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Modeling of mercury sorption by activated carbon in a confined, a semi-fluidized, and a fluidized bed

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Abstract

A process model was developed to simulate elemental mercury sorption by activated carbon in three distinct beds, namely a confined, a semi-fluidized, and a fluidized bed. The model involved the coupling of a kinetic model based on the mechanisms of surface equilibrium and external mass transfer, and a material balance model based on the tank-in-series approach. For surface equilibrium, three different equilibrium laws were used in the model, namely the Henry's Law, the Langmuir isotherm and the Freundlich isotherm. Literature mercury sorption data were used to determine the best-fit values of parameters for these equilibrium expressions. The parameter-fitted model was then used to simulate mercury sorption processes in the three distinct beds. The simulation parameters were mercury concentration, gas flow rate, adsorption temperature and the degree of semi-fluidization.

The simulation results have indicated that the model is capable of describing the literature available mercury sorption data. All the three surface equilibrium laws appear to simulate the adsorption profiles equally well mainly because the sorption process occurs in an extremely low concentration range. The simulation results for the three distinct beds have suggested that the confined bed has the best mercury control performance; however, it generates the highest pressure-drop across the bed. A fluidized bed creates the least pressure drop; however, its sorption performance is poor. A semi-fluidized bed offers acceptable performance with affordable pressure-drops and can be a practical candidate for the process.

1. Introduction

Mercury emissions from coal combustion and waste incineration have been a great environmental concern and are targeted under the Clean Air Act Amendments of 1990 (Keating et al., 1997). Unlike most other trace elements, mercury is highly volatile and exists almost exclusively in the vapor phase of combustion flue gases, either in the form of elemental mercury or mercury salts such as $HgCl_2$, HgO, HgS and $HgSO_4$ (Keating et al., 1997). To protect public health, mercury emission standards of as low as 30 μg/dscm (dry standard cubic meter) have been imposed and are expected to be even stricter in the future (Keating et al., 1997).

A promising method for effective mercury emission control is to employ suitable sorbents to absorb/adsorb mercury from the combustion flue gas (Krishnan et al., 1994, 1997; Keating et al., 1997; Korpiel and Vidic, 1997; Liu and Vidic, 2000). Activated carbon with or without chemical impregnation has been reported to be effective for mercury sorption (Krishnan et al., 1994, 1997; Korpiel and Vidic, 1997). It is generally observed that mercuric chloride is more easily adsorbed by non-chemically-impregnated activated carbons than elemental mercury. However, sulfur-impregnated activated carbons have been found to dramatically enhance elemental mercury sorption (Keating et al., 1997). The other flue gas components, e.g., SO_2, NO_x, CO_2, and moisture, have negligible effect on the sorption process for elemental mercury (Liu and Vidic, 2000).

In addition to experimental investigations, efforts have also been devoted to the modeling of mercury sorption processes (Carey et al., 1998; Meserole et al., 1999). Carey et al., (1998) developed a mass transfer model involving surface equilibrium to simulate mercury removal in a fixed bed. They concluded that the Freundlich isotherm provides a slightly better fit than the Langmuir isotherm during the simulations. Meserole et

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al. (1999) presented a theoretical model that combines the adsorption characteristics measured in the laboratory with mass transfer considerations to predict mercury removal by the duct injection process in actual flue gas streams. In their study, the Freundlich isotherm was used to describe the surface equilibrium. Their simulations were to predict when mercury removal is limited by mass transfer and when it is limited by sorbent capacity when injecting a powdered sorbent upstream of either an electric precipitator or fabric filter.

In this study, a process model was developed to simulate elemental mercury sorption by activated carbon in three distinct beds, namely a confined, a semi-fluidized, and a fluidized bed. The model involved the coupling of a kinetic model based on the mechanisms of surface equilibrium and external mass transfer, and a material balance model based on the tank-in-series approach. Three different equilibrium expressions were used in the model, i.e. the Henry's Law, the Langmuir isotherm and the Freundlich isotherm. Literature mercury sorption data were used to determine the best-fit values of parameters for these equilibrium expressions. The parameter-fitted model was then used to simulated mercury sorption processes in the three distinct beds. The simulation parameters were mercury concentration, gas flow rate, adsorption temperature and the degree of semi-fluidization.

