RHODES 2024
11th International Conference on Sustainable Solid Waste Management
Rhodes, Greece, 19 - 22 JUNE 2024

Modelling of Hg adsorption on activated carbon in WtE plant fabric filters

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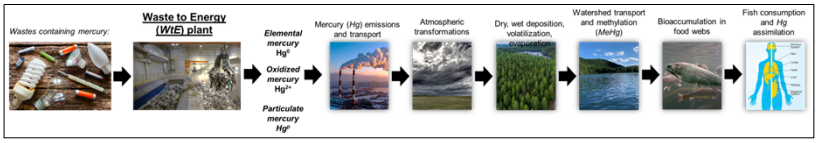
MERCURY PROBLEM



AIMS OF THE STUDY

Development of a model using a kinetic approach to describe the mercury adsorption process on activated carbon based on data from a full-scale solid waste incineration plant equipped with a dry flue gas treatment line. Previous literature on mercury removal with activated carbon was studied and critical points in modelling to go beyond the state-of-the-art were identified and implemented in the present study.

MERCURY ADSORPTION ON ACTIVATED CARBON IN A FABRIC FILTER

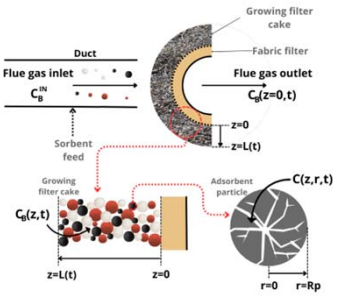


Figure 1. schematics of Hg

Hypothesis

- Activated carbon (AC) particles all spherical, uniform in size, uniformly dispersed in the gas phase, and uniformly distributed within the packed bed.
- Mass transfer boundary layer causes resistance to external mass transfer and intraparticle mass transfer is controlled by pore diffusion.
- q_{max}, k_1, k_2 constants → small variation with temperature
- Only $HgCl_2$ → 70-90% of total Hg.
- Negligible in-duct adsorption → short contact time.
- All fabric filter (FF) modules modelled as one → info on overall pressure drop.
- Filter cake properties based on mass fraction of reactants where only activated carbon can effectively adsorb $HgCl_2$.

MODELLING

The model is based on the pore diffusion mechanism and Langmuir theory for the equilibrium between the gas phase and the surface of activated carbon particles. It neglects in-duct adsorption and focuses on Hg adsorption solely within the growing bed deposited on the fabric filter surface.

Adsorption on activated carbon

$$\frac{\partial q}{\partial t} = k_{1,m}(q_{max,m} - q)C - k_{2,m}q$$

Intraparticle mass transfer

$$\epsilon_{b,tot}\frac{\partial C_B}{\partial t} = u\frac{\partial C_B}{\partial z} - \frac{3\rho_{b,tot}D_e}{\rho_{p,m}R_{p,m}}\frac{\frac{Q_{AC1}}{\rho_{b,AC1}} + \frac{Q_{AC2}}{\rho_{b,AC2}}}{\frac{Q_{bic}}{\rho_{b,bic}} + \frac{Q_{AC1}}{\rho_{b,AC1}} + \frac{Q_{AC2}}{\rho_{b,AC2}}}\frac{\partial C}{\partial r}\Big|_{(z,R_p,t)}$$

External mass transfer

$$\epsilon_{p,m}\frac{\partial C}{\partial t} = D_e\left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right) - \rho_{p,m}[k_{1,m}(q_{max,m} - q)C - k_{2,m}q]$$

Initial conditions

$$IC\begin{cases} q(z,r,t_i=0) = q(z,r,t_{i-1}=t_F) \\ C(z,r,t_i=0) = C(z,r,t_{i-1}=t_F) \\ C_B(z,r,t_i=0) = C_B(z,r,t_{i-1}=t_F) \\ L(t_i=0) = L_0 \end{cases}$$

