



Investigation of adsorption-enhanced reaction process of mercury removal from simulated natural gas by mathematical modeling



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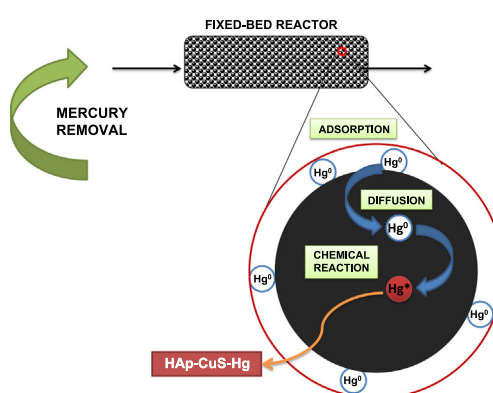
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HIGHLIGHTS

- The proposed model for Hg fixation involves adsorption, diffusion and chemical reaction.
- Experimental data are obtained for low concentration in the gaseous stream.
- Chemical fixation of mercury inside the solid matrix leads to an increase of mercury removal capacity.
- Chemical fixation minimizes the risks of mercury re-emission to environment.

GRAPHICAL ABSTRACT



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ABSTRACT

Hydroxyapatites modified with copper sulfide were studied as sorbents for mercury removal from gaseous streams containing low mercury concentration. A mathematical model was proposed to take into account adsorption, diffusion into the sorbent particle and chemical reaction inside the solid matrix. The chemical reaction mechanism for mercury fixation into the solid matrix is supported by XRD analysis results. The unknown parameters are estimated from experimental data by minimization of the unweighted least-squares function, using a hybrid of Newton-like and Particle Swarm Optimization methods. Results are shown for two hydroxyapatite sorbents developed in our lab. The model, with its optimized parameters, was used to study the dynamic behavior of a fixed bed adsorption process at different operational conditions. Simulation results show that the chemical fixation of mercury inside the solid matrix leads to an increase of mercury removal capacity and it provides insights about operational plant conditions.

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1. Introduction

Combustion of fossil fuels is the main way of mercury emission from anthropogenic sources, especially in coal-burning power plants [1–3]. Currently, mercury is considered as a “global pollutant” because it can be transported globally in its gaseous

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Nomenclature

C	mercury concentration in the fluid phase (kg m^{-3})	HAp	hydroxyapatite
C_o	inlet mercury concentration (kg m^{-3})	<i>PSO parameters</i>	
\bar{q}	average amount of mercury inside the particles (kg m^{-3})	N_{pt}	number of points
q_{RQ}	amount of mercury reacted at time t (kg m^{-3})	N_{iter}	number of iterations
q_{RQm}	maximum amount of mercury fixed by solid (kg m^{-3})	w	initial inertial value
q_{Rp}	amount of mercury adsorbed in equilibrium (kg m^{-3})	c_1	cognition parameter
K	equilibrium constant of the adsorption isotherm	c_2	social parameter
k	specific velocity of Hg fixation ($\text{m}^3 \text{kg}^{-1} \text{s}$)	TOL	tolerance
R_p	particle radius (m)	<i>Dimensionless numbers</i>	
D	diffusivity ($\text{m}^2 \text{s}$)	σ	constant
L	bed length (m)	Γ	dimensionless mercury concentration in the fluid phase
z	axial coordinate (m)	Γ_i^C	calculated dimensionless concentration in the fluid phase at the outlet of the bed
r	radial coordinate (m)	Γ_i^E	experimental dimensionless concentration in the fluid phase at the outlet of the bed
v	linear velocity of the gas (m s^{-1})	τ	dimensionless time
t	time (h)	ϖ	relation between convective and diffusive terms
T	temperature (K)	ξ	dimensionless length
m	sorbent weight (kg)	ψ	dimensionless mercury concentration in the solid phase
S	value of optimized objective function	ϕ	relation between reactive and diffusive terms
NE	number of experimental points	λ	dimensionless related to available sites for mercury fixation
n	number of discretization boxes	κ	dimensionless isotherm constant
ρ_p	particle density (kg m^{-3})	λ_{max}	dimensionless of maximum fixation capacity
ρ_b	bed density (kg m^{-3})		
ε	porosity		
<i>Abbreviations</i>			
PSO	Particle Swarm Optimization		
SQP	Sequential Quadratic Programming		

elemental form [1]. Furthermore, mercury is a substance which has been focus of many studies due to its adverse effects on human health, high toxicity and bioaccumulative properties.

On natural gas, typical concentrations of mercury are between 1 and $200 \mu\text{g m}^{-3}$ [4]. However, there is a significant spatial-temporal variability of mercury concentration in natural gas [5,6] and high amounts of this fuel are processed annually around the world. Therefore, mercury emissions from natural gas require control even though the low mercury concentrations. Furthermore, mercury corrosion is associated with serious failures at natural gas plants [4].

Mercury emissions occur in three forms: elemental mercury (Hg^0), oxidized mercury (Hg^{2+}) and particle-bound mercury (Hg^p) [7]. Elemental mercury is the major chemical form emitted to the atmosphere [8] and it is difficult to capture by the existing air pollution control devices due to both water insolubility and high volatility [9].

Adsorption onto carbon, activated carbon, halide- and sulfur-impregnated activated carbon [10–13], transition metal oxides [14], and supported noble metals have been reported in the literature [15]. The stability of captured mercury is an important issue and desired characteristic of the sorbent, knowing the environmental risks associated with sorbent disposal at the end of adsorption process. Some recent studies have investigated sorbents with ability to retain mercury in stable form [16]. However, only a few studies have focused on modeling the adsorption-fixation mercury from gaseous stream. Chung et al. [17] applied the modeling assuming to different active sites for mercury adsorption on impregnated activated carbon. Ren et al. [18] developed a model based on the mechanism of surface equilibrium and mass transfer, and this model can be used to determine the effects of sorbent properties on mercury removal at different conditions. None of

previous model includes, besides adsorption, the Hg fixation process explicitly.

Here, we provide a model based on the mercury sorption process involving the surface adsorption, the diffusion into the sorbent particle, and the chemical reaction into the solid matrix. The chemical reaction mechanism is added to the model aiming to explain the high mercury fixation capacity of our sorbents, which was previously confirmed by stabilization results to lixiviation and thermal treatment tests. Very low leaching of mercury in water ($\text{pH} = 5$) and no Hg release at high temperatures (up to 60°C) were observed [19]. Simulations using the proposed model are performed to observe the influence of mercury-fixation on the dynamics behavior of the fixed-bed column.

2. Experimental section

2.1. Sorbents

Two different adsorbents developed in our laboratory are used here: sorbent A (Case 1) and B (Case 2). Both sorbents are synthetic non-stoichiometric hydroxyapatites (HAp), $\text{Ca}_{10-2z}(\text{HPO}_4)_2(\text{PO}_4)_{6-z}(\text{OH})_{2-2z}$ [$0 < z < 1$], modified with different copper content (5.4% to solid A and 2.3% to solid B). Hydroxyapatite precursor of sorbent A was prepared by the precipitation method and copper incorporation was performed by the ion exchange method. These methods were described to zinc modified hydroxyapatites in previous work [20], but copper instead of zinc is used in the present work. Sorbent B was prepared by co-precipitation method: copper incorporation already occurs in hydroxyapatite preparation substituting part of calcium nitrate used in hydroxyapatite precipitation by copper nitrate. Both sorbents (A and B) were exposed to a stream with 5%

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