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Phenomenological modeling for elemental mercury capture on hydroxyapatite-based adsorbents: An experimental validation

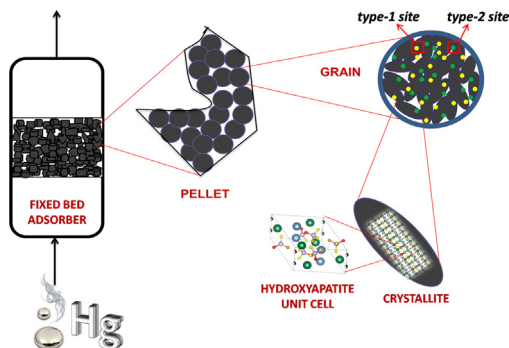
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GRAPHICAL ABSTRACT



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ABSTRACT

The knowledge of the risks associated with the mercury pollution and the presence of mercury in gas processing plants has motivated the development of new efficient technologies for mercury removal from natural gas streams. In this work, the results of the physicochemical characterization of a synthetic adsorbent are used to understand the gaseous mercury adsorption process. The adsorbent is a mesoporous copper sulfide (Cu_xS_y)-hydroxyapatite with well-dispersed active sites presenting high-performance for mercury removal and fixation. Experimental results indicated that mercury migrates by diffusion into the mesopores where it is chemisorbed in two active sites located on the crystalline surface. These experimental results were considered in a phenomenological description of transport and adsorption processes resulting in a novel and more realistic mathematical model. In addition, experimental breakthrough curves at different conditions were used to validate the proposed mechanisms. The integration of experimental and modeling allowed an in-depth understanding of the adsorbents as well as the mercury removal process.

1. Introduction

Mercury represents a major threat to the environment and human

health, which motivates global active discussions. Due to its characterization as a global pollutant, more stringent regulations to limit mercury emissions have been drafted by environmental agencies [1,2].

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Nomenclature

C	mercury concentration in fluid phase ($\text{g}\cdot\text{cm}^{-3}$)
C_f	mercury concentration in fluid phase in the inlet of the bed ($\text{g}\cdot\text{cm}^{-3}$)
C_p	mercury concentration inside the pores ($\text{g}\cdot\text{cm}^{-3}$)
Q	mercury concentration in solid phase ($\text{g}\cdot\text{cm}^{-3}$)
t	time (h)
z	axial length coordinate in the fixed bed (cm)
L	fixed bed length (cm)
r	radial coordinate in the spherical particle (cm)
u	squared radial coordinate in the spherical particle (cm^2)
R_p	particle radius (cm)
D_p	intraparticle diffusion coefficient ($\text{cm}^2\cdot\text{h}^{-1}$)

D_{ax}	bed diffusivity ($\text{cm}^2\cdot\text{h}^{-1}$)
A_s	particle surface area (cm^2)
$S_{\max,i}$	maximum concentration of type- i sites ($i = 1$ or 2) ($\text{g}\cdot\text{cm}^{-3}$)
K_i	specific velocity of chemisorption on type- i sites ($i = 1$ or 2) ($\text{cm}^3\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)
E_i	Hg/S stoichiometric ratio for type- i sites ($i = 1$ or 2) ($\text{g}_{\text{Hg}}/\text{g}_s$)

Greek letters

ε	the bed porosity (-)
ε_p	particle porosity (-)
v	interstitial gas velocity ($\text{cm}\cdot\text{h}^{-1}$)

Mercury and its compounds occur naturally in fossil fuels, such as petroleum, natural gas, and condensed gas [3]. A representative level of mercury concentration on natural gas streams is difficult to be established given its natural variability; values of 1–200 $\mu\text{g}/\text{m}^3$ and 4400 $\mu\text{g}/\text{m}^3$ have been mentioned in the literature [4,5]. Even in low mercury concentrations, aluminum equipment failures at natural gas processing plants can be induced by mercury embrittlement of structures, such as in the catastrophic processing plant accidents occurred in 2004 at Moomba, Australia, and Skikda, Algeria [6]. In addition, condensation and accumulation of elemental mercury, especially in cryogenic process plants make imperative its removal from natural gas streams [7].

