

# Kinetics of cadmium desorption from some soils of Iran

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## Abstract

Cadmium (Cd) is highly toxic and therefore represents a potential threat to the environment and human health. To improve predictions of the toxicity and threat from Cd contaminated soil, knowledge of time-dependent desorption behavior of these soils is crucial. Kinetics of Cd desorption from 15 Cd-spiked surface soil samples (0-30 cm) from the northern part of Iran with a wide range of physical and chemical properties, were studied. Treatments consisted of two levels of Cd (15 and 30 mg/kg as CdCl<sub>2</sub>) with two replications. Samples were incubated under 20% w/w moisture content and 25±°C. After 3 and 6 weeks, Cd desorption pattern was investigated by DTPA (Diethylene-Triamine-Pentaacetic-Acid) extraction with shaking times from 30 to 960 min. Results showed that two-constant-rate, parabolic-diffusion and simple Elovich equations were the best fitted equations among five kinetic models used. The coefficients of kinetic equations had significant correlation with each other. Stepwise multiple regression equations indicated that pH and CEC (cation exchange capacity) were the most important soil characteristics for predicting the rate constants of the kinetic models.

## Key Words

Cadmium, desorption-kinetic, two-constant, parabolic-diffusion, simple Elovich.

## Introduction

Of the heavy metals often found contaminating soil and ground water, cadmium (Cd) is both readily available and highly toxic. Cadmium pollution of the environment has also increased in recent years due to an increase in its use (Alloway 1990). Cadmium (Cd) bioavailability, and hence, potential toxicity depends on its concentration in the soil solution and on the ability of soils to release it from the solid phase to replenish those removed from solution by plants (Backes *et al.* 1995). Although desorption experiments are simple extensions of adsorption experiments, there are relatively few publications have examined Cd desorption, and even fewer that have measured Cd desorption kinetics (Tran *et al.* 2002). Therefore, the objective of the present study were (1) to evaluate different kinetic models in describing Cd desorption from some selected soils with a wide range of soil physicochemical properties and (2) to investigate factors influencing desorption of Cd.

## Methods

Fifteen surface soil samples (0-30 cm), with a wide range of soil physicochemical properties, were collected from Guilan province in northern part of Iran (Table 1). A laboratory experiment was designed with two levels of Cd (15 or 30 mg/kg as CdCl<sub>2</sub>) with two replications. Cadmium was added to 200 g of each soil sample in polyethelene pots. The pots were kept at 25±2°C, and soil moisture was maintained about 20 % w/w. After three and six weeks, 10 g of each soil sample was extracted with 20ml of DTPA extractant (Lindsay and Norvell 1978) for periods of 30, 60, 120, 240, 480 and 960 min at room temperature. Desorbed Cd concentration was determined by atomic absorption spectrophotometry. Kinetic equations including, Zero Order (Dang *et al.* 1994), First Order (Kue and Lotse 1973), Parabolic Diffusion (Khater and Zaghoul 2002), Two Constant Rate (Dang *et al.* 1994) and Simple Elovich (Polyzopoulos *et al.* 1986) were used in soil desorption studies. A relatively high coefficient of determination (R<sup>2</sup>) and low standard error (SE) were used as criteria for the best fit. The relationships between desorption coefficients and soil properties were investigated by correlation and regression analysis using Excel and SPSS software.

**Table 1. Mean and range of physicochemical characteristics of the soils.**

	Clay (%)	pH 1:2.5 (soil:CaCl <sub>2</sub> 0.01M)	OM (%)	CCE (%)	Fe <sub>o</sub> (mg/kg)	CEC (cmol <sub>c</sub> /kg)
Min.	8.00	4.21	1.53	1.59	582	14.18
Max.	52.00	7.61	9.77	16.51	9348	51.94
Ave.	32.00	6.65	4.91	7.78	4833	35.00

### Equations

Desorption data were fitted to Zero order, First order, Parabolic diffusion, Two constant rate and Simple Elovich models.

