures of any given shape. Moreover, the process designed allows the mercury captured on the sorbent to be recovered and the gold to be retrieved after depletion of the sorbent, by burning away the low ash containing carbon foam. More importantly in this preliminary study is that the proposed sorbent represents a new approach to the retention of Hg^0 at industrial scale that will reduce if not totally avoid the generation of toxic wastes in energy production processes.

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Conflicts of Interest: The authors declare no conflict of interest.

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