2. Process description

Fig. 1 describes the three mercury adsorption beds involved in this study. For all three beds, activated carbon is placed between two bed-dividers, a distributor at the bottom and a fine-mesh screen at the top. The difference among the three is the location of the screen. When it is located right at the static bed height, the bed will be a confined bed during operation (Fig. 1a). When it is located well above the static bed height, the bed will be a fluidized bed (Fig. 1c). A semi-fluidized bed will be formed if the screen is located somewhere between the heights of the confined and the fluidized bed (Ho et al., 1987) (Fig. 1b). It should be noted that all three beds can be operated at a wide range of superficial velocities above that of the minimum fluidization velocity (U_{mf}) of the bed particles. This implies that these beds can have a substantially higher throughput than that of a conventional fixed bed, although the pressure-drop can be higher, especially for the confined bed.

3. Theoretical

The proposed process model involved the coupling of a kinetic model and a material balance model based on the tank-in-series approach. The kinetic model was

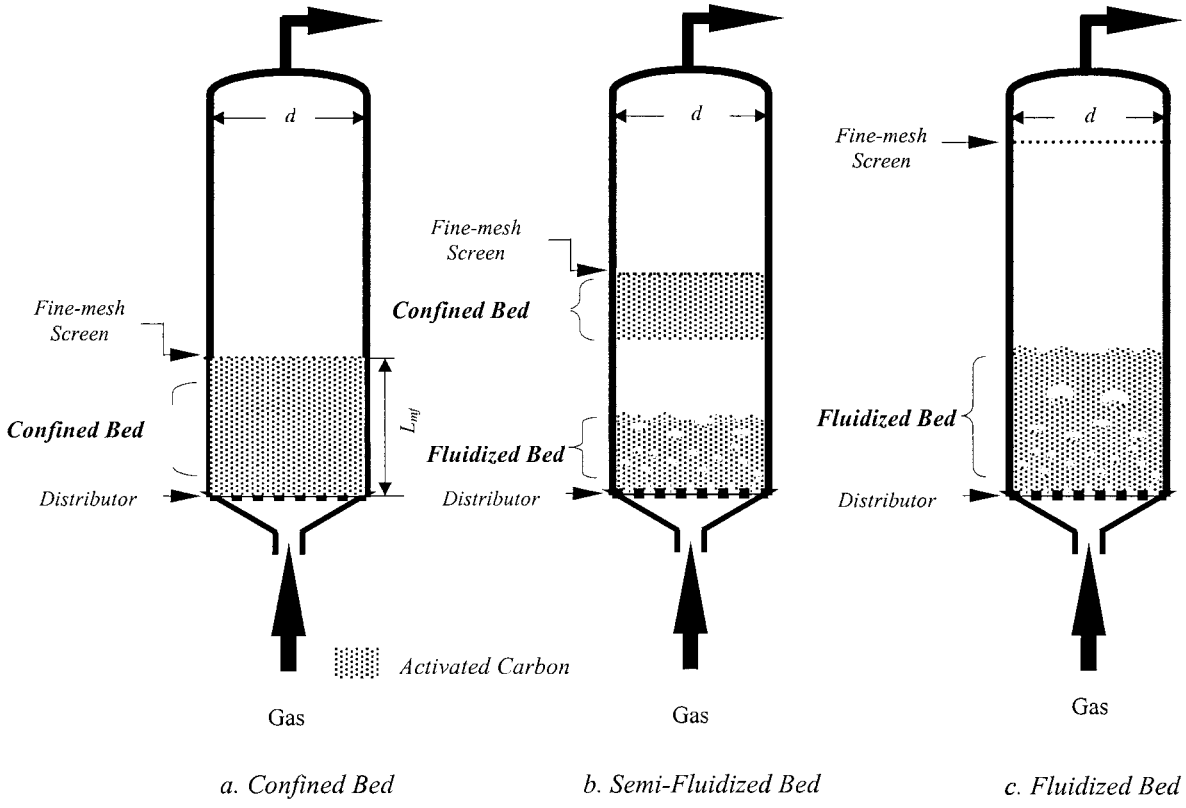

Fig. 1. Schematic diagram of the confined, semi-fluidized and fluidized beds.

based on the mechanisms of surface equilibrium and external mass transfer.