$$\text{Zero Order} \quad q_t = q_0 - k_0 t \quad (1)$$

$$\text{First Order} \quad \ln q_t = \ln q_0 - k_1 t \quad (2)$$

$$\text{Parabolic Diffusion} \quad q_t = q_0 + k_p t^{0.5} \quad (3)$$

$$\text{Two Constant Rate} \quad q_t = a t^b \quad (4)$$

$$\text{Simple Elovich} \quad q_t = 1 / \beta_s \ln \alpha_s \beta_s + 1 / \beta_s \ln t \quad (5)$$

Where  $q_t$  and  $q_0$  are the amounts of Cd desorbed by DTPA (mg/kg) after  $t$  (s) period of extraction and at  $t = 0$ , respectively,  $k_0$  is Zero Order rate constant (mg Cd/kg/s),  $k_1$  is First Order rate constant ( $s^{-1}$ ),  $k_p$  is diffusion rate constant (mg Cd/kg)<sup>-0.5</sup>,  $a$  is initial Cd desorption rate constant (mg Cd/kg/s)<sup>b</sup>,  $b$  is Cd desorption rate coefficient (mg Cd/kg)<sup>-1</sup>,  $\alpha_s$  is initial Cd desorption rate (mg Cd/kg/s),  $\beta_s$  is Cd desorption constant (mgCd/kg)<sup>-1</sup>.

### Results

Results of the statistical analysis showed that Parabolic Diffusion ( $R^2_{\text{mean}}=0.81$ ), Two Constant Rate ( $R^2_{\text{mean}}=0.88$ ), and simple Elovich ( $R^2_{\text{mean}}=0.93$ ) predicted the pattern of the Cd desorption from treated soils better than the other kinetic equations (Table 2). The range of these kinetic model coefficients are shown in Table 2.

**Table 2. Mean and range of values of the rate constants for the kinetic models that best described Cd desorption from soils**

	Parabolic diffusion	Two constant rate		Simple Elovich	
	( $k_p \times 10^3$ ) (mg Cd/kg <sup>-0.5</sup> )	a (mg Cd/kg/s) <sup>b</sup> /(mg Cd/kg)	b (mg Cd/kg)	$\alpha_s \times 10^3$ (mg Cd/kg/s)/(mg Cd/kg)	$\beta_s$ (mg Cd/kg)
Min.	10.85	0.053	0.066	1.33	0.25
Max.	64.92	8.505	0.413	1157.40	1.48
Ave.	31.10	2.187	0.225	226.90	0.67

A plot of the rate of Cd desorption vs.  $t^{0.5}$  (linear form of parabolic diffusion equation) showed that the initial desorption of Cd from these soils was a rapid process (Figure 1). Most of the desorbable Cd desorbed within 2h, although limited Cd desorption was still ongoing after 16h. For instance, the pattern of Cd desorption based on linear form of Parabolic Diffusion equation and the average rates of Cd desorption of the soils after 3 and 6 weeks with two levels of Cd (15 or 30 mg Cd/kg soil), showed a discontinuity in slope at 2h in most soils (Figure 1). The findings of Dang *et al.* (1994) on the studies of kinetics of zinc desorption, revealed that the most desorption of zinc has occurred within 4h. The trend proposed that two different mechanisms are controlling the rate of Cd desorption. Film diffusion was minimized by continuous shaking during the experiment (Sparks *et al.* 1980), and therefore it is likely that at least two particle diffusion mechanisms were involved (Sivasubramaniam and Talibudeen 1972). Probably in the first 2h Cd desorption is occurred from macroaggregates or outer surfaces microaggregates. The low desorbability of Cd may be due to entrapment of Cd in the imperfections/cracks in the structure of soil particles or due to specific adsorption on high energy sites on soil. If the former is true, the desorbability of Cd should decrease with increased time of Cd reaction with soil. This is consistent with the Cd diffusion model of Bruemmer *et al.* (1988); initially, Cd complexes with DTPA, desorbs from external surfaces of adsorbents, and diffuses into soil solution then, Cd from internal binding sites diffuses to external surfaces, or complexes with DTPA and diffuses into soil solution.

