

Kinetic and equilibrium studies of cesium adsorption on ceiling tiles from aqueous solutions

Muhammed Yusuf Miah^{a,b}, Konstantin Volchek^{a,*}, Wenxing Kuang^c, F. Handan Tezel^d

^a Emergencies Science and Technology Section, Environment Canada, 335 River Road, Ottawa, Ontario, Canada K1A 0H3

^b Department of Applied Chemistry and Chemical Technology, Noakhali Science and Technology University, Bangladesh

^c SAIC Canada, 335 River Road, Ottawa, Ontario, Canada K1A 0H3

^d Department of Chemical and Biological Engineering, University of Ottawa, 161 Louis-Pasteur, Ottawa, Ontario, Canada K1N 6N5

ARTICLE INFO

Article history:

Received 11 February 2010

Received in revised form 19 July 2010

Accepted 20 July 2010

Available online 30 July 2010

Keywords:

Cesium adsorption

Construction materials

Adsorption equilibrium

Adsorption kinetics

ABSTRACT

A series of experiments were performed to quantify the adsorption of cesium on ceiling tiles as a representative of urban construction materials. Adsorption was carried out from solutions to mimic wet environmental conditions. Non-radioactive cesium chloride was used as a surrogate of the radioactive ¹³⁷Cs. The experiments were performed in the range of initial cesium concentrations of 0.114–23.9 mg L⁻¹ at room temperature (21 °C) around three weeks. Solution samples were taken after set periods of time and analyzed by inductively coupled plasma mass spectrometry (ICP-MS). The quantity of adsorbed Cs was calculated by mass balance as a function of time.

Two kinetic and three equilibrium models were employed to interpret the test results. Determination of kinetic parameters for adsorption was carried out using the first-order reaction model and the intra-particle diffusion model. Adsorption equilibrium was studied using Langmuir, Freundlich and three-parameter Langmuir–Freundlich adsorption isotherm models. A satisfactory correlation between the experimental and the predicted values was observed.

Crown Copyright © 2010 Published by Elsevier B.V. All rights reserved.

1. Introduction

The radioactive contamination has become a crucial public health, safety, and environmental issue. Even trace amounts of radionuclides can be enough to cause concern [1–5]. The Chernobyl accident in 1986 had wide spread radiation health effects including those caused by ¹³⁷Cs that has a half-life of 30.5 years [6]. Another well-known example is a radiological accident in 1987 in Goiânia, Brazil where a number of people died, many more were injured and environment became contaminated as a result of exposure to ¹³⁷Cs found in an old medical radiation therapy source [7].

The other potential threat from radionuclides may come from radiological terrorism. A radiological dispersal device (RDD), also called the “dirty bomb”, is an explosive device capable of widespread dispersion of radioactive material [8]. An RDD may not necessarily release enough radiation to kill or cause illness, but it will create panic and psychological stress in the general public. The contamination caused to property that would require cleanup may also result in significant economic distress.

Among various radionuclides, cesium (Cs) is a likely candidate for use in RDDs due to its wide availability [9]. Adsorption of Cs

by soil and minerals has been published in the literature [10–14]. Duursma and Eisma [15] reported that Cs enters the interlayers of a mineral such as illite, since its ionic radius matches the interlayer space of the mineral. Komareni and Roy [16] reported the selectivity of Cs on calcium mineral in the presence of various competing alkali metal and alkaline earth cations. Cs uptake behavior for several divalent cations was also investigated by Shrivastava et al. [17,18]. In their study, naturally occurring clay minerals like vermiculite showed remarkably higher pickup for radioactive Cs than that for cadmium or strontium. Crawford et al. [19] reported that ordinary Portland cement had negligible sorption potential for Cs because of the absence of any crystallochemical incorporation of Cs in cement gels. Lee et al. [20] studied an experimental approach for assessing the impact of a cesium chloride RDD.

In general, even though the above data provide valuable information on interaction between Cs and clay–soil, information on interactions between RDDs and urban surfaces is often limited or simply not available. The focus of this paper was on interactions between Cs and ceiling tiles. Among many possible types of construction materials, ceiling tile was used in this study being a common construction material yet representing a challenge for decontamination. Containing minerals such as gypsum and being highly porous, ceiling tiles were expected to have high affinity towards Cs ions as a result of accidental or intentional radiological contamination.

* Corresponding author. Tel.: +1 613 990 4073; fax: +1 613 991 9485.

E-mail address: Konstantin.Volchek@ec.gc.ca (K. Volchek).

