

RESEARCH NOTE

ADSORPTION, DESORPTION AND ISOTOPIC EXCHANGE OF CADMIUM ON ILLITE: EVIDENCE FOR COMPLETE REVERSIBILITY

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Abstract—Adsorption, desorption and isotopic exchange of Cd on illite clay have been studied at low Cd concentrations and low ionic strength. The results indicate that under the conditions of the experiments Cd sorption on illite is completely reversible. Long equilibration times (7–8 weeks) were shown to be essential because of slow desorption kinetics.

Key words—adsorption, desorption, isotopic exchange, cadmium, illite, reversibility of sorption, kinetics of sorption, kinetics of isotopic exchange

INTRODUCTION

The partition of trace metals between solid phases and natural waters is an essential feature of their geochemical behaviour in the environment. Although adsorption and desorption together determine and are equally important for the reversibility of the sorption process, desorption has been given relatively little attention. The extent of the reversibility is of major importance if one is concerned with the release of adsorbed metals into solution during changes in the chemical environment (e.g. concentration gradients, increasing salinity).

Conventional laboratory studies of desorption make use of extractions with a wide variety of often concentrated solutions (Ferrell and Price, 1978; Pickering, 1980; Salomons and Förstner, 1984 and references therein). The choice of a particular solution is however somewhat arbitrary and results are therefore often difficult to compare. A second approach is to resuspend riverine suspended matter in mixtures of fresh water and sea water in order to simulate desorption during estuarine mixing (Van Der Weijden *et al.*, 1977; Li *et al.*, 1984b).

The most direct test of reversibility is obviously to use the same aqueous phase for both adsorption and desorption (Di Toro *et al.*, 1986). This approach has been applied to examine the reversibility of trace metal sorption on suspended matter in sea water (Li *et al.*, 1984a; Nyffeler *et al.*, 1984), but almost no data are available for fresh water systems. The two studies by Li *et al.* (1984a) and Nyffeler *et al.* (1984) were done over long time periods, a factor which we found to be essential when attempting to achieve complete equilibration.

In experiments using heterogeneous solid systems such as soils, suspended matter and sediments, the reversibility of trace metal sorption is difficult to relate directly to specific components. Obviously there is a need for reference data based on single model compounds. This paper describes long-term experiments on the adsorption and desorption of cadmium at low concentrations on the clay mineral illite. A simple fresh water model, containing only Ca^{2+} as competing cation, was used for both adsorption and desorption. Calcium has been shown to play an important role in the adsorption of cadmium on clay minerals because it competes for exchange sites (Tiller *et al.*, 1979; Pickering, 1980 and references therein). Calcium is therefore considered to be the major competing cation in many fresh water systems.

In addition to adsorption and desorption, we studied the isotopic exchange of ^{109}Cd with adsorbed stable cadmium in order to find out what fraction of cadmium on the solid was in kinetic equilibrium with the solution.

MATERIALS AND METHODS

A Ca-form illite from the Carentan Basin (Normandy, France), pre-treated as described by Van Der Weijden (1975), was used for this study. The cation exchange capacity of this clay mineral was 39 m-equiv 100 g^{-1} (Van Der Weijden, 1975) using the sodium saturation method of Chapman (1965) at pH 7. The specific surface area (BET-analysis) was $152\text{ m}^2\text{ g}^{-1}$. The clay mineral was stored as a stock suspension in $10^{-3}\text{ M Ca}(\text{NO}_3)_2$ with known solid/solution ratio.

A relatively simple electrolyte solution, containing only Ca^{2+} as competing cation, HCO_3^- as a natural pH buffer and NO_3^- (non-complexing), was prepared by dissolution of CaCO_3 (Merck, suprapur) in HNO_3 (Merck, suprapur) in

appropriate amounts to establish a predetermined pH of 7.8. $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Merck, suprapur) was added to obtain an ionic strength of 2×10^{-3} M, which is representative for average fresh water.

Adsorption experiments

To acid-cleaned 100 ml polyethylene sample bottles we added 75 ml of the ionic medium containing 7.5 mg illite and initial cadmium concentrations ranging from 10 to $80 \mu\text{g l}^{-1}$, labelled with 4 kBq (108 nCi) ^{109}Cd (Amersham, $1000 \mu\text{Ci } \mu\text{g}^{-1} \text{Cd}$): illite was added by pipetting a known volume of the homogenized stock suspension; both stable and radioactive cadmium were added from stock solutions in 10^{-2} M HNO_3 . The simultaneous addition of H^+ was compensated for by the addition of equivalent amounts of 10^{-3} M $\text{Ca}(\text{OH})_2$ (Merck, pro-analyse) solution. The initial pH of the samples was $7.79 (\pm 0.06)$.