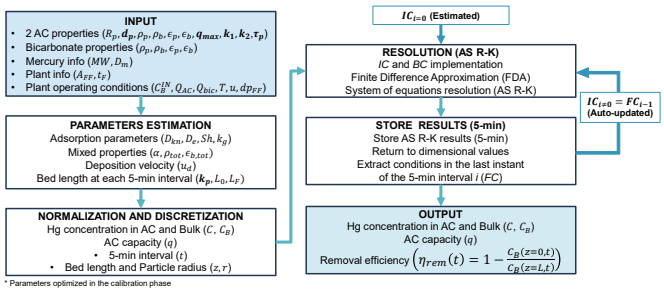
Boundary conditions

$$BC\begin{cases} C_B(z=L,t) = C_B^{IN} \\ q(z=L,r,t) = 0 \\ C(z=L,r,t) = 0 \\ \left.\frac{\partial C_B}{\partial z}\right|_{(z=0,t)} = 0 \\ \left.\frac{\partial C}{\partial r}\right|_{(z,r=R_p,t)} = \frac{k_g}{D_e}[C_B(z,t) - C(z,R_p,t)] \\ \left.\frac{\partial q}{\partial r}\right|_{(z,r=0,t)} = 0 \\ \left.\frac{\partial C}{\partial r}\right|_{(z,r=0,t)} = 0 \end{cases}$$

C = HgCl2 concentration in the gas phase of the internal pore (kg of HgCl2/m3
C_B = HgCl2 concentration in the bulk gas phase of the filter cake (kg of HgCl2/m3)
D_e = effective pore diffusion coefficient (m^2/s)
k_1 = Adsorption rate constant (m^3 kg^(-1) s^(-1))
k_2 = Desorption rate constant (s^(-1))
k_g = Gas-phase mass-transfer coefficient (m/s)
k_p = bed constant ($m/mbar\ s$)
L = Filter cake thickness (m)
Q_{AC} = Sorbent loading in the flue gas (kg/m^3)
Q_{bic} = Bicarbonate loading in the flue gas (kg/m^3)
q = Hg adsorbed on the sorbent (kg_{Hg}/kg_{AC})
q_{max} = maximum adsorption capacity (kg_{Hg}/kg_{AC})
R_p = Radius of the particle (m)
r = Sorbent radial distance (m)
u = superficial gas velocity (m/s)
ϵ_b = bed porosity (-)
ϵ_p = particle porosity (-)
ρ_b = bed density (kg/m^3)
ρ_p = sorbent particle density (kg/m^3)
d_p = pore diameter (Å)
τ_p = tortuosity factor
m = mixed properties
tot = total

MODEL IMPLEMENTATION

The coordinate transformation technique and finite difference approximation was applied to make the system of differential equations (i.e., Langmuir equation, Hg mass balance along the bed and inside the AC particle) more tractable and solvable with an adaptive step size Runge-Kutta solver. With respect to previous studies which considered static operating conditions, the model developed in the present study takes into consideration the Hg concentration variability at the FF inlet and the simultaneous injection of two different types of activated carbon



* Parameters optimized in the calibration phase

RESULTS

- ❑ The model has undergone calibration and subsequent validation using datasets particularly chosen including high and low Hg concentrations (19'500 five-minute average data points)
- ❑ When employing consistent Langmuir constants (i.e., q_{max}, k_1, k_2) across different inlet Hg concentrations, the calculated Hg removal efficiency seemed to be underestimated, particularly for low Hg inlet concentrations (below 20 µg/m³).

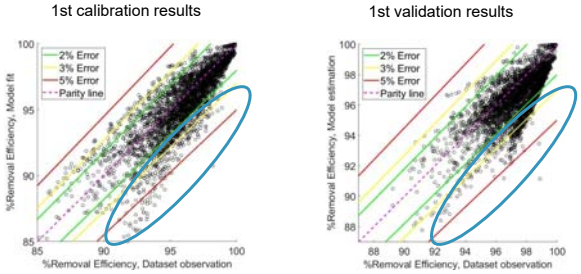


Figure2. First calibration and validation results: for Hg inlet concentration under 20 ug/Nm³ (blue curve) the model tends to underestimate the removal efficiency.

- ❑ As a result, the model was recalibrated independently for inlet Hg concentrations above and below the abovementioned threshold. The outcome notably improved.
- ❑ Overall, the model demonstrated the capability to estimate Hg removal efficiency in the FF unit with a maximum absolute error margin of ±3% and a mean absolute percentage error of 0.87%.