Nomenclature

b	Langmuir or three-parameter Langmuir–Freundlich constant (L mg^{-1})
C_A	concentration in the liquid phase at time t (mg L^{-1})
C_{A0}	initial concentration of cesium in solution (mg L^{-1})
C_{Ae}	concentration of cesium in solution at equilibrium (mg L^{-1})
dq/dt	rate of adsorption ($\text{mg g}^{-1} \text{h}^{-1}$)
k	Freundlich constant (mg g^{-1}) (L mg^{-1}) ^{1/n}
k_1	first-order rate constant for adsorption (h^{-1})
k_2	first-order rate constant for desorption (h^{-1})
k'	overall rate constant (h^{-1})
K_c	equilibrium constant (dimensionless)
k_p	intra-particle diffusion rate constant ($\text{mg g}^{-1} \text{h}^{-1/2}$)
m	mass of the coupon (g)
n	Freundlich or three-parameter Langmuir–Freundlich constant (dimensionless)
q	amount of Cs adsorbed at time t (mg g^{-1})
q_e	amount of Cs adsorbed at equilibrium (mg g^{-1})
q_m	maximum saturation capacity at the isotherm temperature (mg g^{-1})
Q_T	total mass of Cs adsorbed in the ceiling tile at equilibrium (mg)
t	contact time (h)
U	Fractional uptake defined by Eq. (2)

Weather conditions (humidity, precipitation, temperature, and wind direction and speed) play an important role in the spread of the radionuclide materials and their deposition on urban surfaces. In particular for Cs, the presence of moisture plays a crucial role. The interaction between Cs and surface materials is much stronger in wet conditions as opposed to dry environment. The objective of this study was to determine the adsorption kinetic and equilibrium parameters of Cs adsorption by ceiling tiles from aqueous solutions by using CsCl as surrogate at room temperature, in order to mimic Cs contamination in wet environmental conditions.

2. Experimental

2.1. Materials

Cesium chloride (CsCl) 99.99% was purchased from Sigma Aldrich. Mineral fiber ceiling tiles (GRENADA type) were purchased from Rona Inc. Tiles were cut into test coupons with dimensions of 5.0 cm × 5.0 cm × 1.5 cm. De-ionized water was used for the preparation of stock solutions and sample dilution.

2.2. Adsorption experiments

2.2.1. Sample preparation

All of the solutions were prepared with de-ionized water. After measuring the weight (g), ceiling tile coupons were secured into 1000-mL Fisher brand polypropylene beakers using clamps so that coupons would be completely immersed in 1 L test solutions of cesium chloride with initial concentrations ranging from 0.114 to 23.9 mg L⁻¹. Table 1 shows sample identification (left column in this table) and the initial concentrations (second left column) for the experiments carried out. Samples identified with the same letter, such as A1 and A2, indicate repeats. The temperature was maintained at 21 °C for all of these experiments. Test solution samples were mixed at a constant speed of 600 rpm using magnetic stirrers.

2.2.2. Kinetic and equilibrium experiments

At the beginning of each set of experiments, before inserting the ceiling tile coupon into the Cs solution beaker, 10 mL of sample was taken and analyzed to determine initial Cs concentration. After the ceiling tile was inserted, 10 mL of solution samples were taken after set periods of time from the same beaker, until equilibrium was reached. The samples were preserved in polystyrene test tubes. The beakers and the test tubes used in this study were made from plastics, rather than glass, to avoid Cs adsorption on the glass. The time to reach equilibrium was determined to be the time after which the solution concentration does not change significantly. A series of experiments were performed at room temperature (21 °C) using the same coupons to generate kinetic and equilibrium data for the following initial Cs concentrations: 0.114, 0.501, 0.767, 4.59, 9.44, and 23.9 mg L⁻¹. In order to generate an adsorption isotherm for Cs, the adsorption capacity of the coupon (mg of cesium per g of coupon) was determined by calculating the mass of Cs adsorbed (mg) and dividing it by the weight of the coupon (g) for each different initial concentration (mg L⁻¹). The mass of Cs adsorbed (mg) was determined by taking the difference between the initial and final (after reaching equilibrium) mass of Cs (mg) in the solution.

The pH measurements were performed using a pH electrode (Denver Instrument, Model 225, pH ISE Meter) calibrated with standard buffer solutions. The pH value of the initial solution was 4.95 while at equilibrium it ranged from 7.0 to 7.87.

2.3. Porosity measurement

The coupon was dried overnight at 100 °C to remove moisture and then weighed at room temperature. The volume of coupon was calculated based on its dimensions. The coupon was immersed in a beaker containing de-ionized water for 24 and 48 h at room temperature to fill the pore space to a saturation state. After wiping the wet coupon surface with tissue paper to remove free surface water, it was weighed and the water-filled part of the coupons was determined by weight difference. The porosity was determined by using the density of de-ionized water, and the same value was obtained for 24 and 48 h immersion in water.

$$\text{Porosity} = \frac{\text{water filled pore volume (cm}^3\text{)}}{\text{total coupon volume (cm}^3\text{)}} \quad (1)$$

2.4. ICP-MS analysis

The Cs aqueous samples were analyzed in a fully quantitative analytical method on Thermo X Series II ICP-MS in standard mode. An internal standard of 0.1 mg L⁻¹ rhodium in 4% hydrochloric acid was used to monitor the analysis. The instrument was calibrated by 0.1 and 1 mg L⁻¹ Cs standard solutions before running samples and checked by the same solutions after running samples. Each sample was analyzed 3–5 times and average was taken. The relative standard deviation (RSD) of multiple measurements was less than 1.5% and in most cases, less than 1.0%.