Triplicate samples for each initial Cd^{2+} concentration were placed in a reciprocating shaker kept at $298 (\pm 1)$ K, and were equilibrated for 54 days. At intervals during equilibration we measured the pH of the suspensions and collected a 2 ml sample of the homogeneous suspension. Samples were taken under continuous stirring in order to maintain a constant solid/solution ratio. After centrifugation at $1.6 \times 10^4 \text{ ms}^{-2}$ for 20 min, the aqueous ^{109}Cd activity was determined by gamma-counting of 1 ml of the clear supernatant. An LKB 1280 gamma-counter with a NaI well-type detector was used, set at counting times of 1200 s. The aqueous and the sorbed Cd concentration were calculated as follows:

$$C_L = (C_L^*/C_{L0}^*)C_{L0} \quad (1)$$

$$C_s = (C_{L0} - C_L)/m \quad (2)$$

where

C_{L0} = initial aqueous Cd concentration ($\mu\text{g l}^{-1}$)

C_L = aqueous Cd concentration after equilibration ($\mu\text{g l}^{-1}$)

C_{L0}^* = initial aqueous ^{109}Cd activity (Bq l^{-1})

C_L^* = aqueous ^{109}Cd activity after equilibration (Bq l^{-1})

C_s = sorbed Cd concentration ($\mu\text{g g}^{-1}$)

m = solid/solution ratio (g l^{-1}).

After 54 days, the pH of the samples was $7.22 (\pm 0.05)$ and the samples were split into two equal volumes for the desorption and isotopic exchange experiments.

Desorption experiments

One half of the sample volumes was transferred with a pipette, under continuous stirring, to acid-cleaned 50 ml polypropylene centrifuge tubes. The tubes were centrifuged at $1.6 \times 10^4 \text{ ms}^{-2}$ for 20 min and the Cd^{2+} containing aqueous phase was carefully removed. About 0.5 ml was left at the bottom of the tube to prevent removal of the solid phase and was corrected for. The solids were resuspended into an equal volume of the same electrolyte solution without Cd^{2+} and the suspensions transferred to 100 ml acid-cleaned sample bottles. The bottles were placed in the reciprocating shaker (kept at 298 ± 1 K) and also allowed to equilibrate for 54 days. At intervals during equilibration the pH of the suspensions was measured and, if necessary, adjusted to pH 7.2 by dropwise addition of 10^{-2} M HNO_3 or $\text{Ca}(\text{OH})_2$ solution. Sampling and determination of C_L and C_s took place as described for the adsorption experiments. After 54 days the pH of the samples was $7.13 (\pm 0.05)$.

Isotopic exchange experiments

A spike of 28.5 kBq (770 nCi) ^{109}Cd (Amersham, $1000 \mu\text{Ci } \mu\text{g}^{-1} \text{Cd}$) was added to the second half of the sample volumes after adsorption equilibration. The samples were again placed into the reciprocating shaker (kept at 298 ± 1 K) and were also equilibrated for 54 days. Sampling and pH adjustment were done as described for the desorption experiments. The activity of the tracer was determined