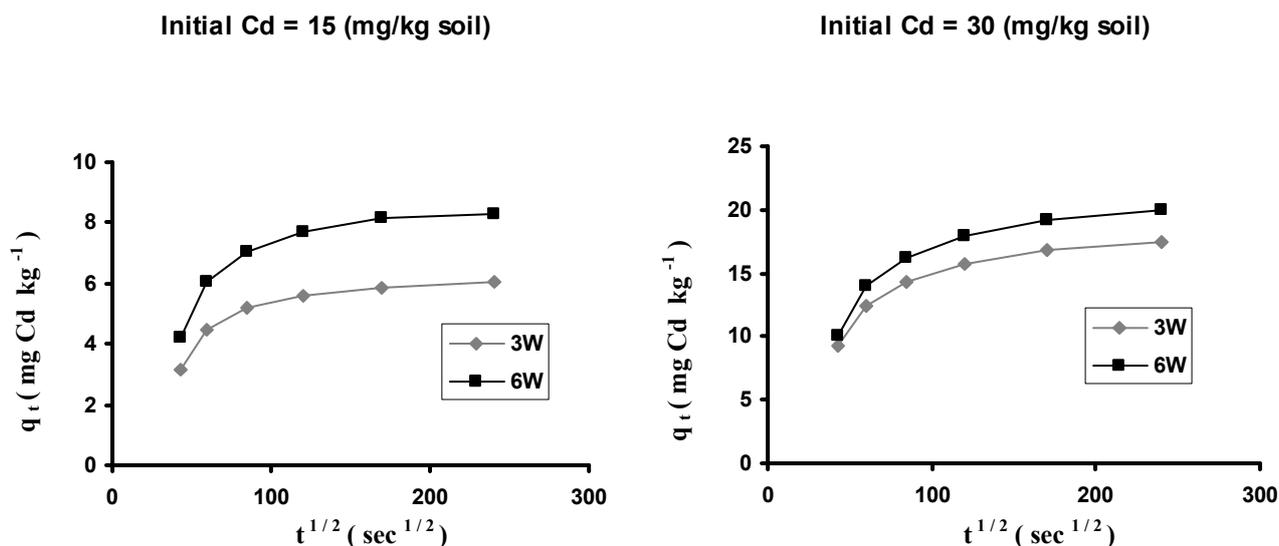


Figure 1. Kinetics of initial Cd desorption (15 or 30 mg Cd/kg oil) by DTPA from the average rates of Cd desorption of the soils after 3 and 6 weeks as described by linear form of Parabolic Diffusion equation.

The constant rates of these different kinetic models had significant correlation with each other (Table 3).

Table 3. Correlation coefficient (r) between constant rates of kinetic models

Constant rates	Constant rates			
	$\beta_s$ (Simple Elovich)	$\alpha_s$ (Simple Elovich)	b (Two constant rate)	a (Two constant rate)
$k_p$ (Paraboli Diffusion)	-0.834**	NS	NS	NS
a (Tow constant rate)	NS	0.780**	-0.608*	
b (Tow constant rate)	NS	-0.556*		
$\alpha_s$ (Simple Elovich)	NS			

\* and \*\* significant at  $p \leq 0.05$ , and  $p \leq 0.01$ , respectively.

NS : not significant

The negative sign of a correlation coefficient between  $\beta_s$ , value of the Simple Elovich equation that relates to the mount of Cd desorption, and  $k_p$ , value of the Parabolic Diffusion equation that relates to the mount of Cd diffusion, indicated that the rate of Cd diffusion increased as the value of  $\beta_s$  decreased, which confirm the findings of pavlatou and polyzopoulos (Pavlatou and Polyzopoulos 1988). There had a significant negative correlation between a. and b, coefficient of Two Constant Rate equation. Dang *et al.* (1994) proposed that an increase in the value of a, and a decrease in the value of b in Two Constant Rate equation probably indicates an increase in the rate of desorption from soils.

## Conclusion

This study showed that Cd desorption was characterized by a rapid initial desorption, which lasted for about 2h, followed by a slower desorption, which was still proceeding after 960 min (16h). The trend well describes the relatively high ability of the DTPA soil test in predicting Cd availability in these soils. The Cd desorption by DTPA from these soils was adequately described by the Parabolic Diffusion, the Two Constant Rate, and the Simple Elovich. Moreover, the constant rates of these kinetic models have shown significant correlation with each other.

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