2.5. Quality assurance and quality control

The control and blank tests, as well as the repeats were done for each set of different initial concentration experiments. For the control, the beakers just contained the Cs solution without coupon. This control beaker was used to check Cs solution evaporation and/or adsorption by the beaker until the equilibrium is reached. No change in Cs concentration was observed, indicating no evaporation or adsorption by the beaker in all experimental conditions studied.

For the blank, the beaker just contained de-ionized water with a coupon. This blank was used to check the possible release of Cs

Table 1
Adsorption of Cs on ceiling tiles for different initial concentrations of Cs in solution at 21 °C.

Sample	C_{A0} (mg L ⁻¹)	C_{Ae} (mg L ⁻¹)	m (g)	Q_T (mg)	q_e (μg g ⁻¹)	K_c	k_1 (h ⁻¹)	k_p (mg g ⁻¹ h ^{-1/2})
A1	0.114	0.027	7.83	0.081	10.39	385	0.0831	0.0014
A2	0.114	0.028	7.69	0.075	9.79	350	0.1037	0.0014
B1	0.501	0.157	7.67	0.322	41.98	267	0.1633	0.0064
C1	0.767	0.261	7.75	0.479	61.81	237	0.2335	0.0119
C2	0.767	0.260	7.94	0.480	60.49	233	0.2384	0.0110
D1	4.59	3.550	7.28	1.011	138.87	39.6	0.2450	0.0286
E1	9.44	7.530	7.73	1.840	238.11	31.0	0.3148	0.0841
E2	9.44	7.540	7.80	1.840	235.89	31.3	0.2614	0.1006
F1	23.90	20.050	7.85	3.271	416.73	21.0	0.6037	0.2097
F2	23.90	20.120	7.70	3.778	490.65	24.3	0.6072	0.2395

from ceiling tile coupon into de-ionized water. The results from this blank experiment revealed that Cs concentration was 0.105 μg L⁻¹ after 19 days of contact time, at room temperature. The above Cs concentration was found to be more than 1000 times lower than the lowest Cs initial concentration used for the adsorption tests (0.114 mg L⁻¹) and considered to be negligible. Two repeats were done for most initial concentrations of Cs to determine reproducibility. Results of these repeats are also presented in Table 1 with the same letter in sample numbers.

3. Theoretical section

3.1. Kinetic models

3.1.1. First-order kinetic model

The kinetics of Cs adsorption process can be considered similar to the kinetics of first-order reaction [21–24]. The rate of a chemical reaction may be defined as the change in the concentration of a reactant (or product) in a given time interval. Average rate of reaction is a function of time. At a fixed temperature the rate of a given reaction depends on concentrations of reactants.

Bhattacharya and Venobachar [21] developed an adsorption model similar to first-order reversible reaction kinetic model. The adsorption of Cs on a solid surface can be hypothesized as a reversible reaction. This model approach was used to determine the rate of adsorption of Cs in this study. In this model, the relationship between fractional uptake (U), and overall rate constant (k') can be expressed as:

$$\ln(1 - U) = k't \quad (2)$$

$$U = \frac{(C_{A0} - C_A)}{(C_{A0} - C_{Ae})} \quad (3)$$

$$k' = k_1 + k_2 \quad (4)$$

$$K_C = \frac{q_e}{C_{Ae}} = \frac{k_1}{k_2} \quad (5)$$

where k_1 and k_2 are the first-order rate constants for adsorption and desorption, respectively, and K_C is the equilibrium constant, C_{A0} is the initial concentration of Cs in solution, C_A is concentration of Cs in solution at any time t , C_{Ae} is the concentration of Cs in solution at equilibrium and q_e is the amount of Cs adsorbed in coupon at equilibrium.

By plotting the value of $\ln(1 - U)$ vs. contact time t , the rate constant k' can be determined from the experimental data, from the initial slope of this curve within the first hour of adsorption (see Eq. (2)). The concentration of Cs in solution decreases with time due to adsorption. When the system reaches equilibrium then the rate of adsorption is equal to that of desorption. The equilibrium constant, K_C , is defined as the ratio of equilibrium concentration of Cs in the ceiling tile and the aqueous phase. The K_C value can be determined from Eq. (5) by determining the amount of Cs adsorbed on the coupon (q_e) and the amount of Cs remaining in

the solution at equilibrium (C_{Ae}). After calculating k' , the k_1 value, which is the rate constant for adsorption, can be determined from Eqs. (4) and (5).