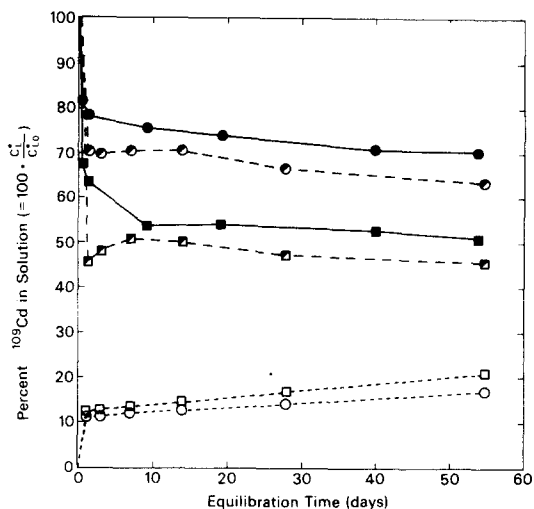


Fig. 1. Adsorption, desorption, and isotopic exchange as a function of equilibration time. The ordinate represents the activity of ^{109}Cd in solution, expressed as a percentage of the amount of radiotracer originally added to the solution $[= 100(C_L^*/C_{L0}^*)]$. ■—adsorption, $C_{L0} = 10 \mu\text{g l}^{-1}$; ●—adsorption, $C_{L0} = 80 \mu\text{g l}^{-1}$; □—desorption, $C_{L0} = 10 \mu\text{g l}^{-1}$; ○—desorption, $C_{L0} = 80 \mu\text{g l}^{-1}$; ■—isotopic exchange, $C_{L0} = 10 \mu\text{g l}^{-1}$; ●—isotopic exchange, $C_{L0} = 80 \mu\text{g l}^{-1}$. The plotted symbols represent the average values of triplicate samples.

as described for the adsorption experiments. The isotopic exchangeable fraction of total adsorbed cadmium (E) was calculated from the mass balance of Cd in the experiments (2) and from the fraction $f = C_L^*/C_{L0}^*$ of the radiotracer that remained in solution after equilibration. According to the principles of isotopic dilution f is also equal to

$$f = C_L/[C_L + (E C_s m)]. \quad (3)$$

After rearrangement we obtain for E

$$E = (1 - f)C_L/fC_s m. \quad (4)$$

A correction was made for the residual activity of ^{109}Cd after adsorption equilibration. The pH of the samples after 54 days was $7.22 (\pm 0.04)$.

RESULTS AND DISCUSSION

Kinetics

Adsorption, desorption and isotopic exchange are shown as a function of equilibration time in Fig. 1. The ordinate represents the activity of ^{109}Cd in solution, expressed as a percentage of the amount of radiotracer originally added $[= 100(C_L^*/C_{L0}^*)]$. All three processes are slow: even after weeks of equilibration there was still some continuation. Adsorption approaches equilibrium faster than desorption. The ^{109}Cd percentages for adsorption show only very small differences after 9 and 54 days, whereas the desorption values, after an initial rapid increase, continue to increase slightly with time. Similar observations were reported for the partition of several trace metals, including Cd, between red clay and sea water (Li *et al.*, 1984a) and between Narraganset Bay surface sediments and sea water (Nyffeler *et al.*, 1984).

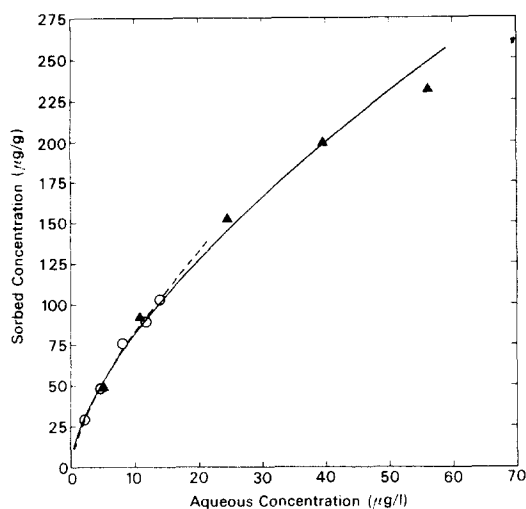


Fig. 2. Isotherm plot of the concentrations of cadmium in solution and on the solid after 54 days of equilibration. Freundlich isotherms based on the separate adsorption (\blacktriangle) and desorption (\circ) data are indicated: — represents the adsorption isotherm $C_s = 18.07 C_L^{0.65}$ ($r^2 = 0.989$ for the log-transformed equation); --- represents the desorption isotherm $C_s = 16.93 C_L^{0.68}$ ($r^2 = 0.996$ for the log-transformed equation). Plotted symbols represent the average values of triplicate samples.

Isotopic exchange equilibration shows some slight fluctuation but it seems that, within experimental errors, isotopic exchange and adsorption show a similar equilibration pattern. In the literature very few data have been reported on the isotopic exchange of trace metals. Bourg and Filby (1976) demonstrated however that 100% isotopic exchangeability of ^{65}Zn with stable zinc adsorbed during 1 h equilibration on illite, montmorillonite and kaolinite, was achieved within 1 h. Fujii and Corey (1986) showed that isotopic equilibrium between ^{109}Cd and ^{65}Zn and stable Cd and Zn respectively in two soils, both with and without addition of sewage sludge, was not attained in 16 h and possibly not even in 72 h.

