Journal of Hazardous Materials 183 (2010) 712–717

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

# 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 $^{137}$Cs. 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.

## 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 $^{137}$Cs 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 $^{137}$Cs 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).

0304-3894/$ – see front matter. Crown Copyright © 2010 Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2010.07.084

**Nomenclature**

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

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

### 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 $\mathrm{mg\,L^{-1}}$ rhodium in 4% hydrochloric acid was used to monitor the analysis. The instrument was calibrated by 0.1 and 1 $\mathrm{mg\,L^{-1}}$ 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