3.1.2. Intra-particle diffusion model

Another kinetic model that can be considered is the isothermal intra-particle diffusion model [25–27]. The rate parameter (k_p) is defined as the intra-particle diffusion constant, as the initial slope of the graph for the amount of Cs adsorbed at time t per gram of adsorbent, q , vs. $t^{1/2}$:

$$q = k_p t^{1/2} \quad (6)$$

The initial slope of the plot q vs. $t^{1/2}$ will give the intra-particle diffusion constant, k_p .

3.2. Equilibrium models

An adsorption isotherm describes the relationship between the amount of adsorbate, which is taken by the adsorbent, and the concentration of adsorbate in the liquid at equilibrium. In this study, the relationship between Cs adsorbed by ceiling tile and concentration of Cs remaining in solution at equilibrium is described by Langmuir [28], Freundlich [29] and Langmuir–Freundlich isotherm [30,31] models in the concentration range from 0.114 to 23.9 mg L⁻¹ at 21 °C. These models were used to interpret the experimental adsorption isotherms obtained according to the following equations:

The Langmuir model is given by:

$$q_e = \frac{q_m b C_{Ae}}{1 + b C_{Ae}} \quad (7)$$

This equation can be rearranged to give:

$$\frac{1}{q_e} = \frac{1}{q_m} + \left(\frac{1}{b q_m}\right) \left(\frac{1}{C_{Ae}}\right) \quad (8)$$

where b is Langmuir constant, and q_m is the maximum saturation capacity at the isotherm temperature and these parameters can be determined from the slope and the intercept of $1/q_e$ vs. $1/C_{Ae}$ plot.

The Freundlich isotherm model is given by:

$$q_e = k C_{Ae}^{1/n} \quad (9)$$

or

$$\log q_e = \log k + \frac{1}{n} \log C_{Ae} \quad (10)$$

where k and n are Freundlich constants and they can be determined from the slope and the intercept of $\log q_e$ vs. $\log C_{Ae}$ plot.

Three-parameter Langmuir–Freundlich isotherm:

$$q_e = \frac{q_m (b C_{Ae})^{1/n}}{1 + (b C_{Ae})^{1/n}} \quad (11)$$

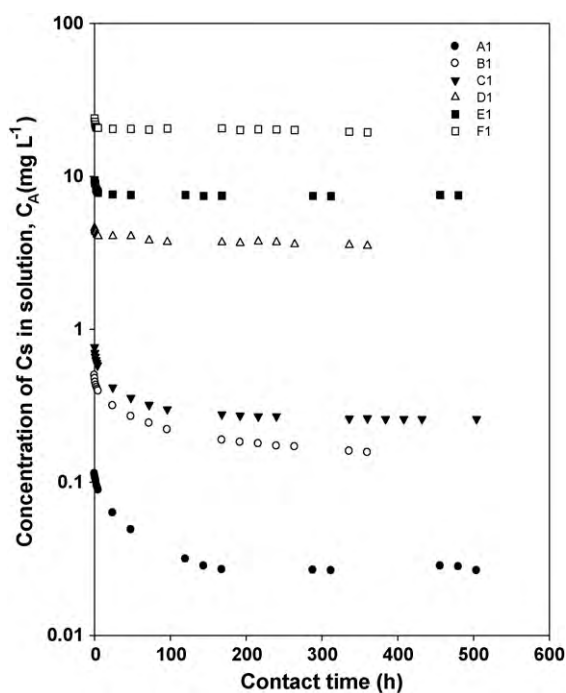


Fig. 1. Change of Cs concentration in solution, C_A , as a function of time, t , for different initial concentrations as indicated by the legend, for adsorption of Cs by ceiling tile at 21 °C (see Table 1 for the initial concentration of samples).

where b , q_m and n are three-parameter Langmuir–Freundlich constants and they can be determined from a non-linear regression of the q_e vs. C_{Ae} data.

4. Results and discussion

4.1. Physical properties of the ceiling tile

Ceiling tiles are manufactured from composite porous material that includes a mixture of cellulose fibers and gypsum. Pores in ceiling tiles serve to reduce the effective density of the board material and to increase the noise insulation by the tile [32]. The diameter of most cellulose fibers observed under a microscope in this study was found to be around 1–2 μm . The tiles contain both intra-fiber and inter-fiber pores. Inter-fiber pores are actually the spaces that are randomly distributed between fibers. Intra-fiber pores are randomly distributed throughout the interior of a fiber and have a mean pore diameter from about 0.1–1 μm [32]. A wide variation of pore diameters for the ceiling tile for both intra- and inter-fiber pores was reported to be between 1.5 nm and 20 μm [33]. Levit and Teather reported the void fraction of the ceiling tile (defined by the ratio of the pore volume to the total volume) to be between 0.5 and 0.7 [33]. As described in Section 2.3, the porosity of the ceiling tile was determined using the volume of water that occupies the pores. The calculated porosity was 0.72, which was in good agreement with the literature data [33]. Density of the coupon was calculated to be 0.21 g cm^{-3} .