Reversibility

An isotherm plot of the Cd concentrations in solution (C_L) and on the solid (C_s) after 54 days equilibration is presented in Fig. 2. Freundlich isotherms (used here only for curve-fitting purposes) based on the separate adsorption and desorption data are indicated, showing almost complete overlap. It should be noted that after 54 days the desorption process still shows a slight increase with time (Fig. 1). Consequently the slope of the desorption isotherm might still show a slight decrease. The fact that, within experimental errors, the adsorption and desorption isotherms overlap implies that for this clay mineral and under the conditions of this experiment the sorption process is completely reversible.

The results of the isotopic exchange experiments (Table 1), although showing relatively large experimental errors, support this observation. It can be said

Table 1. Isotopic exchangeability (E -value) of ^{109}Cd with stable Cd adsorbed on illite* at different initial aqueous Cd^{2+} concentrations (C_{L0})

C_{L0} ($\mu\text{g Cd l}^{-1}$)	E -value ($\pm 1\sigma$)
10	1.26 (± 0.18)
20	1.12 (± 0.07)
40	1.22 (± 0.23)
60	1.14 (± 0.22)
80	1.40 (± 0.09)

*"Native" Cd content $< 0.3 \mu\text{g Cd g}^{-1}$ clay.

that (at the 95% confidence limit), except for the highest C_{L0} value, the isotopic exchangeabilities are approx. 100%. The apparent trend towards E -values higher than 1 is non-significant, except for $C_{L0} = 80 \mu\text{g Cd l}^{-1}$. The reason for the erroneously high E -value (with relatively low standard deviation) of the latter sample is unclear. E -values above 1 suggest a "hidden" Cd source. We were however unable to trace such a source because suprapur chemicals were used and the "native" Cd content of the illite clay was found to be $< 0.3 \mu\text{g Cd g}^{-1}$ clay. Because the isotopic exchangeabilities are approx. 100% ($E \approx 1.00$) all adsorbed cadmium is apparently in kinetic equilibrium with the solution, on the time scale of these experiments (7–8 weeks). Therefore, the same distribution of cadmium between the solid and the solution as was observed after adsorption can be restored after desorption.

Reversibility of trace metal sorption on clay minerals, hydrous metal oxides or heterogeneous systems such as soils, suspended matter and sediments, has often been found to be incomplete (Ferrell and Price, 1978; Tiller *et al.*, 1979; Pickering, 1980 and references therein; Di Toro *et al.*, 1986). In some systems however, this apparent lack of reversibility might be due to slow desorption kinetics. Quite often such sorption experiments were terminated within a few days. As can be seen in Fig. 1, desorption at $t = 7$ days could perhaps have been interpreted as having virtually reached equilibrium. Slow progress of desorption after 7 days results however in the release of significant amounts of Cd from the solid, leading to complete reversibility after 54 days. This suggestion is supported by the results of Nyffeler *et al.* (1984). These authors describe a similar time dependence for Cd on a comparable time scale and suggest, on the basis of similarity of adsorption and desorption distribution coefficients (K_d 's), that within their experimental errors reversible equilibrium was established in the sorption reaction. Because of the extremely low concentrations used, their results may however be somewhat biased by isotopic exchange reactions.

The slowness of the adsorption, desorption and isotopic exchange processes may indicate the formation of hydroxy particles on variable charge surfaces on the clay mineral (Farley *et al.*, 1985). The available data do not allow a more definite conclu-

sion to be drawn as to the specific sorption mechanism. It is not yet clear whether the suggested mechanism determines sorption of trace metals on clay minerals and what role it plays in the reversibility of the sorption process.

SUMMARY

Under the conditions of our experiments, we demonstrated the complete reversibility of cadmium sorption on illite as a single solid phase in a simple fresh water model. The results for this system show that long time periods are required to achieve virtually complete equilibration. The kinetics of more complex heterogeneous systems may indeed (Nyffeler *et al.*, 1984) require similar long equilibration periods. The apparent lack of reversibility reported in some earlier studies may in some cases be due to the fact that the experiments were terminated prematurely.

More reference data on single "model" solids should help to establish the relation between reversibility of trace metal sorption and the composition of the solid phase in natural aquatic systems.

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