3.1. Model derivation

The transport rate for mercury between the bulk of the fluid phase and the outer surfaces of the sorbent granules is given by (Perry and Chilton, 1973)

$$dN/dt = K_g S_{ex}(C - C^i) \quad (1)$$

For a segment of an adsorption system, the following material balance principle must be satisfied:

$$dN/dt = (FC_i - FC_e) \quad (2)$$

Eqs. (1) and (2) can be combined to yield:

$$K_g S_{ex}(C\text{-}C^i) = (FC_i - FC_e) \quad (3)$$

With the assumption that the segment of the bed acts like a complete stirred tank reactor (i.e. $C = C_e$), Eq. (3) may be rearranged to yield

$$C = (K_g S_{ex} C^i + FC_i)/(K_g S_{ex} + F) \quad (4)$$

Eq. (4) describes the concentration of mercury in a segment of the bed at any bed location. The C^i appearing in Eqs. (1), (3) and (4) is estimated by one of the three surface equilibrium expressions described below.

3.2. Surface equilibrium expressions

Three surface equilibrium laws were proposed to estimate C^i in the model. They were: Henry's Law, Langmuir isotherm, and Freundlich isotherm. The corresponding equations are expressed below:

3.2.1. Henry's Law

In this approach, the C^i in the model was estimated using the ideal gas law expressed as:

$$C^i = P^i/RT \quad (5)$$

where P^i in the above equation was estimated by the following Henry's Law expression:

$$P^i = xH \quad (6)$$

3.2.2. Langmuir Isotherm

In this approach, the C^i in the model was estimated using the following Langmuir expression:

$$q = nC^i/(1 + kC^i) \quad (7)$$

After rearrangement, the above equation becomes

$$C^i = q/(n - kq) \quad (8)$$

3.2.3. Freundlich Isotherm

In the Freundlich isotherm approach, the C^i in the model was estimated using the following expression:

$$q = [1/k][C^i]^{1/n} \quad (9)$$

After rearrangement, the above equation becomes

$$C^i = [k]^n[q]^n \quad (10)$$

3.3. Model simulation

The tank-in-series model was employed for all three beds. When a confined bed was simulated, a 50-tank model was used; while for a fluidized bed, a one-tank model was assumed. The assumption implies that a fluidized bed is assumed to behave like a complete stirred tank reactor (CSTR), which may be over-simplified but is adequate for serving the purpose in this study (Kunii and Levenspiel, 1991). A semi-fluidized bed was considered to have a fluidized bed section at the bottom and a confined bed at the top having the same amount of particles in each tank as that in the confined bed simulation. The mass transfer coefficients (K_g) for the simulations were estimated by the experimental measurements reported by Resnick and White (1949) (Fig. 2). Note that the Modified Henry's Law Constant (H) and the values of parameters for Langmuir (n and k) and Freundlich (n and k) isotherms for different

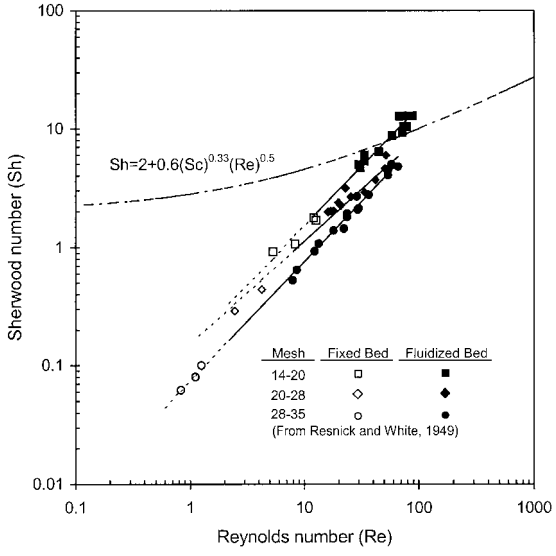

Fig. 2. Sherwood number for fixed and fluidized bed (Resnick and White, 1949).

mercury-sorbent pairs were evaluated by fitting experimental observations reported in the literature to the model. Note that in each simulation, the initial and boundary conditions were set up as follows:

Initial conditions:

$$t = 0,\ C_i = C_o \text{ All Tanks}$$

$$x(\text{or}\quad q) = 0 \text{ All Tanks}$$

$$\text{Boundary Conditions}: t > 0,\ C_i = C_o \text{ Tank 1}$$

The simulation was to determine C_e and x (or q) at each tank at any time t. The Δt used in the simulation was 1 min.