4.2. Kinetic study

The change of Cs concentration in solution as a function of contact time is shown in Fig. 1 for different initial concentrations. The repeats (A2, C2, E2 and F2 samples given in Table 1) are not shown in this figure to avoid overlap. The decrease of Cs concentration was the result of its adsorption by the coupon. An overall decline in Cs concentration of 16–76% was observed for initial Cs concentration

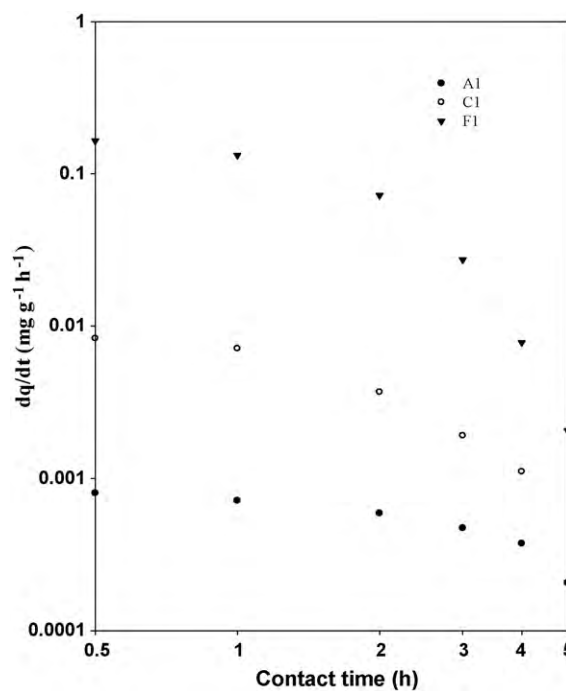


Fig. 2. The rate of adsorption of Cs as a function of contact time for different initial concentrations by ceiling tile at 21 °C.

range of 0.114–23.9 mg L^{-1} as can be seen more clearly from Table 1 by comparing the initial (C_{A0}) and final equilibrium concentrations (C_{Ae}) measured. As expected, Cs concentration initially decreased rapidly and then continued decreasing at a slower pace until equilibrium was achieved. The quantity of adsorbed Cs was calculated based on a mass balance. Fig. 2 shows the rates of Cs adsorption (dq/dt) for the initial 5 h determined by calculating the derivative of the amount adsorbed vs. time data (taken from Fig. 1). This figure shows that the rate of adsorption decreased with time with the rates being orders of magnitude higher for higher initial concentrations. Adsorption equilibrium was observed to be attained around 10 days (240 h) for all initial concentrations as can be seen from Fig. 1. This relatively long time to reach equilibrium is likely due to the very small pores existing in the ceiling tiles and a slow diffusion. Smaller pores result in a slower pore diffusion which likely becomes a determining step in the mass transfer. As previously mentioned, the size of pores in the ceiling tiles varies in the range of 1.5 nm to 20 μm [33]. Due to the heterogeneity of pores in the coupons, Cs initially fills more easily accessible larger pores very fast, and then slowly keeps filling the smaller pores that are difficult to access. Similar trends for kinetics of Cs adsorption on granite were observed by Tsai et al. [22,23]. Roostaei and Tezel [24] also reported this kind of adsorption process for phenol with porous activated carbon.

The curves in Fig. 1 were correlated well with the two models used in this study: the first-order kinetic model and the intra-particle diffusion model. The corresponding kinetic model constants, k_1 and k_p , for both of these models are listed in Table 1 and plotted against equilibrium concentration, C_{Ae} , in Fig. 3. k_1 was calculated from Eqs. (4) and (5), and k_p was calculated from the initial slopes of q vs. $t^{1/2}$, for each sample, as mentioned in Section 3.1. As shown in this table and Fig. 3, the parameter of the first-order kinetic model, k_1 , shows an increasing trend as Cs concentration increases, indicating that the Cs adsorption is faster at higher concentrations. The rate constants k_1 increased from 0.0831 to 0.6072 h^{-1} within the range of initial concentrations used in this study (0.114–23.9 mg L^{-1}).

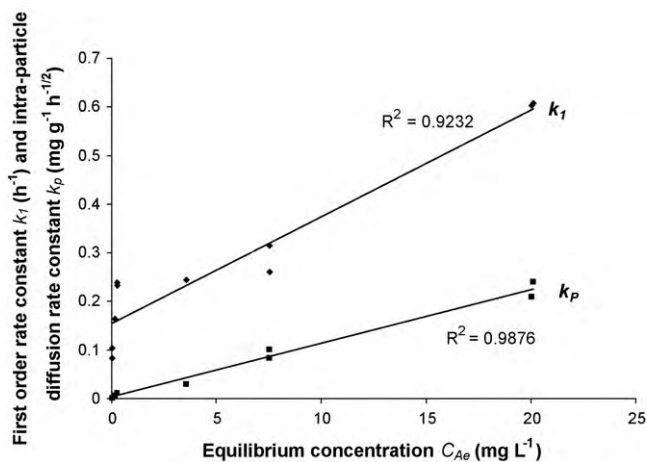


Fig. 3. First-order rate constant k_1 and intra-particle diffusion rate constant k_p vs. equilibrium concentration C_{Ae} for Cs adsorption by ceiling tile at 21 °C.