Elemental mercury capture technologies include the use of regenerative adsorbents, mainly those based on activated carbon and transition metal oxides [8–12]. The possibility of regeneration is an interesting feature as far as the financial aspect is concerned. However, the stability of mercury captured on the adsorbents must be tested to meet the stricter leaching and thermal stability requirements for storage and disposal of mercury-containing wastes [13]. Thus, stabilization/solidification (S/S) processes are often required prior to disposal of spent adsorbents into a secured landfill [14,15]. Taking advantage of the sulfur-mercury chemical affinity, sulfide-induced mercury stabilization has been reported as an effective technology to stabilize mercury-containing wastes, converting mercury into mercury sulfide, a compound with low solubility and high thermal stability [16–18]. Similarly, non-regenerable sulfur-containing adsorbents have been found to be very effective for simultaneous mercury removal and stabilization, producing less hazardous wastes and minimizing mercury reemission [19,20].

In our previous works, hydroxyapatite modified with copper sulfide has been pointed out as a high capacity adsorbent for mercury removal from gaseous streams, including the fixed-bed mercury adsorption from simulated natural gas [21,22]. Two mathematical models were proposed by considering different mercury uptake as well as transport mechanisms in the packed-bed and inside the adsorbent particles. In those works, we have mentioned that additional experimental information should be obtained to elucidate all involved phenomena and to choose the most appropriate mathematical model.

Here, we provide a new phenomenological modeling approach integrating experimental and simulation data in the following steps: (1) obtaining new experimental data of physicochemical characterization of the hydroxyapatite-based adsorbents, and evaluating of the dynamic mercury adsorption behavior on these adsorbents; (2) proposal of a novel phenomenological model based on the obtained morphology and crystalline structure of the adsorbents, and (3) experimental validation of the proposed model by new breakthrough curves obtained using simulated natural gas at different operational conditions.

2. Methodology**2.1. Experimental****2.1.1. Adsorbent preparation**

Hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] was synthesized by the precipitation method using 0.30 M phosphate of ammonium (solution A) and 0.50 M calcium nitrate (solution B). During the slow addition ($2.5\text{ mL}\cdot\text{min}^{-1}$) of solution B on solution A, the pH was adjusted at 10–11 using a 0.30 M ammonium hydroxide solution. The mixture was mechanically stirred at a temperature of $80 \pm 5^\circ\text{C}$ for two hours and then filtered off. The precipitate was washed with hot water ($80 \pm 5^\circ\text{C}$), dried at 100°C for 24 h, and calcined in air flow ($50\text{ mL}\cdot\text{min}^{-1}$) at 300°C for two hours.

As the hydroxyapatite structure allows ionic substitutions, a copper nitrate solution was used to incorporate into its crystalline matrix a copper content about 5%wt by ion-exchange method (samples were named Cu-HAp[TI-1] and Cu-HAp[TI-2]) and 2%wt by co-precipitation method (sample was named Cu-HAp[CP]). By using the ion-exchange method, 5 g of the synthetic hydroxyapatite was kept in contact with a 0.14 M copper nitrate solution under constant magnetic stirring (250 rpm) for four hours. Then, the mixture was filtered off and the precipitate was dried at 100°C for 24 h, and calcined in air flow ($50\text{ mL}\cdot\text{min}^{-1}$) at 300°C for two hours. In the co-precipitation method, copper is already added in the hydroxyapatite precipitation step, by replacing part of the volume of the calcium nitrate solution with a copper nitrate solution. Using the co-precipitation method, the obtained copper-modified hydroxyapatite is usually characterized by a high specific surface area and the substituting ions are incorporated into the hydroxyapatite lattice [23].

In order to activate the mercury removal sites, all copper-modified hydroxyapatite samples were exposed for 2 h to a stream with 5% H_2S diluted in helium at room temperature, immediately before the adsorption tests.

2.1.2. Physicochemical characterization

Textural properties of the adsorbents were evaluated by N_2 adsorption at 77 K using a Micrometrics® ASAP 2000 equipment. The specific surface area was calculated using the BET equation [24,25]. Barret-Joyner-Halenda (BJH) method was used to calculate the average mesoporous volume from adsorption/desorption isotherms [26]. The chemical composition of adsorbent samples was determined by X-ray fluorescence (XRF) using a Rigaku RIX 3100 equipment with a rhodium tube (4 kW). Microscopy images were obtained by means of a Field Emission Gun Scanning Electron Microscope (FEG-SEM), FEI Company Quanta 400 equipment operated under high vacuum at 20 kV and a

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