3.4. Pressure drop estimation

The Ergun equation expressed as:

$$\Delta P/L = 150\left[(1-\varepsilon)^2/\varepsilon^3\right]\left[(\mu U)/\left(\Phi_s d_p\right)^2\right] + 1.75\left[(1-\varepsilon)/\varepsilon^3\right]\left[\left(\rho_g U^2\right)/\left(\Phi_s d_p\right)\right] \quad (11)$$

was used to estimate the pressure drop across the bed in all three beds. The sphericity (Φ_s) of activated carbon was assumed to be 0.9 and the void fraction (ϵ) in the confined bed was assumed to be 0.44 (Kunii and Levenspiel, 1991).

4. Results and discussion

Both equilibrium simulations and process simulations were performed in this study. The results are reported in three sub-sections discussed below.

4.1. Equilibrium simulation results

Equilibrium simulations were performed to identify the predominant mercury species during coal combustion and waste incineration. Fig. 3 shows a typical set of simulation results involving coal-mercury-air-sulfur. The results clearly indicate that elemental mercury is the predominant species during coal combustion at high temperatures. However, when chlorine is present as in waste incineration, mercuric chloride is seen to become the predominant species as shown in Fig. 4. Note that mercuric chloride is water-soluble and can be effectively controlled by wet scrubbers. Elemental mercury, however, is not water-soluble and requires alternative control strategies such as activated carbon sorption described in this study.

4.2. Evaluation of model parameters

Experimental results for mercury adsorption from two different research groups (Krishnan et al., 1997; Korpiel and Vidic, 1997) were used to evaluate the model parameters, i.e., the Henry's Law constant and the parameters appearing in the Langmuir and Freundlich isotherm expressions. It was found that all three equilibrium expressions describe the literature data equally well and the best-fit values of the parameters for all the three expressions are summarized in Table 1. The primary reason for this observation is that the mercury sorption process occurs in an extremely low concentration range where the Henry's Law and the Langmuir isotherm behaves identically (see Fig. 5). In addition, the Freundlich isotherm is identical to the Henry's Law when $n = 1.0$.

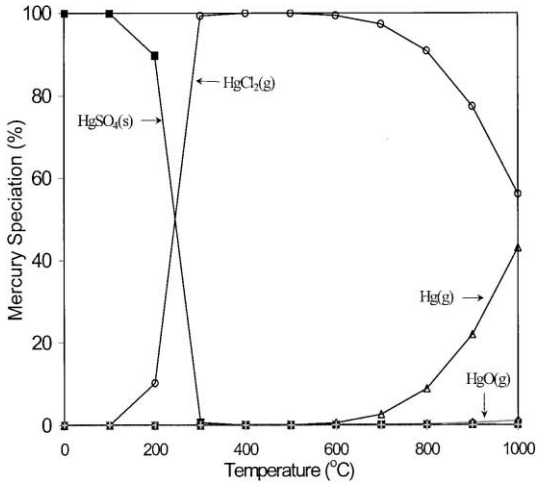

Fig. 3. Equilibrium mercury speciation in a $HgCl_2$–air-system (Hg^o: 1.5 wt.%; air: 94.5 wt.%; sulfur: 4.0 wt.%; chlorine: 1.5 wt.%).

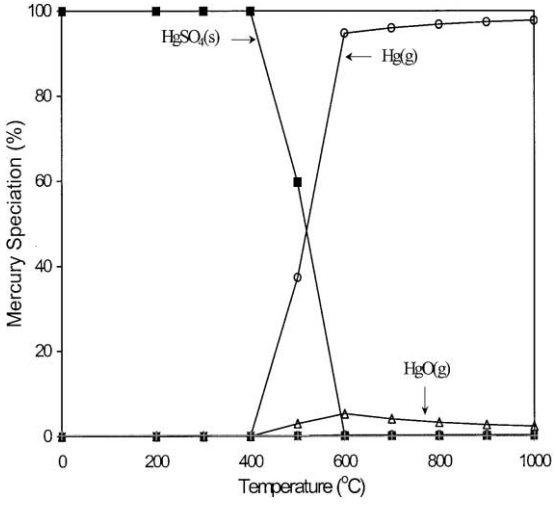

Fig. 4. Equilibrium mercury speciation in a Hg^o–air–Sulfur system (Hg^o: 1.5 wt.%; air: 94.5 wt.%; sulfur: 4.0 wt.%).