Table 1 and Fig. 3 show that the calculated values of the intra-particle diffusion rate constant, k_p , changed linearly from 0.0014 to 0.24 ($\text{mg g}^{-1} \text{h}^{-1/2}$) within the studied concentration range. This corresponds to a 171-fold increase in k_p , which is in good agreement with the increase in the initial rates of adsorption (dq/dt as shown in Fig. 2). Within the same range of initial concentrations, dq/dt increased from 0.000825 to 0.174 ($\text{mg g}^{-1} \text{h}^{-1}$), i.e. by a factor of 210. It is therefore concluded that Cs adsorption by ceiling tile is well represented by the intra-particle diffusion model.

4.3. Equilibrium study

Equilibrium concentration, C_{Ae} , and equilibrium capacity, q_e , were determined for each initial concentration as shown in Table 1 and in Fig. 4. The Langmuir isotherm model parameters b and q_m were obtained from the slope and the intercept of the plot $1/q_e$ vs. $1/C_{Ae}$ according to Eq. (8). The Freundlich isotherm parameters k and $1/n$ were determined by plotting $\log q_e$ vs. $\log C_{Ae}$, as per Eq. (10). The three parameters Langmuir–Freundlich model q , b and $1/n$ were calculated by performing a non-linear regression to the experimental data using Eq. (11). The parameters are listed in Table 2.

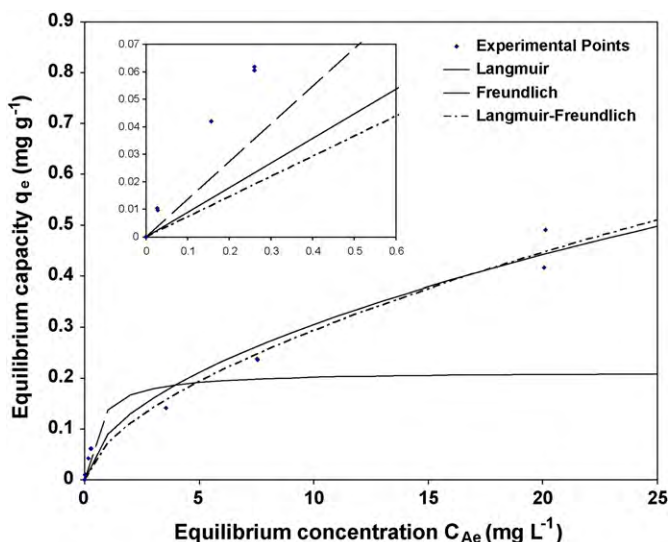


Fig. 4. Comparison of equilibrium isotherm models with experimental results obtained for Cs adsorption by ceiling tile at 21 °C.

Table 2

Equilibrium model parameters for adsorption of Cs on ceiling tiles at 21 °C.

Isotherm model	Parameters	Unit	Constant
Langmuir	q_m	mg g^{-1}	0.2128
	b	L mg^{-1}	1.8035
Freundlich	k	$(\text{mg g}^{-1})(\text{L mg}^{-1})^{1/n}$	0.0894
	$1/n$		0.5334
Langmuir–Freundlich	q_m	mg g^{-1}	50.00
	b	L mg^{-1}	2.11×10^{-5}
	$1/n$		0.6060

Fig. 4 shows the experimental data as well as the calculated values by the three isotherm models. In this figure, an insert figure was added to highlight the trends at very low Cs concentrations at equilibrium. At these very low concentrations, the Langmuir model gave the closest fit, although it still deviated from the experimental points. Freundlich and Langmuir–Freundlich models showed similar trends in this concentration range. On the other hand, at higher concentration range, Langmuir–Freundlich model showed slightly better fit compared to the Freundlich model. If only one isotherm model had to be chosen, Freundlich isotherm is the best one for the whole equilibrium concentration range considered in this study (from 0.027 to 20.12 mg L^{-1}) for Cs adsorption by ceiling tile at room temperature. Although the Langmuir model gave a better fit at lower concentrations, it deviates considerably from the experimental data at higher concentrations as can be seen from Fig. 4.

The Langmuir model is based on the concept of a mono-layer adsorption which is usually the case of adsorption at lower concentrations. This is likely why this model produced a better correlation with experimental results in the lower range of concentrations. At higher concentrations, the Freundlich and the three-parameter models fit better as they consider a multi-layer adsorption.

