

Elovich and Freundlich Power-Like Equations Applied to the Uptake of Some Heavy Metals by Synthetic Calcium Carbonate for a Short Time Scale.

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(Accepted 6/8/2004)

□ ABSTRACT □

100 mgs of synthetic calcium carbonate were suspended into 50 ml containing an initial quantity of Mn, Zn, Cd or Pb: 3.1 mg of Mn as $MnSO_4 \cdot 2H_2O$, or 3.2 mg of Zn as $Zn(NO_3)_2$ or 35 mg of Cd as $Cd(NO_3)_2$, or 125 mg of Pb as $Pb(NO_3)_2$. The suspension was agitated at the ambient temperature (23-25°C) for a period of time ranging between 2 and 240 minutes, before being filtered to measure the concentration of metallic ions in the filtrates by atomic absorption spectrophotometry. The data were treated by the use of two kinetic models: Elovich and Freundlich power-like. We found out that experimental results fitted nearby equally with both Elovich and Freundlich power-like equation. The uptake kinetic of Pb appeared poorly fitted with the two models. It was succeeded by Cd retention. The uptake kinetics of Mn and Zn were well fitted with the two models.

Key words: heavy metals, calcium carbonate, uptake, kinetic, Elovich equation, Freundlich power-like equation.

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تطبيق معادلتَي إلفويتش وفرندليش الأسيية في دراسة حركية إزاحة بعض العناصر المعدنية من قبل كربونات الكالسيوم "الصنعية"

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(قبل للنشر في 2004/8/6)

□ الملخص □

درست حركية إزاحة أربعة عناصر معدنية هي: المنغنيز والزنك والكامبيوم والرصاص من قبل كربونات الكالسيوم الصنعية. وكان ذلك بمعاملة 100 مغ من مسحوق الكربونات بحجم ثابت (50 مل) من محلول أحد العناصر المذكورة لفترة زمنية تراوحت ما بين 2 - 240 دقيقة. وضعت العينات خلال الفترة المذكورة للرج الهادئ على درجة حرارة المخبر، ثم رشحت وقيست تراكيز العناصر المعدنية في الرشاحات باستعمال جهاز الامتصاص الذري. طبقت معادلتَي إلفويتش وفرندليش الأسيية في دراسة المنحنيات الحركية لإزاحة العناصر الأربعة، وأظهرت نتائج تحليل المعطيات التجريبية مقدرة متقاربة لهذين النموذجين الحركيين على التنبؤ بحركية إزاحة العناصر الأربعة وتوصيفها. كانت حركية امصاص الرصاص من أقل الحركيات استجابة للنموذجين، تلاه في ذلك الكامبيوم، ولكن بفارق واضح. وأما المنغنيز والزنك، فكانت استجابة حركيتهما للنموذجين على السواء عالية.

الكلمات المفتاحية: العناصر الثقيلة، كربونات الكالسيوم، إزاحة، حركية، معادلة إلفويتش، معادلة فرندليش الأسيية.

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INTRODUCTION:

Kinetics processes, including dissolution precipitation, sorption and desorption, play a determinant role in soil chemistry, and they affect the transport, toxicity and bioavailability of metallic ions. Many studies have recently been conducted to investigate the kinetic of sorption and desorption of metallic ions (Elzinga and Sparks, 2001; Scheckel and Sparks, 2001a; Strawn and Sparks, 2000). McLaren and al (1998) conducted a study about cadmium and cobalt kinetic desorption from soil clay minerals. They studied the effect of sorption period and found out that the desorption kinetics for Cd and Co may well be described by a two – site first-order model. It is well known that the reactivity of soil mineral surfaces is a determining factor in the reaction of soil metallic ions Manning and Suarez (2000). These authors showed that the rate of As(III) adsorption on soils is heavily depends on soil properties which reflects the reactivity of mineral surfaces. The sorption of metals onto natural materials leads to the formation of new mineral-like precipitate phase, the stability of this phase increases with aging time. The effect of time aging on the pathway of metal adsorption onto a precipitate has already been studied McBride et al (1998). Scheckel and Sparks (2001b) believe that the basic kinetic and the thermodynamic parameters for the formation of metal precipitates have not been examined. In this respect, those authors examine Ni-sorption kinetics on pyrophyllite, talc, gibbsite, amorphous silica, and a mixture of gibbsite and amorphous silica over a temperature range of 9 to 35°C. Less attention has been given to the sorption of metals on calcium carbonate, compared with oxides, clay, and organic matter. The precipitation of carbonate minerals like calcite in natural mediums provides an important pathway of metals scavenging by adsorption of metal ions and coprecipitation during crystal growth. Thus the investigation of metal interactions with carbonate minerals provides both deeper knowledge about the biogeochemical cycles of the metals and better understanding of the ecological pathways of metals. Complexation of copper(II) with carbonate ligands in aqueous solution and at CaCO₃ surfaces has recently been studied (Schosseler and al, 1997). These authors demonstrated that Cu(II) ions form different stable inner-sphere complexes with several surface carbonate ligands at the vaterite surface, then they incorporate into the crystal lattice of calcite. It is obvious that this incorporation reaction is a kinetic process that may be discussed with respect to the mechanism and kinetic of calcite crystal growth.

This study focused on the kinetic aspects of some metallic ions uptake by synthetic calcium carbonate, where two kinetic models were applied.

THEORETICAL CONSIDERATIONS:

In many cases the kinetic data obtained by the experience do not fit well with theoretical equations. For these cases the empirical expressions can be used to provide a useful analysis of kinetic phenomenon. Many equations are available, and two of them have been reviewed by Aharoni and Sparks (1991):

2- The power equation or Freundlich like equation which can be represented by the expression:

$$q_{(t)} = kt^n \quad (1)$$

where $q_{(t)}$ is the quantity measured at a given time (t), k and n are constants with $n < 1$. This kind of equations has widely been applied to study the dissolution of minerals as well as to describe sorption of solutes in soils and sediments. The applicability of this equation can be simply tested by the linear plots of $\log q$ vs. $\log t$.

2- The Elovich equation

$$\frac{dq}{dt} = a \exp(- bq) \quad (2)$$

where q is the quantity taken up in time (t), a is a constant relating to the initial velocity of reaction, and b is a constant relating to activation energy. The integral form of equation (19) with the boundary conditions $q = 0$ at $t = 0$ is

$$q = b^{-1} \{ \ln(t + k) / k \} \quad (3)$$

where $k = (ab)^{-1}$. This equation can also be represented as a more simplified form (Aharoni and Sparks., 1991)

$$q = B + (1/b) \ln t \quad (4)$$

where B is a constant still relating to activation energy while b becomes a constant relating to the initial velocity and to activation energy. The Elovichian model is rarely used to analyze the data for dissolution, but it is frequently applied to sorption, specially to chemisorption of gases (Anderson and Rubin.,1981), and many theoretical studies. The applicability of this equation can be verified, as it was illustrated Anderson and Rubin (1981) by the linear plots q vs. $\ln t$.

MATERIALS AND METHODS:

100 mg of synthetic calcium carbonate were suspended into 50 ml containing an initial quantity of each metallic ion alone: 3.1 mg of Mn as $MnSO_4 \cdot 2H_2O$, or 3.2 mg of Zn as $Zn(NO_3)_2$ or 35 mg of Cd as $Cd(NO_3)_2$, or 125 mg of Pb as $Pb(NO_3)_2$ at the ambient temperature (23-25°C). The suspensions was then gently agitated for a period of time varying from 1 to 240 minutes, before being filtered to measure the concentrations of metallic ions in the filtrates by atomic absorption. A blanc suspension of distilled water and calcium carbonate has been used.

RESULTS AND DISCUSSION

The uptake of Mn, Zn, Cd and Pb by calcium carbonate as a function of time, is given in Figure1.