Table 1
Best-fit parameters for the three equilibrium expressions

Sorbent type	Temp. (°C)	Hennry's law Eq. H (mmHg)	Langmuir Eq. n (m^3/g)	Langmuir Eq. k ($m^3/\mu g$)	Freundich Eq. k (g/m^3)	Freundich Eq. n
PC-100	23	0.6	3.08	3.4×10^{-4}	0.32	1.0
PC-100	80	1.2	2.04	2.5×10^{-4}	0.49	1.0
PC-100	140	2.0	1.26	1.8×10^{-4}	0.79	1.0
FGD	23	3.6	0.51	5.7×10^{-4}	1.95	1.0
FGD	140	6.7	0.18	2.6×10^{-5}	5.59	1.0
HGR	25	0.02	154.98	1.1×10^{-2}	0.006	1.0
HGR	140	0.6	6.32	6.3×10^{-6}	15.83	1.0
BPL-S	25	0.4	6.20	5.2×10^{-4}	0.16	1.0
BPL-S	140	4.2	0.67	8.4×10^{-5}	1.49	1.0

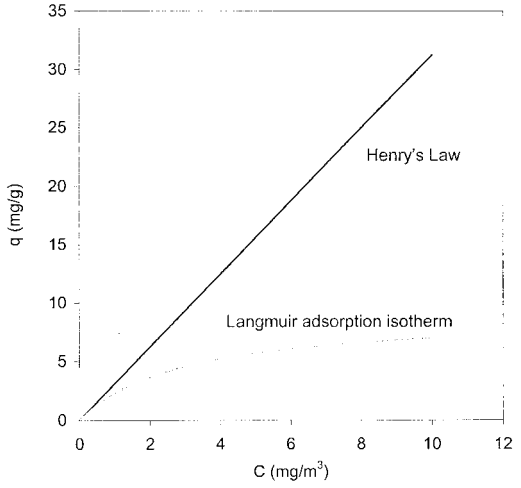

Fig. 5. Comparison between the Henry's Law and the Langmuir adsorption isotherm.

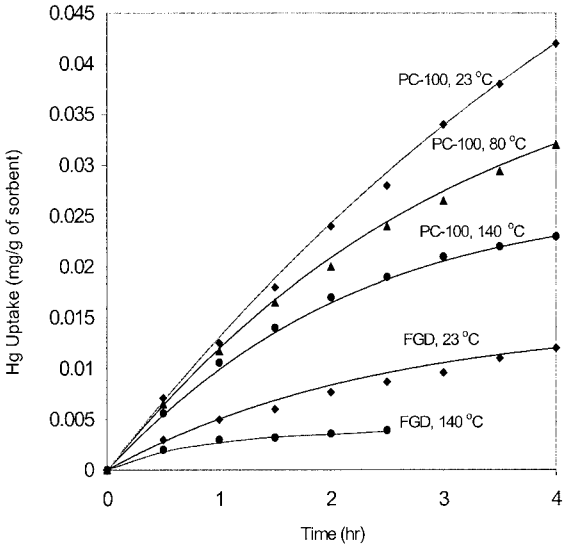

Fig. 6. Adsorption profiles (Hg^o-PC-100 and Hg^o-FGD by Krishnan et al., 1994).

The corresponding simulation results based on the values displayed in Table 1 are shown in Figs. 6 and 7. As can be seen, the model is capable of describing the experimental results extremely well. The best-fit values of the Henry's Law constant (H) are plotted against the temperature in Fig. 8. As indicated, the H value increases with temperature and the range of H for the different activated carbons appears to be in the same order of magnitude.

4.3. Process simulation results

The established model was used to perform simulations on elemental mercury sorption in the three beds. The simulations were based on the same total amount of activated carbon (74.5 kg) and the same total incoming mercury (11.8 μg/s). Note that the bed diameter and the static bed height for most of the simulations were 0.5 and 1 m, respectively, and the superficial velocity was 0.1 m/s at 25 °C (about 7 U_{mf}). Other simulation parameters were: inlet mercury concentration, bed temperature, type of activated carbon, and fraction of semi-fluidization. Table 2 summarizes the simulation conditions.

The simulation results for the confined bed are shown in Figs. 9–12. The sorbent type, sorption temperature, and inlet mercury concentration are seen to affect the results the most. The HGR (Korpiel and Vidic, 1997) is clearly a better sorbent than the BPL-S (Korpiel and Vidic, 1997) for mercury sorption. A lower temperature is in favor of the sorption process indicating that surface equilibrium is an essential mechanism. A lower inlet concentration substantially reduces the mercury uptake. Smaller particles are seen to moderately improve the sorption process due mostly to larger available exterior surface areas. The simulation results also indicate that the superficial velocity only marginally affect the results indicating that external mass transfer is not the dominant controlling mechanism.