4.4. Cesium adsorption and role of ion exchange

An attempt was made to link the adsorption of cesium to its likely ion exchange reaction with calcium and other cations. As mentioned in Section 2, de-ionized water was used to prepare all test solutions. It was hypothesized that if adsorption is mainly due to this ion exchange reaction, then a quantity of the released cations (in gram-equivalent) would be close to that of the adsorbed cesium. Test results revealed however that cations were released into solutions in much greater quantities compared to cesium. For example, even when the initial Cs concentration was just 0.114 mg L^{-1} , the concentration of Ca in solution would increase from a few $\mu\text{g L}^{-1}$ to 10 mg L^{-1} or more within two weeks. The adsorption of such small quantity of cesium alone would not cause the release of 10 mg of calcium. It was therefore concluded that the release of Ca and other cations into solution was mainly due to their dissolution rather than ion exchange with Cs.

5. Conclusions

The behavior of adsorption of Cs from aqueous solutions on ceiling tile coupons was studied using CsCl as a surrogate of radioactive ^{137}Cs . The initial concentration of Cs ranged from 0.114 to 23.9 mg L^{-1} . It required around ten days to reach equilibrium. As expected, a higher initial rate of adsorption corresponded to a higher Cs concentration.

Kinetic results show that Cs adsorption correlates well with the intra-particle diffusion and the first-order reaction models. The rate of adsorption decreased with time while the rates being higher for higher initial concentrations. The rate constants k_1 increased from 0.0831 to 0.6072 h^{-1} within the range of initial concentrations used in this study. At the same time, the calculated values of the intra-

particle diffusion rate constants k_p changed linearly from 0.0014 to 0.24 ($\text{mg g}^{-1} \text{h}^{-1/2}$).

Three adsorption isotherm models were applied to interpret experimental equilibrium data. At low concentrations, the Langmuir model gave the closest fit among the models considered. At high concentration range, the Langmuir–Freundlich model was the best to represent the data. Overall, Freundlich isotherm is the best one to be used for the whole equilibrium concentration range considered in this study (from 0.027 to 20.12 mg L^{-1}) for Cs adsorption by ceiling tile at room temperature.

Acknowledgements

Funding for this research is provided by the Chemical, Biological, Radiological, Nuclear, and Explosive Research and Technology Initiative (CRTI) under Project 06-0156RD. The authors thank Ali Khalifa, Ken Li, Vladimir Blinov and Pervez Azmi (Environment Canada), Dario Velicogna and Geneviève Thouin (SAIC Canada), Emily Snyder and Sangdon Lee (US Environmental Protection Agency), and Marc Desrosiers (DRDC Canada) for their valuable contributions.