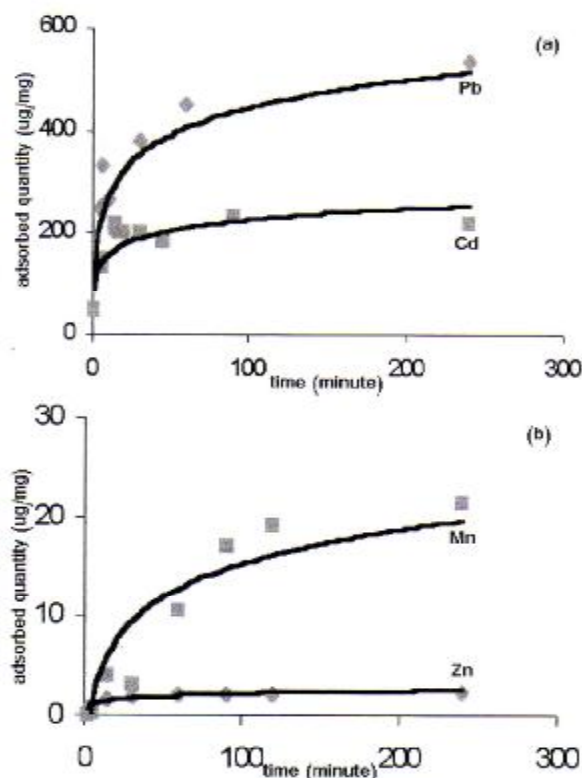


Fig.1. The retained quantity ($\mu\text{g} / \text{mg}$) of metallic ions by calcium carbonate as a function of time: (a) Cd, Pb; (b) Mn, Zn.

The experimental results were also plotted according to equations 1, 2, 3...(Fig.2). they indicate that the kinetic of Mn and Zn retention may be well fitted by both the Freundlich power-like and Elovich equations. Analysis shows that there are no big differences between these two models. The kinetic of Cd uptake can also be described, but for a less extended degree, by the Freundlich power-like and Elovich models. Here the Elovich model is likely being more convenient. In the case of Pb retention, the two models adjust the experimental results but less conveniently.

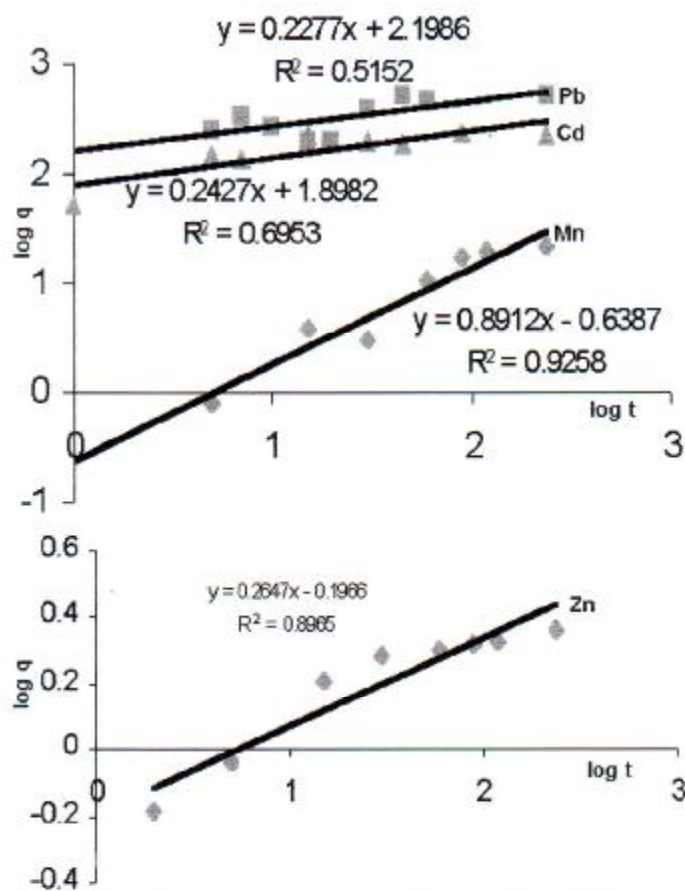


Fig 2. Freundlich power-like equation plot $\log q$ vs $\log t$. (t = time in minute, q = quantity adsorbed in $\mu\text{g}/\text{mg}$).