Table 1. Calibration parameters, optimal ranges and optimized values for the fabric filter mercury adsorption model

Calibration parameter	Optimization range	1st optimized value	2nd optimized value	
			<20 µg/m³	>20 µg/m³
$q_{max,AC1}$ (kg/kg)	$10^{-5} - 5 \cdot 10^{-1}$	$4.88 \cdot 10^{-1}$	$4.95 \cdot 10^{-1}$	$4.81 \cdot 10^{-1}$
$k_{1,AC1}$ (m^3kgs)	$10^1 - 5 \cdot 10^3$	10^2	$1.04 \cdot 10^2$	$1.08 \cdot 10^2$
$k_{2,AC1}$ (s^{-1})	$10^{-8} - 10^{-1}$	$3.63 \cdot 10^{-3}$	$2.85 \cdot 10^{-3}$	$2.69 \cdot 10^{-3}$
$q_{max,AC2}$ (kg/kg)	$10^{-5} - 5 \cdot 10^{-1}$	$6.09 \cdot 10^{-2}$	$5.17 \cdot 10^{-2}$	
$k_{1,AC2}$ (m^3/kgs)	$10^1 - 5 \cdot 10^3$	$1.01 \cdot 10^3$	$1.11 \cdot 10^3$	
$k_{2,AC2}$ (s^{-1})	$10^{-8} - 10^{-1}$	$5.44 \cdot 10^{-2}$	$5.48 \cdot 10^{-2}$	
$d_{p,AC1}$ (m)	$5 \cdot 10^{-10} - 5 \cdot 10^{-8}$	$8.27 \cdot 10^{-9}$	$9.31 \cdot 10^{-9}$	
$d_{p,AC2}$ (m)	$5 \cdot 10^{-10} - 5 \cdot 10^{-8}$	$2.05 \cdot 10^{-8}$	$2.03 \cdot 10^{-8}$	
k_p ($m/mbar\ s$)	$10^{10} - 10^5$	$9.64 \cdot 10^6$	$8.49 \cdot 10^6$	
$\tau_{p,AC1}$	$5 \cdot 10^0 - 65 \cdot 10^1$	$5.00 \cdot 10^0$	$5.21 \cdot 10^0$	
$\tau_{p,AC2}$	$5 \cdot 10^0 - 65 \cdot 10^1$	$8.16 \cdot 10^0$	$8.01 \cdot 10^0$	
Mean absolute percentage error (MAPE)		1.32%	0.87%	

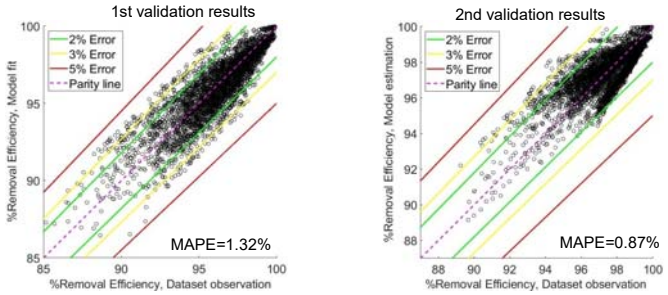


Figure 3. Validation comparison of the recalibrated model: (left panel: 1st model - 328 validation data points outside 3% error band; right panel: recalibrated model - only 59 data points outside 3% error band)

CONCLUSIONS

- ❑ The model performance indicators confirmed the effectiveness of the applied methodology but there is potential for further improvement.
- ❑ A critical review of the initial hypotheses could amplify the complexity of the phenomenon's description.
  - ❑ This could involve incorporating elemental mercury, currently overlooked, and accounting for the packing phenomenon in the filter cake.
  - ❑ Additionally, investigating the delay between flue gas entry and exit from the FF presents another point for exploration.
  - ❑ Further refinement of the model includes optimizing the algorithm employing more robust resolution techniques, enhancing the accuracy and minimizing the computation time.

FUTURE DEVELOPMENTS

- ❑ The model was developed with the intention of integrating it into phenomenological models for the creation of virtual sensors, specifically for mercury monitoring in Waste-to-Energy plants. These virtual sensors serve as backups in the event of stack mercury analyzer failures, bridging the monitoring gap until the physical analyzers are reinstated.
- ❑ The model has also the potential to play a key role in a data-driven activated carbon feed control strategy, thereby contributing to increased economic and environmental sustainability in WtE plants.

Related paper: Speroni et al., 2024. Mercury adsorption on activated carbon in Waste-to-Energy: model development and validation on real plant data. Waste Management 184:72-81.

MODELLING APPROACH REFERENCES

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