Figs. 13 and 14 summarize the effect of different beds on the mercury sorption process. The results indicate that the confined bed produces the highest mercury

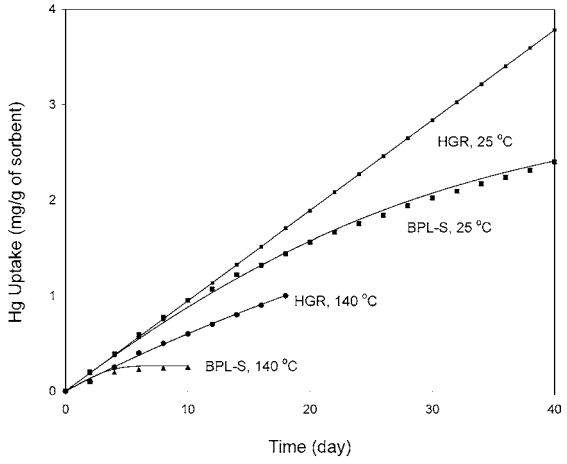

Fig. 7. Adsorption profiles (Hg°-HGR and Hg°-BPL-S, Korpiel and Vidic, 1997).

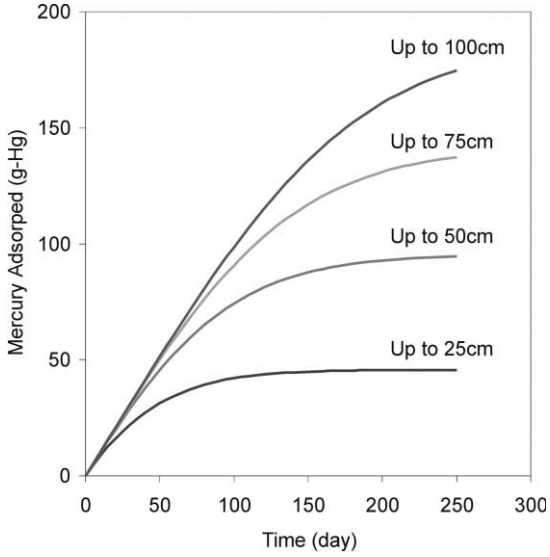

Fig. 9. Mercury adsorbed at different bed elevation under Run 1 condition.

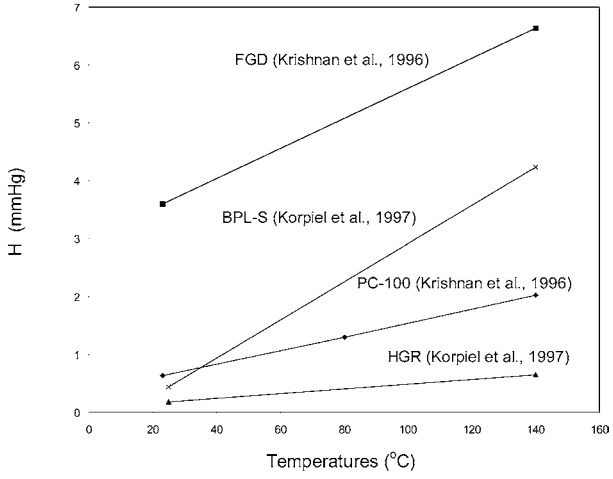

Fig. 8. Best-fit Henry's Law constants.

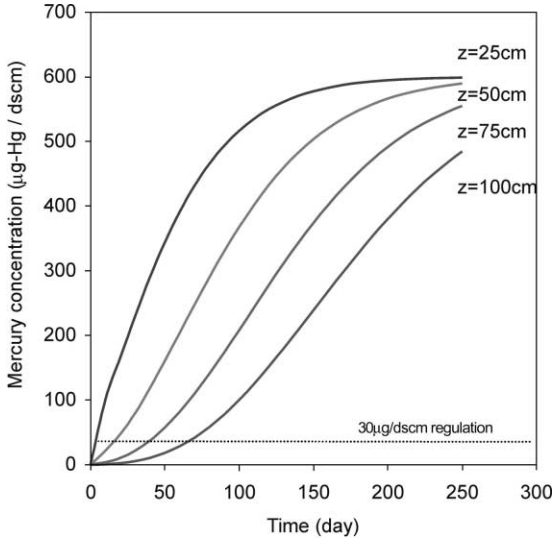

Fig. 10. Mercury concentration at different bed elevation corresponding to Fig. 9.

