



Study of elemental mercury removal from flue gases using Tetravalent manganese Feroxyhyte

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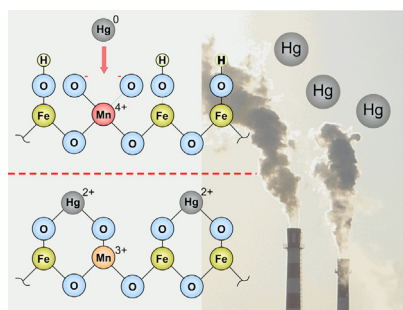
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HIGHLIGHTS

- The high oxidation potential of TMFx ensures Hg(0) oxidation.
- Adsorption capacity
 $Q_{50} = 13.9 \text{ mg Hg/g}$ at 120°C .
- Exothermic behavior of the process.
- EBCT strongly influences Q_{50} value.
- Effective TMFx regeneration by KI at room temperature.

GRAPHICAL ABSTRACT



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ABSTRACT

An innovative material, namely Tetravalent Manganese Feroxyhyte (TMFx), was synthesized and tested for its capacity to capture elemental mercury, Hg(0), from boiler flue gases. TMFx presents characteristics well-suited for this purpose, since it incorporates high oxidation capacity, high surface area and high negative surface charge density. Results show that the Hg(0) uptake capacity (Q_{50}) at break through concentration equal to the EU emission limit ($50 \mu\text{g}/\text{m}^3$) was essentially affected by synthesis pH, temperature and Empty Bed Contact Time (EBCT). The significantly high Hg(0) uptake capacity of 13.9 mg Hg/g , was determined for the material prepared at pH 9, and tested in a fixed bed reactor at $T = 120^\circ\text{C}$ and $\text{EBCT} = 40 \text{ ms}$. Uptake capacity was reduced at higher temperatures of $150\text{--}180^\circ\text{C}$, due to the exothermic nature of the process and degradation of the TMFx's surface properties. An XPS study and regeneration tests indicated oxidation of Hg(0) in its bivalent form that allows for regeneration of spent TMFx samples under mild chemical conditions (KI solution) at room temperature. These mild regeneration conditions result in preserving TMFx uptake capacity. The presence of flue gas constituents affected positively the TMFx's uptake capacity for Hg(0). Oxygen alone increased adsorption yield by 180%, NO by 80%, and HCl by 64%. In contrast, SO_2 had a strong negative effect, almost zeroing the Hg(0) uptake. The effect became positive when oxygen was added and yield increased by 25%. Contact time significantly influenced mercury uptake capacity, since by increasing the EBCT from 40 ms to 90 ms at 150°C , the Q_{50} value almost tripled.

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1. Introduction

Annual worldwide mercury emissions are estimated to exceed 2×10^3 tons, and this figure will increase if current trends in industry continue in the future[1]. 30% of these mercury emissions are

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generated from human activity and only 10% from natural sources. The remaining 60% is attributed to re-emissions of existing environmental mercury [2]. Of all the anthropogenic activities, coal burning power plants emit the most mercury. Although mercury is a trace element of coal (0.01–3.3 mg/g), environmental emissions are considerable due to the large quantities coal burned to meet high global energy demands [3].

In 2005, the European Commission launched a mercury strategy that aims to address the problem of mercury pollution, both in the EU and globally. The strategy contains measures to reduce mercury emissions, lower supply and demand, and protect from mercury exposure [4]. The strategy also identifies large lignite combustion plants as the largest emitters [5]. According to the most recent EU directive, the regulation limit for mercury emissions remains at 50 $\mu\text{g}/\text{m}^3$, although the global community does plan a further reduction [6].

The process of coal combustion results in elemental Hg(0), oxidized Hg(I)/Hg(II), and particulate Hg(p) mercury. Elemental mercury is primarily released since the thermodynamic equilibrium favors this form at high temperatures while oxidation is kinetically limited [7]. As the temperature reduces when passing through the stack, Hg(0) is partially oxidized to $\text{HgCl}_2/\text{Hg}_2\text{Cl}_2$ by chloride ions of flue gases which are presumed to be the dominant oxidation mechanism [8]. The percentage of oxidized mercury, which is easier to remove, depends on the coal fraction and its chloride content.

Oxidized and particulate mercury are usually retained by conventional air pollution control devices, such as electrostatic precipitators or fabric filters, flue gas desulphurization processes and scrubbers [9]. Depending on the process applied, up to 98% of mercury can be removed, although the actual yield is much lower and averages 40% [7]. This low removal efficiency should be attributed to the fact that these processes were not specifically developed for mercury treatment but were designed for other pollutants. In contrast, many recent studies focus on the synthesis of adsorbents for the specific removal of elemental mercury [10–19].