The data treatment indicates that different models fit with the same process, and dissimilar processes fit with the same model. This fact was mentioned by Aharoni and Sparks (1991). Those authors believe that there is no correlation between the applicability of any of these equations and the nature of the process. They explain this by the fact that equations are an approximation to which the generalized equation reduces at certain limited ranges of coverage. Hence they propose a generalized equation based on diffusion mechanisms as alternative model. A diffusion-controlled reaction has also been applied for the adsorption and desorption of anions at solution-solid surface (Huang, 1975; Hingston and Raupach, 1967). Anderson and Rubin (1981) think that it is impossible to decide which of these possible models gives the best representation of the reactions of anions at solid-aqueous solution interfaces. In fact this requires more understanding of reaction mechanisms.

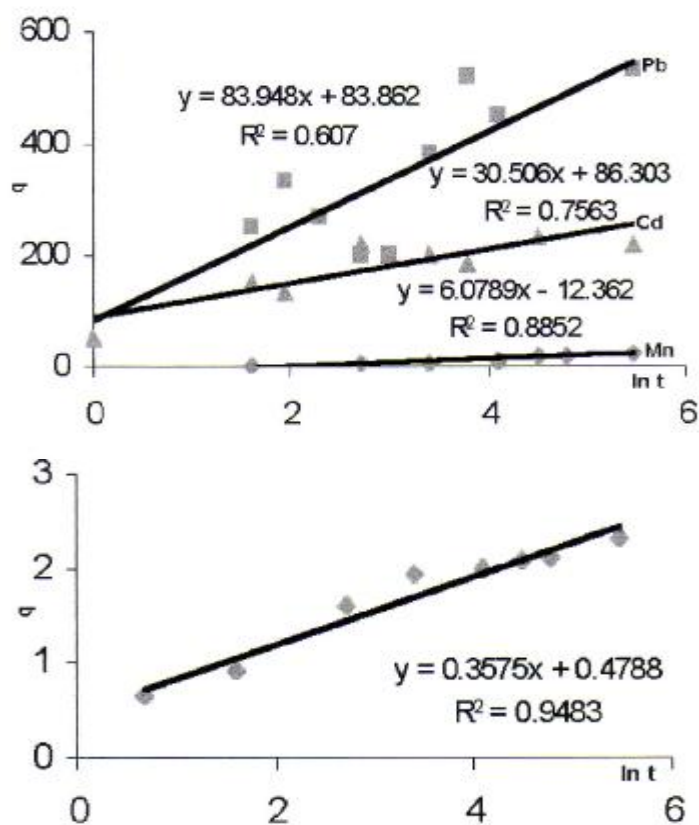


Fig 3. Elovich equation plot q vs $\ln t$. (t = time in minute, q = quantity adsorbed in $\mu\text{g}/\text{mg}$)

CONCLUSION

Calcareous soils are the main element of the pedological cover in Syria. By its properties and buffering effect, calcium carbonate may deeply affect the behavior of soil and become the controlling factor of soil contamination, release and migration of toxic metals. Many researchers have recently been interested in the interaction of metals with calcium carbonate for geochemical, ecological, plant nutrition and contamination issues (Van Cappellen et al, 1993; Schosseler et al, 1997).

The identification of adsorption mechanisms is of prime importance for the determination of calcium carbonate role in soils, and hence to identify the contribution of soil as a purifying and buffering agent. The processes of interaction of metallic ions, like precipitation dissolution, adsorption and desorption, in soils go rarely at thermodynamic equilibrium. This is why the kinetic model is very interesting for the study of metals transformation processes in soils, sediments and aquatic mediums. Indeed, kinetic model permits to evaluate the evolution character of a given process as a function of time, and to elucidate its mechanism. For this purpose, the analysis of adsorption and retention data, using different kinetic models, is recommended. Our results show here that both Elovich and Freundlich power-like models are valuable to describe Mn, Zn, Cd and Pb kinetic uptake by calcium carbonate. A more exhaustive analysis of data, per example by breaking-up the kinetic curves in different steps of retention, is necessary to know which one of the two models tested here is more appropriate.

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