Table 2
Simulation conditions for the confined, semi-fluidized and fluidized beds

	Run No.									
	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10
Bed type (% fluidized)	C (0)	C (0)	C (0)	C (0)	C (0)	C (0)	S (25)	S (25)	S (25)	S (25)
A.C. Type	HGR	HGR	HGR	HGR	HGR	BPL	HGR	HGR	HGR	HGR
Inlet mercury concentration (µg/dscm)	600	600	300	600	600	600	600	600	600	600
Temperature (°C)	140	25	140	140	140	140	140	140	140	140
Superficial velocity (m/s)	0.14	0.1	0.25	0.25	0.14	0.14	0.14	0.14	0.14	0.14
Column diameter (m)	0.5	0.5	0.5	0.35	0.5	0.5	0.5	0.5	0.5	0.5
Particle diameter (µm)	213	213	213	213	113	213	213	213	213	213
Height of confined bed (m)	1.0	1.0	1.0	2.0	1.0	1.0	0.25	0.5	0.75	0

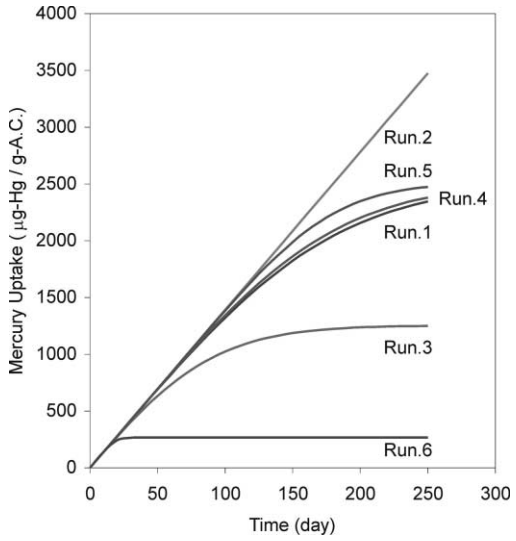

Fig. 11. Effect of simulation conditions on mercury uptake.

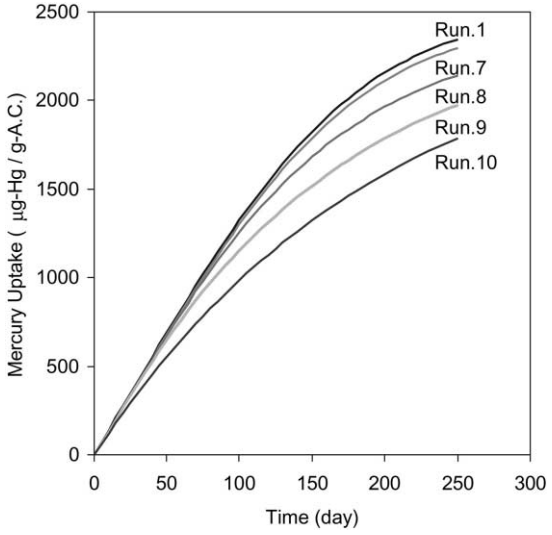

Fig. 13. Effect of semi-fluidized conditions on mercury uptake.

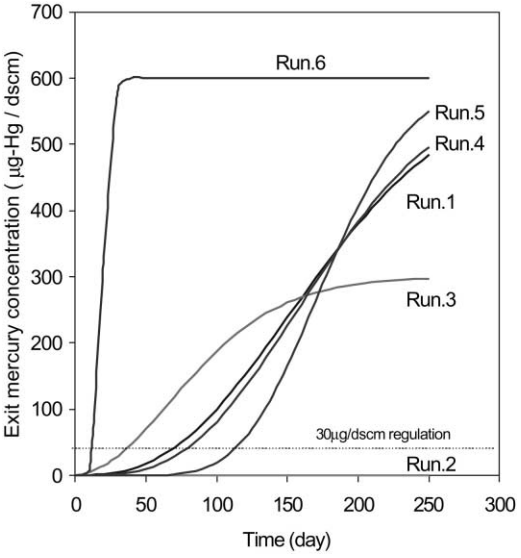

Fig. 12. Effect of simulation conditions on exit mercury concentration, corresponding to Fig. 11.