References

- [1] A.A. Bulgakov, A.V. Konoplev, V.E. Popov, A.V. Stcherbak, Dynamic of the long-lived radionuclide wash-off from soils at the area around Chernobyl NPP, *Eurasian Soil Sci. (Pochvovedenie)* 4 (1990) 47–54.
- [2] K.G. Andersson, J. Roed, C.L. Fogh, Weathering of radiocaesium contamination on urban streets, walls and roofs, *J. Environ. Radioact.* 62 (9) (2002) 49–60.
- [3] E.M. Korobova, S.L. Romanov, A Chernobyl ^{137}Cs contamination study as an example for the spatial structure of geochemical fields and modeling of the geochemical field structure, *Chemom. Intell. Lab. Syst.* 99 (1) (2009) 1–8.
- [4] E. Lima, I.A. Ibarra, V. Lara, P. Bosch, S. Bulbulian, Cesium leaching from γ -irradiated CsA and CsX zeolites, *J. Hazard. Mater.* 160 (2008) 614–620.
- [5] E. Korobova, V. Linnik, N. Chizhikova, The history of the Chernobyl ^{137}Cs contamination of the flood plain soils and its relation to physical and chemical properties of the soil horizons (a case study), *J. Geochem. Explor.* 96 (2–3) (2008) 236–255.
- [6] M.I. Balonov, L.R. Anspaugh, A. Bouville, I.A. Likhtarev, Contribution of internal exposures to the radiological consequences of the Chernobyl accident, *Radiat. Prot. Dosim.* 127 (1–4) (2007) 491–496.
- [7] R.M. Anjos, N.K. Umisedo, A. Facure, E.M. Yoshimura, P.R.S. Gomes, E. Okuno, Goiânia: 12 years after the ^{137}Cs radiological accident, *Radiat. Prot. Dosim.* 101 (2002) 201–204.
- [8] K.G. Andersson, T. Mikkelsen, P. Astrup, S.T. Nielsen, L.H. Jacobsen, L.S. Jensen, S.C. Hoe, S.P. Nielsen, Estimation of health hazards resulting from a radiological terrorist attack in a city, *Radiat. Prot. Dosim.* 131 (3) (2008) 297–307.
- [9] H. Shin, J. Kim, Development of realistic RDD scenarios and their radiological consequence analyses, *Appl. Radiat. Isot.* 67 (7–8) (2009) 1516–1520.
- [10] J.M. Zachara, S.C. Smith, C. Liu, J.P. Mckinley, R.J. Serne, P.L. Gassman, Sorption of Cs^+ to micaceous subsurface sediments from the Hanford site, USA, *Geochimica et Cosmochimica* 66 (2) (2002) 193–211.
- [11] T. Wang, M. Li, W. Yeh, Y. Wei, S. Teng, Removal of cesium ions from aqueous solution by adsorption onto local Taiwan laterite, *J. Hazard. Mater.* 160 (2–3) (2008) 638–642.
- [12] G. Kosakowski, S.V. Churakov, T. Thoenen, Diffusion of Na and Cs in montmorillonite, *Clays Clay Miner.* 56 (2) (2008) 190–206.
- [13] J.F. Real, F. Persin, C. Claret, Mechanisms of desorption of ^{134}Cs and ^{85}Sr aerosols deposited on surfaces, *J. Environ. Radioact.* 62 (2002) 1–15.
- [14] S. Staunton, C. Dumat, A. Zsolnay, Possible role of organic matter in radiocaesium adsorption in Soils, *J. Environ. Radioact.* 58 (2–3) (2002) 163–173.
- [15] E.K. Duursma, D. Eisma, Theoretical, experimental and field studies concerning reactions of radioisotopes with sediment and suspended particles of the sea. Part C. Applications to field studies, *Neth. J. Sea Res.* 6 (1973) 265–324.
- [16] S. Komareni, D.M. Roy, Tobermorites: a new family of cation exchangers, *Science* 221 (4611) (1981) 647–648.
- [17] O.P. Shrivastava, V. Taruna, P.K. Watal, Intrinsic sorption potential of aluminum-substituted calcium silicate hydroxyl hydrate for $^{137}\text{Cesium}$, *Adv. Cem. Bas. Mater.* 2 (1995) 80–83.
- [18] O.P. Shrivastava, R. Shrivastava, Cation exchange applications of synthetic tobermorite for the immobilization and solidification of cesium and strontium in cement matrix, *Bull. Mater. Sci.* 23 (2000) 515–520.
- [19] R.W. Crawford, C. McCulloch, M. Angus, F.P. Glasser, A.A. Rahman, Intrinsic sorption potential of cement components for $^{134}\text{Cesium}$, *Cem. Concr. Res.* 14 (1984) 595–599.
- [20] S. Lee, E. Snyder, J. Barzyk, J. McGee, Experimental approaches to assessing the impact of cesium chloride radiological dispersal device, in: *Proceedings of Thirty-first AMOP Technical Seminar on Environmental Contamination and Response*, Environment Canada, Ottawa, 2008, pp. 415–428.
- [21] A.K. Bhattacharya, C. Venkobachar, Removal of cadmium (II) by low cost adsorbents, *J. Environ. Eng.* 110 (1) (1984) 110–122.
- [22] S. Tsai, T. Wang, Y. Wei, W. Yeh, Y. Jan, S. Teng, Kinetics of Cs adsorption/desorption on granite by a pseudo first order reaction model, *J. Radioanal. Nucl. Chem.* 275 (3) (2008) 555–562.
- [23] S. Tsai, T. Wang, M. Li, Y. Wei, S. Teng, Cesium adsorption and distribution onto crushed granite under different physicochemical conditions, *J. Hazard. Mater.* 161 (2009) 854–861.
- [24] N. Roostaei, F.H. Tezel, Removal of phenol from aqueous solutions by adsorption, *J. Environ. Manage.* 70 (2004) 157–164.
- [25] D.M. Ruthven, *Principles of Adsorption and Adsorption Processes*, Wiley-Interscience Press, New York, 1984.
- [26] W.J. Weber, J.C. Morris, in: W.W. Eckenfelder (Ed.), *Advances in Water Pollution Research*, Pergamon Press, Oxford, 1964.
- [27] G. McKay, The adsorption of dyestuffs from aqueous solutions using activated carbon: analytical solution based on batch adsorption based on external mass transfer and pore diffusion, *J. Biochem. Eng.* 27 (1983) 187–194.
- [28] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc.* 40 (1918) 1361–1403.
- [29] H. Freundlich, *Kapillarchemie*, Akademische Bibliothek, Leipzig, 1909.
- [30] R. Sips, On the structure of a catalyst surfaces II, *J. Chem. Phys.* 18 (1950) 1024–1026.
- [31] M. Jaronice, A. Derylo, A. Marezewski, The Langmuir–Freundlich equation in adsorption from dilute solutions on solids, *Monatshefte fur Chemie* 114 (1983) 393–397.
- [32] M.A. Baig, Ceiling tile construction, US Patent Application 20080216936 (2008).
- [33] N.V. Levit, E.W. Teather, Acoustically absorbent ceiling tile having barrier facing with diffuse reflectance, US Patent Application 20090173570 (2009).