The main processes practiced are physisorption and/or chemisorption onto activated carbon, which is the adsorbent that has been studied the most widely. Carbon that has been chemically modified by either metals [10] or sulfur [11], is injected into exhaust gas and captured by control devices used for fly ash removal. The main disadvantage of activated carbon, and that of some inorganic materials, is their inability to oxidize Hg(0). Additionally, Hg(0) binding to the adsorbent's active sites is also limited. A higher uptake can be achieved by the presence of a compound that acts as an oxidant during the adsorption process, such as H_2S [12], O_2 [13] or HCl [14], which can transform Hg(0) to Hg(I)/Hg(II).

A significant number of inorganic adsorbents have also been investigated for mercury removal. However, in almost all cases the studies focused on maximum adsorption capacity, while failing to investigate their effectiveness to meet emissions standards, or determine their adsorption capacity at the regulation limit of mercury [15–17]. Moreover, there are also reports of inorganic materials that are capable of both oxidizing and capturing mercury [18]. These materials are based on the presence of manganese in their structure which aids the efficient oxidation of Hg(0) [15]. However, besides their ability to achieve residual concentration lower than the regulation limit for mercury emissions, their corresponding uptake capacities are limited. This may be attributed to their low surface area and their low $[\text{Mn}]/[\text{Fe}]$ molar ratio. On the other hand, Tetravalent Manganese Feroxyhyte (TMFx) is a material with high oxidation capacity, as well as high surface area and charge density, which has already been proved very effective in mercury adsorption from water [19] and, to the best of our knowledge, have not been previously investigated for Hg(0) uptake.

This study aims to investigate the efficiency of TMFx for the removal of Hg(0) from flue gases. The evaluation criteria include: ability to reduce the residual concentration to below the current emission limit of 50 $\mu\text{g}/\text{m}^3$, the influence of temperature and contact time of typical flue gas components on adsorption capacity, verification of Hg(0) oxidation using XPS, and the regeneration and leaching characteristics of the spent materials.

2. Materials and methods

2.1. Adsorbent synthesis

TMFx was prepared by precipitating FeSO_4 (40 g/L) under a highly oxidative environment defined by KMnO_4 (25 g/L) in a two-stage continuous flow (10 L/h) reactor working at 1 h retention time, as described in detail by Kokkinos et al., 2016 [20]. A NaOH solution (30% w/w) was continuously added to both reaction tanks to maintain pH at the targeted values of 4, 6, 9 and 12. The produced solid suspension was thickened for 24 h, washed several times with distilled water, centrifuged, dried for 4 h at 90 °C, then ground and sieved to obtain a fine powder (<63 μm).

The iron content of the synthesized samples was measured as 39 ± 1 wt%, manganese was 12.5 ± 0.2 wt%, and the bulk density was 0.55 ± 0.1 kg/L. The negative charge densities were determined as 0.1, 0.7, 1.8, and 1.1 mmol H^+/g for the samples synthesized at pH 4, 6, 9 and 12, respectively, while the recorded corresponding specific surface areas were 85, 183, 301 and 272 m^2/g , respectively.

2.2. Adsorption evaluation

Adsorbent evaluation for mercury removal was carried out using a down-flow packed bed reactor located within a tubular furnace with a temperature regulation ranging from 50 to 250 °C. The elemental mercury inflow concentration was maintained at 400 $\mu\text{g}/\text{m}^3$ by adjusting the N_2 flow rate passing through the mercury saturator (100 mL/min) and the temperature of the furnace into which the mercury permeation tube was placed (Fig. 1). A second inflow line allowed the passage of different, typical components of combustion flue gases, such as O_2 , HCl, SO_2 , and NO, in order to observe their effect on the absorption capacity of the material.

A cold vapor atomic absorption spectrometer (CVAAS-Mercury Instruments Analytical Technologies: Mercury Vapor Monitor VM 3000) and an online data acquisition system were used to record the effluent concentrations. The adsorbent weight was calculated in relation to its bulk density in order to run an experiment under the eligible Empty Bed Contact Time (EBCT). The effectiveness of the adsorbents was evaluated according to their uptake capacity (Q , mg Hg/g adsorbent) at the breakthrough concentration of the international emission limit of 50 $\mu\text{g}/\text{m}^3$, which will hereafter be abbreviated as Q_{50} . The mercury content in spent TMFx samples was determined as follows: A 10 mg dry sample was placed in a 100 mL PTFE beaker. Then 20 mL of 6 N HCl were added and boiled for about 1 h until the sample had been completely dissolved. The solution was cooled and transferred to a 100 mL volumetric flask. The mercury concentration was determined by graphite furnace atomic absorption spectrophotometry using a Perkin Elmer AAnalyst800 instrument.

2.3. Mercury speciation

X-ray Photoelectron Spectroscopy (XPS) was applied to identify the mercury speciation after its uptake by TMFx. The spectrum was acquired in an Axis Ultra DLD system by KRATOS. A monochromated Al-K α 1 X-ray beam was used as the excitation source. The pass energy was 160 eV for survey scans and 40 eV for high resolu-

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