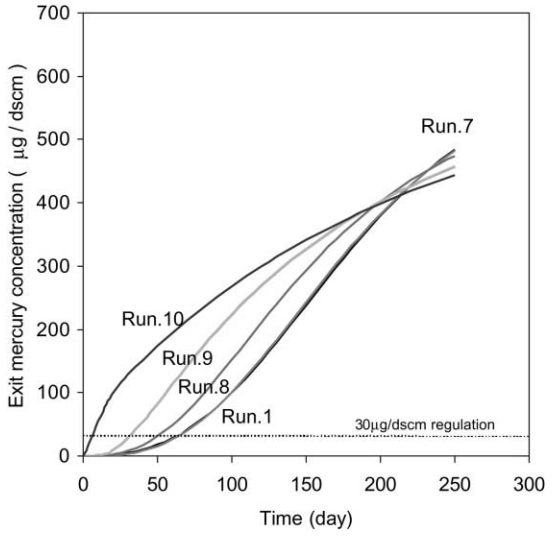

Fig. 14. Effect of semi-fluidized conditions on exit mercury concentration, corresponding to Fig. 13.

uptake and the lowest emission level, and is clearly the best candidate for the process from the mercury sorption point of view. A semi-fluidized bed with 75% confined has a very similar performance as that of the confined bed, followed by the bed with 50% confined, and then 25% confined. As expected, the performance of the fluidized bed is the worst. The results also indicate that it takes about 70 days for the exit mercury concentration to exceed the mentioned emission standard, i.e. 30 μg/dscm, for both the confined bed and the semi-fluidized bed with 75% confined; 55 days for the semi-fluidized bed with 50% confined; 35 days for 25% confined; and less than 10 days for the fluidized bed. It is worth pointing out that one great advantage of a semi-fluidized bed over that of a confined bed can be the pressure-drop across the bed. A rough estimate of the pressure-drop under the current simulation conditions is: 35 kPa for the confined bed; 27 kPa for the semi-fluidized with 75% confined; 19 kPa for the semi-fluidized bed with 50% confined; 12 kPa for the semi-fluidized bed with 25% confined; and 4 kPa for the fluidized bed. This implies that a semi-fluidized bed can be a good candidate for the sorption process when the pressure drop is a concern.

5. Conclusions

A kinetic model coupled with a tank-in-series model has been employed to simulate the mercury sorption process in three distinct beds, namely a confined bed, a semi-fluidized bed, and a fluidized bed. The developed

model has been demonstrated to describe extremely well the mercury sorption results reported in the literature. All the three surface equilibrium laws, i.e. Henry's Law, Langmuir isotherm, and Freundlich isotherm, appear to simulate the adsorption profiles equally well. The simulation results for the three distinct beds have suggested that the confined bed has the best mercury control performance; however, it generates the highest pressure-drop across the bed. A fluidized bed creates the least pressure drop; however, its sorption performance is poor. A semi-fluidized bed offers acceptable performance with affordable pressure-drops and can be a practical candidate for the process.

6. Notation

C	mercury concentration in gas phase; C_e: in exit stream of a bed segment; C_i: in inlet stream of a bed segment; C^i: at gas–particle interface, C_o: in incoming flue gas, kg-mole/m^3
C^i	mercury concentration at gas–particle interphase, μg/m^3
d_p	particle size, m
F	volumetric flow rate, m^3/min
H	Modified Henry's Law Constant, mm Hg
K_g	mass transfer coefficient, m/min
k	constant in Langmuir isotherm expressed in Eqs. (7) and (8), m^3/μg
k	constant in Freundlich isotherm expressed in Eqs. (9) and (10), g/m^3
L	bed height, m
L_{mf}	static bed height, m
N	moles of solute (mercury), kg-mole
n	constant in Langmuir isotherm expressed in Eqs. (7) and (8), m^3/g
n	constant in Freundlich isotherm expressed in Eqs. (9) and (10)
P^i	partial pressure of solute at gas–particle interface, mm Hg
ΔP	pressure drop across the bed, kPa
q	mercury concentration in sorbent, mg/g
S_{ex}	total external surfaces of sorbent particles, m^2
T	Temperature, °C or K
t	time, min
U	superficial velocity, m/s
U_{mf}	minimum fluidization velocity, m/s
x	mercury mole fraction in sorbent
z	distance above the distributor, m
ϵ	void fraction
μ	viscosity, kg/(m s)
Φ_s	sphericity
ρ_g	density of gas, kg/m^3

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